GARDEN

REVITALIZING IDEAL NECESSITIES

Editors

Dr. Suchita Khodke | Dr. Dinesh Khedkar | Dr. Rekha Maggirwar
Dr. Shashank Deshmukh | Dr. Ganesh Hedawoo | Mr. Subhash Bhave
Dr. Gajendrasingh Pachlore | Dr. Umesh Kanerkar



Publisher

Indian Rose Federation Affiliated

Amravati Garden Club, Amravati

Registered Public Trust under Maharashtra Public Trusts Act, 1950

Edition : October 2021

ISBN : 978-93-200-0000-6

www.agca.webs.com

INDEX

Sr. No.	Contents	Page No.
1.	संपादक मंडळ - Editorial Board	1
2.	Forward – Dr. V.R. Ghurde, Advisory Member of Amravati Garden Club, Amravati	2-3
3.	Editorial - Dr. Suchita P. Khodke	4
4.	Message by Hon. Vice-Chancellor of Dr. Panjabrao Deshmukh Agricultural University, Akola.	5
5.	Message by Hon. Vice-Chancellor of Sant Gadge Baba Amravati, Amravati.	6
6.	Message by Hon. Dean of Dr. Panjabrao Deshmukh Agricultural University, Akola.	7
7.	Message by Hon. Dean of Sant Gadge Baba Amravati, Amravati.	8
8.	About Amravati Garden Club of Amravati	9-10
9.	GRIN COURSE Brochure	11-15
10.	List of Collborator Colleges and Co-Organiser	16
11.	Inguration Card	17
12.	Validictory Function	18
13.	Methods of Propagation – Dr. Suchita P. Khodke	19-29
14.	शेवंती लागवड आणि संवर्धन – डॉ. रेखा मग्गीरवार	30-34
15.	Bulking Decorative Foliage Plants – Dr. Dhanshri Patil	35-39
16.	Terrarium and Dish Garden – Mrs. Deepali Taiwade	40-42
17.	पुष्परचनेची संकल्पना – प्रा. डॉ. शर्मिला कुबडे	43-48
18.	वामनवृक्षा – सुनीती देशमुख	49-54
19.	Cultivation of Succulent, Cacti and Adenium – Dr. Suruchi Kadu	55-66
20.	मोसमी फुलझाडांची लागवड – डॉ. विलास आर. देशमुख	67-73
21.	Hanging Basket Care & Maintenance Tips – Mrs. Shital Chitode	74-77
22.	Interior Scaping Hard and Soft Scaping – Mrs.Pallavi Kulkarni	78-83
23.	Plan Your Own Garden – Prof. Chandrashekhar Deshmukh	84-88
24.	रोपवाटिकेचे महत्व व आवश्यकता – श्री सुभाष भावे	89-93
25.	Career & Entrepreneurship Opportunities in Gardening – Dr. Umesh Kanerkar	94-100
26.	पर्यावरण संवर्धन आणि देशी प्रजातीतील पळस वृक्षाचे महत्त्व – डॉ. गणेश हेडावू	101-106
27.	A Garden for Butterfly – Dr. Gajendrasingh Pachlore	107-113
28.	Indoor Plants and Their Benefits – Dr. Minal Keche	114-118
29.	Palms: The Beauty of Garden - Dr. M. U. Ghurde	119-125
30.	जलवनस्पती: कमळाची लागवड व नैसर्गिक संवर्धन – डॉ. युगंधरा राजगुरे-गुल्हाने	126-131
31.	Medico-Garden: "An Ancient Tradition but Future Need" – Dr. Shrikant Patil	132-146
32.	Tools and techniques for cultivation and propagation of Orchids. - Mr. Gokul Bajaj	147-154
33.	Best Performer of the Course	155-156
34	Youtube Links	157

GARDEN REVITALIZING IDEAL NECESSITIES (GRIN 2021)

EDITORS

Dr. Suchita Khodke
Ex-President and Advisor, Amravati Garden Club &
Asst. Professor in Botany, Vinayak Vidnyan Mahavidyalaya, Nandgaon Kh.

Dr. Dinesh Khedkar
President, Amravati Garden Club &
Professor in Botany, Shri Shivaji Science College, Amravati

Dr. Rekha Maggirwar
Secretary, Amravati Garden Club &
Associate Professor in Botany, Shri Shivaji Science College, Amravati

Dr. Shashank Deshmukh
Treasurer, Amravati Garden Club &
Principal, Shri Shivaji Horticulture College, Amravati

Dr. Ganesh Hedawoo
Jt. Secretary, Amravati Garden Club &
Asst. Professor in Botany, Shri Shivaji Science College, Amravati

Mr. Subhash Bhave
Vice-President, Amravati Garden Club, Amravati &
Director, Kiran Nursery and Gardens, Amravati

Dr. Gajendrasingh Pachlore
Executive Member, Amravati Garden Club &
Asst. Professor in Zoology,
Vinayak Vidnyan Mahavidyalaya, Nandgaon Kh.

Dr. Umesh Kanerkar
Executive Member, Amravati Garden Club &
Asst. Professor in Botany, G. S. Tompe Mahavidyalaya, Chandur Bz.

- Published by -
Amravati Garden Club
H. No. 6, Shakuntal Colony
V.M.V. Road, Amravati, MS - 444 604 (India)

- Printed at -
Grow n Glow Cyberpark
19, District Sports Complex, Nagpur Road
Shivaji Nagar, Amravati MS - 444 604 (India)

ISBN No. 978-93-200-0000-6

ALL RIGHTS RESERVED
Article in this book is published with copyright holders and obtained permissions. While every effort has been made to trace copyright holders and obtain permission, this has not been made to every cases; any omissions brought to our attention will be remedied in future.

The moral rights of the authors has been asserted. This is book is provided to the participants of the two Certificate Course in Garden Revitalizing Ideal Necessities (GRIN) 1st August to 3rd October, 2021 on virtual platform of Amravati Garden Club, Amravati. It is subject to the condition that, it shall not, by way of trade or otherwise, be lent, resold, hired out, circlated without prior permission of the publisher, in any form of binding or cover other than that in which it is published.

Forward

Dr. V. R. Ghurde
Founder Member and Senior Advisor, Amravati Garden Club, Amravati
Bageshree N/82, Congress nagar, Amravati

Garden club is maintaining its aim to make citizens aware of the usefulness of gardening as a hobby, to retrieve all tensions of life to have rapo with nature, increase creativity provide work for all three 'H' i.e. Head, Heart and Hands. It is useful for all, from children to old age onces. Apart from global environmental benefits, it is a great thing to be with plants, enjoying and admiring the creation of nature.

Due to lock down and the Covid-19 period, to continue these activities was a great problem. No Garden visits, no workshop or no exhibitions.

Modern development paved the way and garden club took full advantage of it to reach our members as well as all interested ones irrespective of distance.

As a further step involving youth, formulation of a course on gardening is framed and executed. As a result a series of 10 chapters of workshops took place.

First one on propagation was the basic one, which gave new ones the ease of collection of plants, apart from nurseries.

Second one was regarding most enchanting and like plant the *Chrysanthemum*. Most of the details of *Chrysanthemum* culture, including perennation or propagation were covered.

Third one deviated attention from the flowers to foliage and one could understand the beauty of foliage as an integral part of the gardening.

Forth step took both flowers and foliage together into making of decorative, colourful arrangements and different type of themes.

The next step was more dedicated to creativity with patience and perseverance i.e. 'The Art of Bonsai'.

The next step came again as a more natural, beautiful in shape, sizes, colours and flowering i.e. Cacti, succulents and Adenium (The desert Rose).

The next step was again pertaining to beautiful, heavy flowering plants i.e. seasonals and hanging baskets involving, creativity with test of time.

The next step was interior hard and soft scaping comparatively a new concept but still familiar one in some homes who love dolls, pots driftwood etc.

The ninth one was suitably on gardening planning. It reminded you to plan before starting. Thinking before implementing and require proper knowledge of available space and the type of garden one wishes to have.

The last one is to boost entrepreneurs.

In every such workshops care is taken to provide maximum details with practicals. But still problem remains as to the purpose, achievement and skill in the procedures.

Present day culture of use and throw will hamper further progress. Inquisitiveness, search understanding science behind every step, imbibing love for plants, appreciation creativity will give ample returns.

This course should not be taken as a final or last word in gardening. At every step one will come across difficulties. Your love for plants and persistence, patience is required. Every good gardener is basically a good, observer, searcher and learner from failure only one learns the correct path.

In future much more detailed and deeper workshops will take place which will reply all doubts arising during personal work and the science behind it.

Happy Gardening !

Editorial

Dr. Suchita P. Khodke
Head & Asst. Professor in Botany,
Vinayak Vidnyan Mahavidyalaya, Nandgaon Kh.
E-mail ID: khodke.suchita@gmail.com (9823165900)



Dear plant Lovers,

Greetings to you all!

"A writer only begins a book, a reader finishes it" these words of Samuel Johnson still proves true every time a book meets with its true reader. I feel overjoyed to present before the reader community this assorted compilation of the insightful lectures conducted during the two month long Garden Revitalizing Ideal Necessities (G.R.I.N) certificate course in the form of a book.This book is an outcome of consistent affection and love showered by the Garden lovers on the Amravati Garden Club, Amravati. It was a long awaited demand and suggestion from the members and associated garden lovers to pen down the experience of the experts in the form ofbook, which could be used as a ready reference guide. Amravati garden club prioritise this long awaited suggestion and it has reflected in the wonderful creation "GREEN". This Book is in an electronic format so as to make a maximum reach to the ardent garden lovers. I am happy to mention that this E-Book covers vivid aspect of Gardening,art of bonsai making, landscaping, floral arrangement and entrepreneurial aspects of the gardening trade. This book will definitely help the garden enthusiast to find solution and remedial measure to the common problems and issues faced by them during gardening practise.

Amravati Garden club has made a revolutionary change in its approach during the lock down and has made an optimum use of innovative techniques. The online approach for seminar and workshop has been excellently utilize by the executive members and through G.R.I.N.has made it possible to connect the garden lovers across the India. The success of this book is equally shared by garden clubs institutional members along with Advisory and executive members, life time members and associated garden lovers. This book is cooperative efforts of all its contributors who have selflessly shared their expertise and experience in the form of their respective articles. I am happy to share that the book has ISBN number and contain a legitimate material contributed from the experts.

I proudly present this book to the reader with a sense of great responsibility and happiness and I assure that this book will definitely help its reader to explore and understand the science, technique and most importantly the fine art of gardening from "Soul to Soil".

Message



Dr. V. M. Bhale
Vice-Chancellor
Dr. Panjabrao Deshmukh Krishi Vidyapeeth,
Akola

I am delighted that Amravati Garden Club, in collaboration with many educational institutes, has organized Two Month Certificate Course entitled "Garden Revitalizing Ideal Necessities" (GRIN) from 1st August and concluding on 3rd October 2021. It is a splendid endeavour, a noble venture, and a creative step on the path for generating interest in gardening among students, researchers, and lay persons and opening new vistas for career opportunities. The course contents are very relevant in the present scenario and can achieve many goals.

Devoted efforts are needed to attain academic excellence by imparting quality education to develop professional human resources with entrepreneurial skills. Furthermore, addressing the thrust areas of research to develop advanced technologies and promote the farmer-centric transfer of technology for holistic growth of the horticulture sector is the need of the hour. Amravati Garden Club is striving hard to attain this vision by organizing such quality events. Therefore, I am more confident that the club must be unique through dedicated and concentrated efforts in all endeavours.

Today, India is one of the youngest countries globally, with more than 62% of the working-age group (15-59 years) and more than 54% of the population below 25 years of age. If the energy of our youth is channelized in the proper direction, then they can do wonders. I hope many youngsters must have been motivated in this course and realized the importance of conserving our nature.

I convey my best wishes to all the students and heartily congratulate the Executive Members of the club and all organizers of this course mammoth event.

Message



Dr. Dileep N. Malkhede
Vice-Chancellor
Sant Gadge Baba Amravati University, Amravati

I am gratified with the initiative by Amravati Garden Club, Amravati, to conduct a highly demanded course focused on developing apt skills for the young generation. At the dawn of National Education Policy, this Two Month Certificate Course in Garden Revitalizing Ideal Necessities is the best fit as expected anticipated. Our National Education Policy is envisioning integration of a variety of sectors in assimilating education with special emphasis on experiential learning with eventual earning of the skill to generate employers instead of job seekers.

Amravati Garden Club is a nationally acknowledged non-government organization transforming and emerging as an institution supporting academic establishments. The course structure was adopting multiple entry-exit, dynamic skill components, participatory learning and joyful continuous and comprehensive evaluation process, reflected novel thoughts of this institution. I am sure that the dedicated, enthusiastic, and proficiency bestowed participants of this course will definitely pursue their passion and exemplify to vigorously develop their own world. I appreciate the initiative, vision and scientific approach planned by Course Conveners and Coordinators.

I presume that Amravati Garden Club will carry out similar professional development-based tasks. It is the remarkable thing I found in the execution of this course is the involvement of various colleges across the state as course collaborators. Sant Gadge Baba Amravati University will also support every such resourceful enterprise in future.

I convey my sincere wishes to all the resource persons, authors and participants of the course.
Kind regards.

Medico-Garden
"An Ancient Tradition but Future Need"



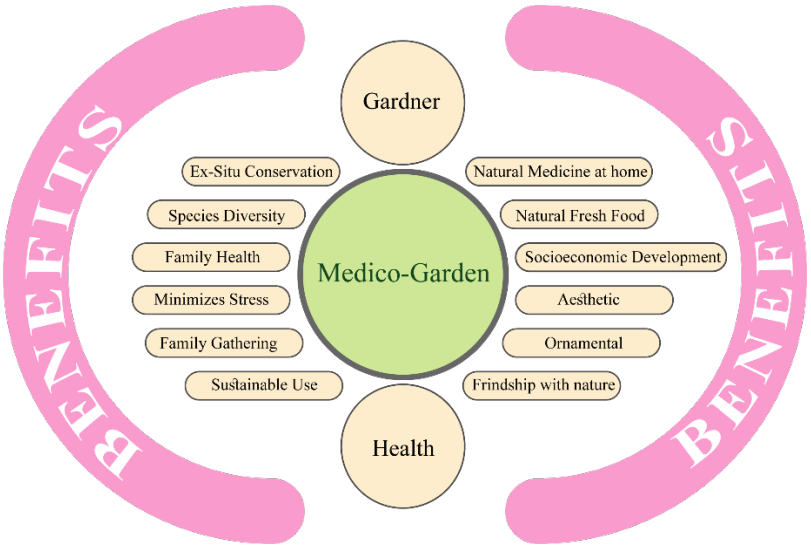
Mr. Shrikant Patil
Assistant Professor in Botany
Aadarsh Mahavidyalaya, Dhamangaon Rly.

E-mail ID: bionicshri@gmail.com (9011123037)

Abstract:

This article offers solution for promoting healthy lifestyle by taking help of ancient remedies available in the hands of nature through home gardening, ideal strata wise structure of medico-garden and how gardening activities and medicinal, food, aesthetic, ornamental properties of garden plants can be exploit for sustainable living of the humans in this dynamic structure of the society.

Due to the current COVID–19 pandemic situations, everyone in the world has a special kind of fear in their mind about the uncertain future of upcoming generations. Everyone in the society, everyone around your own world has become extremely cautious about the health. You can sense the pinch of fear in everybody's mind about health and remedy.Now a days we all are frequently listening the words related to the immunity, disease, hospital, etc., following and closely observing the data related to pandemic and diseased peoples around us and in the country or even around the globe also. Most of us in fact all of us are trying to find possible remedy on the basis of Ayurveda. This desire of humans can be easily fulfilled by using the ancient medicinal knowledge about the plants which are literally present around us or being domesticated by humans since thousands of years.



This article begins by reviewing the general information of garden plants in terms of their names, strata wise distribution, and medicinal properties followed by the method used by the author to gather information related to the garden plants. This article argues that beyond the skill and knowledge, self-inspiration is the key to develop and sustaining the home medico garden. The terminal part of the article will explain the relationship between your garden plant and Gardner can be considered as relationship we share with our family doctor and pharmacist. Where, role of the doctor or pharmacist is played by the group of medicinal plants planted in the home garden and role of the patient is played by the Gardner and his entire family members and sometime neighbours also and how you can choose medicinal plants to plant in your home-garden according to your need of medicine will be suggested.

Introduction:

Home-gardens are part of agriculture and food production system in the tropical as well as subtropical countries as a remedy to eliminate hunger, malnutrition, and diseases (Chakravarty *et al.*, 2018). These man-made gardens provide multiple goods to satisfy social cultural, and economic goods of the owners such as food, medicine, ornamental and spiritual wellbeing, fodder, fuel wood etc. (Qadir and Oster, 2004) and acts as a conduit between biological and social components of the society and ultimately conserving the species and genetic diversity (Hammer, Arrowsmith and Gladis, 2003). Home gardens are one of the most important hot spots for ex-situ conservation of plant (Das and Das, 2005). The garden reflects the wisdom of traditional culture and ecological knowledge that have traveling from one generation to the another over the years (Perrault-Archambault and Coomes, 2008). This study was undertaken in Amravati District, Dhamangaon Railway tahsil to understand the current status of home gardens in terms of diversity of the plants and how they are providing natural medicines to the peoples around followed by construction of an idea that anyone can develop a medico garden at their own place most likely home for fresh, hand-made, natural ayurvedic preparations.

Material and Methods:

The present study was conducted in Dhamangaon Tahsil District Amravati, Maharashtra state of India during August 2019 to June 2021. The study area is spread 18 km^2 in the south west of district Amravati, Maharashtra state, with coordinates as 20.7933° N, 78.1393° E. the average population is near about 21000 individuals.

Methodology:

Data was collected from different areas of Dhamangaon Tahsil including nearby villages, in which 50 respondents (Home-made Garden owners) were randomly selected from the whole samples by asking questionnaire and face to face interview. The data was collected and analyzed for the diversity of the plants in gardens and their traditional medicinal use. During the construction of the questionnaire, respondents' profile such as occupation, education, family size, homemade garden size, traditional medicinal knowledge etc. have been asked.

Plant overview was performed by utilizing perceptions, plant recognizable proof with neighborhood names, fundamental photos for additional ID. Information identifying with the variety and course of action of the plant species was done layers savvy in the chose home nursery.

Table No. 1: Strata wise prearrangement and diversity of the species in home garden

Sr. No.	Strata	Plants
1	First	Vegetables Potato, Pumpkin, Bottle gourd, Bitter gourd, Brinjal, Lady's finger, Bean, Cucumber, Radish, Carrot, Pea; medicinal/aromatic like Tulsi, *Aloe vera*, Mint, Garlic, Onion, Chilli, Coriander and flowers like Rose, *Chrysanthemum* and Marigold
2	Second	Fruits like Lemon, Banana, Papaya; flowers like *Hibiscus*, *Bougainvillea*, and medicinal/fencing like *Jatropha*, *Moringa*.
3	Third	Fruit/fodders like Jackfruit, Litchi, Bel, and timbers like Karanj
4	Fourth	Fruits like Mango, Jamun; timber/fodder, etc. like Shisham, Babhool, Neem, Siris, Teak, Neem, *Eucalyptus* and Bamboos.

Table No. 2: Details of Plant Species present in the home gardens

Sr. No.	Botanical Name	Local Name	Family	Plant Part used as Medicine	Uses
1	*Azadirecta indica*	Kadu Nimb, Neem	Meliaceae	Whole plant	Leaves has insect repellent properties; Inner bark helps against stomach problems

2	*Ocimum sanctum*	Tulas, Tulsi	Lamiaceae	Leaves	Plant is the symbol of religious and leaves are used with black pepper during cold & cough
3	*Adhatoda vasica*	Adulsa	Acanthaceae	Leaves	Excellent against cold cough and for tonic
4	*Spinacia oleracea*	Palak	Amaranthaceae	Leaves	Vegetable, excellent source of vitamins and minerals
5	*Allium cepa*	Kanda, Pyaaj	Liliaceae	Bulb, Leaves	Vegetable, anthelmintic, anti-inflammatory, antiseptic, antispasmodic, carminative, diuretic, expectorant
6	*Allium sativum*	Lasoon	Liliaceae	Bulb, Leaves	Vegetable, fevers, diabetes, rheumatism, intestinal worms, colic, flatulence, dysentery, liver disorders, tuberculosis, facial paralysis, high blood pressure, against high cholesterol, and bronchitis
7	*Mangifera indica*	Amba	Anacardiaceae	Fruit	Unripe fruit as pickle and ripe fruit as table purpose, high level of antioxidants supports heart health, digestion, eye health, skin health
8	*Annona reticulate*	Sitafal	Annonaceae	Fruit	Ripe fruit used as table purpose, anthelmintic, analgesic, anti-inflammatory,

					antipyretic, wound healing and cytotoxic effects
9	*Michelia champaca*	Champa	Annonaceae	Flower	Flower decorations.
10	*Coriandrum sativum*	Kothimbir, Sambar, Dhania	Apiaceae	Leaves, Seeds	Leaves as a vegetable and seed as a spice, stomach pain, constipation, diarrhea, gas (flatulence), nausea
11	*Daucus carota*	Gajar	Apiaceae	Root	Vegetable, pickle, excellent source of carotene and dietary fibers
12	*Cathranthus roseus*	Sadafuli, Sadabahar	Apocynaceae	Flower	Flower used for decoration and religious purpose; it has antimitotic properties
13	*Nerium indicum*	Kanher, Ganeri	Apocynaceae	Flower	Flower used for decoration and religious purpose
14	*Thevetia peruviana*	Kaner, Ghanti	Apocynaceae	Flower	Ornamental
15	*Amorphophallus paeoniifolius*	Suran, Suraskand	Araceae	Tuber	Vegetable, excellent against joint pain and good for gaining physical strength
16	*Colocasia esculanta*	Pekchi sag	Araceae	Tuber	Vegetable
17	*Eclipta prostrata*	Bhringraaj	Asteraceae	Leaves	Excellent brain tonic, improving the memory and hair growth
18	*Helianthus annuus*	Suryaful, Surajmukhi	Asteraceae	Seed	Flowers are large and showy, seeds are oil yielding, excellent source of fat

19	*Basella alba*	Poi	Basellaceae	Leaves	Vegetable, gastro-protective activity, ulcer healing, anti-inflammatory activity, wound healing activity
20	*Brassica nigra*	Mohari	Brassicaceae	Leaves, Seeds	Black mustard oil is used for the common cold, painful joints and muscles (rheumatism)
21	*Brassica oleracea*	Phoolgobi	Brassicaceae	Flower	Vegetable, pickle and dried for using in rainy season
22	*Brassica oleracea*	Bandhgobi	Brassicaceae	Flower	Vegetable, pickle and dried for using in rainy season
23	*Raphanus sativus*	Mula, Muli	Brassicaceae	Root	Vegetable, pickle
24	*Bauhinia variegata*	Koinar	Caesalpiniaceae	Leaves and Flowers	Vegetable
25	*Calendula officinalis*	Genda	Calenduleceae	Leaves, flower	Leaf juice used during ear pain. Flower are used for decoration as well as for religious purpose
26	*Chenopodium album*	Bhatua	Chenopodiaceae	Leaves	Vegetable
27	*Commelina bengalensis*	Kenna	Commelinaceae	Leaves	Vegetable
28	*Cucurbita pepo*	Kaddu	Cucurbitaceae	Fruit	Vegetable
29	*Lagenaria ceraria*	Lauki	Cucurbitaceae	Fruit	Vegetable

30	*Luffa acutangula*	Dodka	Cucurbitaceae	Fruit	Vegetable
31	*Luffa aegyptiaca*	Dodka chopda	Cucurbitaceae	Fruit	Vegetable
32	*Momordica charantia*	Karela	Cucurbitaceae	Fruit	Vegetable
33	*Jatropha curcas*	Ratanjyoti	Euphorbiaceae	Whole plant	Tooth stick and fencing around home garden
34	*Pedilanthus tithymaloides*	Sij	Euphorbiaceae	Leaves	Malaria
35	*Acacia nilotica*	Babool	Fabaceae	Wood	Fuel wood, tooth related problems
36	*Butea monosperma*	Palash	Fabaceae	Leaves	Good against boils, pimples can be controlled.
37	*Cajanus cajan*	Arhar, Tur	Fabaceae	Leaves and Seed	Leaves anaemia, diabetes and seeds for flour
38	*Cassia fistula*	Amaltas	Fabaceae	Flowers	Flowers are excellent against stomach related problems like dysentery, ornamental
39	*Cassia tora*	Tarota	Fabaceae	Leaves	Excellent early monsoon vegetable, acrid, laxative, antiperiodic, anthelmintic, ophthalmic, liver tonic, cardiotonic and expectorant
40	*Cicer arietinum*	Chana	Fabaceae	Leaves, Seeds	Leaves as vegetable and seeds for other various purpose
41	*Dalbergia sissoo*	Shisam	Fabaceae	Stem	Excellent for house hold use and furniture

42	*Indigofera tinctoria*		Fabaceae	Leaves	Vegetable
43	*Lablab purpureus*	Waal	Fabaceae	Fruit	Vegetable, excellent source of vitamins and minerals
44	*Pongamia pinnata*	Karanj	Fabaceae	--	Ornamental, fencing of the garden
45	*Mimosa pudica*	Laajwanti, Lajalu	Fabaceae	Root	Leprosy, dysentery
46	*Phaseolus vulgaris*	Common bean, chawali	Fabaceae	Fruit	Vegetable, excellent source of vitamins and minerals
47	*Pisum sativum*	Matar	Fabaceae	Fruit	Vegetable, excellent source of vitamins, dietary fiber and minerals
49	*Trigonella foenum - graecum*	Methi	Fabaceae	Leaves, Seeds	Very popular vegetable, managing diabetes, increasing breast milk production, improving sex drive and performance, aiding digestion, relieving menstrual pain, and managing weight
50					
51	*Marjorana hortensis*	Marwa	Lamiaceae	Leaves	Essential oil, improve appetite
52	*Mentha arvensis*	Pudina	Lamiaceae	Leaves	Leaves used during summer for preventing sun stroke
53	*Tectona grandis*	Sagwan	Lamiaceae	Timber	Furniture
54	*Vitex negundo*	Nirgundi	Lamiaceae	Leaves, fruit	Leaf juice for reducing fat and ulcers. Flowers are useful in fever and diarrhea

55	*Punica granatum*	Dalimb	Lythraceae	Fruit, Flowers	Ripe fruit used as table purpose, Fruits used against cough, Appetizer, against acidity
56	*Hibiscus rosa-sinensis*	Jaswand	Malvaceae	Flowers	Flowers and leaves used to treat against cancer, to lower blood pressure and good skin cleanser
57	*Grewia asiatica*	Phasla	Malvaceae	Fruits	Pickle
58	*Bombax cieba*	Silk Cotton	Malvaceae	Seed, Spikes on Bark	Used against stomach problems
59	*Abelmoschus esculentus*	Bhindi	Malvaceae	Fruit	Vegetable
60	*Tinospora cordifolia*	Gulwel	Menispermaceae	Stem, Root	Root extract helps in stomachache, boosts immunity
61	*Albizia lebbeck*	Shiras	Mimosaceae	Stem	Ornamental, furniture
62	*Ficus elastic*	Rubber	Moraceae	Leaves	Fodder, religious purpose
63	*Zingiber officinalis*	Zingiber officinalis	Zingiberaceae	Rhizome	Paste of ginger with sugar, salt and black pipper are used during cold and cough
64	*Curcuma longa*	Haldi	Zingiberaceae	Rhizome	Powder of turmeric used with milk as an antibiotic
65	*Aloe barbandensis*	Aloe vera	Asphodelaceae	Leaves	Leaves gel applied on burn
67	*Cissus quadrangularis*	Hadjod	Vitaceae	Stem	Stem paste used in bone fracture
68	*Solanum melongana*	Baingan, wange	Solanaceae	Fruit	Vegetable

69	*Solanum lycopersicum*	Tomato	Solanaceae	Fruit	Vegetable and sauce
70	*Cestrum nocturnum*	Ratrani	Solanaceae	Flower	Flower used for decoration and religious purpose
71	*Capsicum annum*	Mirchi	Solanaceae	Fruit	Vegetable, pickle
72	*Madhuca longifolia*	Mahuwa, Moh	Sapotaceae	Fruit, Flower, Leaves	Leaf of the plant used as fodder. Local bear prepared from the fruit
73	*Aegle marmelos*	Bel	Rutaceae	Fruit, Leaves	Leaves used for religious purpose, juice during summer season, Used against stomach related problems
74	*Jasminium oleaceae*	Chameli	Rubiaceae	Flower	Flower used for decoration and religious purpose
75	*Rosa multiflora*	Gulaab	Rosaceae	Flower	Flower used for decoration and religious purpose; Petals of flower have medicinal properties to prepare gulkand protect against body heat
76	*Gardenia jasminoides*	Gandhraj, Batmogra	Rubiaceae	Flower	Flower used for decoration and religious purpose
77	*Ziziphus mauritiana*	Bor	Rhamnaceae	Fruit	Ripped fruit has excellent digestive properties
78	*Bambusa vulgaris*	Banbmoo	Poaceae	Stem, leaves	Fencing, agriculture implements
79	*Phyllanthus niruri*	Bhuiamla	Phyllanthaceae	Leaves	Extract Helps in constipation

80	*Sesamum indicus*	Til	Pedaliaceae	Seed	Acne
81	*Boerhavia diffusa*	Punarnava	Nyctaginaceae	Leaves and root	Leaves and root extract helps in jaundice
82	*Syzygium cumini*	Jambhool	Myrtaceae	Fruit and seed	Fruit and seed are used for diabetic purpose. Leaf of the plant used as fodder
83	*Psidium guajava*	Amrut, Jaamb	Myrtaceae	Fruit	Ripe fruit used as table purpose
84	*Eucalyptus globules*	Nilgiri	Myrtaceae	Leaves, Stem	Agricultural implements and leaf as medicinal purpose.
85	*Musa acuminate*	Banana, keli	Musaceae	Fruit	Vegetable, unripe fruit as pickle and ripe fruit as table purpose
86	*Ficus religiosa*	Pimpal	Moraceae	Leaves, Roots, inner bark of stem	Leaf as fodder and religious purpose
87	*Tabernaemontana divaricata*	Swastik, Chandini	Apocynaceae	Flower	Flower used for decoration and religious purpose, ornamental use.

Result and Discussion:

Strata in home garden

Strata wise distribution of garden plants has been presented in the table no. 1. In which plant species layered into the four strata. The first strata consist of annuals and herbaceous plants i.e., vegetables, ornamental, and medicinal. The second strata commonly included Papaya, Lemon, Banana, Ornamental shrubs and medicinal plants also. Third strata included Jack fruit, Litchi, Bel and timber species such as Karanja and Kachnar and last strata consist taller fruit and timber yielding species like Mango, Jamun, Shisham, Teak, Neem. Home gardens exhibit complex arrangement of plants both vertically and

horizontally. Vertical arrangement is as a result of variation in total height of the plants at their maturity and horizontal arrangement is because of intermixing of the species and individuals. The gardens are designed and managed on indigenous knowledge. These gardens harbour a wide diversity of local crops suited to social and traditional significance and are most promising and ecologically feasible option for the community The indigenous knowledge used by the communities after repeated trial and error is now being regarded as an invaluable resource of a Agri-diversity (Galluzzi et al. and Negri, 2010). It is believed that traditional home garden practices depend on the type of human community, tradition, needs and beliefs (Chakravarty *et al.*, 2018). Home gardens are the sites that have long been considered as signs of prestige and pride. They are complex, multi-storied environments with very high species diversity and a wide range of varied ecological micro-niches (Galluzzi, Eyzaguirre and Negri, 2010) traditionally integrated within a larger surrounding ecosystem (Chakravarty *et al.*, 2018). The choice of plant species, their arrangement and management vary between and within tropical home gardens in the same community (Méndez et al., 2001). Medicinal plants are planted in the lower strata of multistrata systems such as home gardens (Rao et al., 2004).

Plant diversity in the home gardens:

The plant diversity in the form of local (vernacular) names, botanical name, family and their uses has been mentioned in the table number 2. In the current study, there are 87 species, 41 families and their medicinal, ornamental, aesthetic, food, uses has been recorded. The dominating family recorded is Fabaceae with 15 species. Genera *Ficus* and *Solanum* was represented by three species. Similarly, many studies across the world have been recorded wide diversity in the home gardens (Méndez et al., 2001). Diversity in the species, their size, shape and plant density vary from place to place depending on cultural ecological and socio-economic factors. Species diversity of perennial plants was reported higher in-home gardens located in slopes while diversity of annuals was greater in-home gardens at flat land (Nuberg et al., 1994). Predominance of trees is common especially the fruit species particular when these are crucial for the diet of household members in terms of vitamins and fibres. Other edible species, wild or domesticated are the next most represented category (Perrault-Archambault and Coomes, 2008).

Utilization of the garden plants also recorded in the table no. 2. In which nearly all plants have medicinal importance, some of them are ornamental and 90% of them are edible as a food to human beings and as a fodder for the live stalk. Some of them can be useful as a timber yielding plants. Medicinal plant species was identified as one of the key

characteristics of traditional home gardens (Rao et al., 2004). Medicinal plants in home gardens are either deliberately cultivated or they come up spontaneously as wild and weedy species (Rao et al., 2004). These gardens are not only important sources of food, fodder, fuel, medicines, spices, construction materials and income in many countries around the world, but are also important for in situ conservation of a wide range of plant genetic sources (Das and Das, 2005). In terms of composition, high diversity of species with an immediate use in the home is the most prominent feature of home gardens (Perrault-Archambault and Coomes, 2008).

So, with this study common citizens who are really want to construct a home medicinal garden can plant strata 1 vegetable or shrub grade plants if they have very limited area at their home (Urban peoples). Those who have moderate area for plantation of medico-garden, can chose vegetable, herb, shrub and perennials. At last, those peoples have large space for plantation, can plant every kind of plant including vegetable, herb, shrub, or even large size biennial trees also.

The main advantage that can emerge from Medico-planting isn't just getting normal medications yet additionally expanded social capital and associations. As kids cooperate to plant and make something significant, the outcome is a further developed connection between them. Moreover, cultivating can be an extraordinary chance for guardians and youngsters to hang out. The associations can be reinforced significantly encourage through trading and sharing these developed plants. Sharing plants is a gift that has life span and reason behind it. These plants could last years and give medications, foods grown from the ground to kids and their families, further encouraging appreciation for giving and cultivating.

References:

1) Chakravarty, S. *et al.* (2018) ‘Homegardens: Drops to sustainability’, *Agroforestry: Anecdotal to Modern Science*, (April), pp. 517–527. doi: 10.1007/978-981-10-7650-3_20.
2) Das, T. and Das, A. K. (2005) ‘Inventorying plant biodiversity in homegardens: A case study in Barak Valley, Assam, North East India’, *Current Science*, 89(1), pp. 155–163.
3) Galluzzi, G., Eyzaguirre, P. and Negri, V. (2010) ‘Home gardens: Neglected hotspots of agro-biodiversity and cultural diversity’, *Biodiversity and Conservation*, 19(13), pp. 3635–3654. doi: 10.1007/s10531-010-9919-5.
4) Hammer, K., Arrowsmith, N. and Gladis, T. (2003) ‘Agrobiodiversity with emphasis

on plant genetic resources', *Naturwissenschaften*, 90(6), pp. 241–250. doi: 10.1007/s00114-003-0433-4.

5) Méndez, V. E., Lok, R. and Somarriba, E. (2001) 'Interdisciplinary analysis of homegardens in Nicaragua: Micro-zonation, plant use and socioeconomic importance', *Agroforestry Systems*, 51(2), pp. 85–96. doi: 10.1023/A:1010622430223.
6) Nuberg, I. K., Evans, D. G. and Senanayake, R. (1994) 'Future of forest gardens in the Uvan uplands of Sri Lanka', *Environmental Management*, 18(6), pp. 797–814. doi: 10.1007/BF02393611.
7) Perrault-Archambault, M. and Coomes, O. T. (2008) 'Distribution of agrobiodiversity in home gardens along the Corrientes River, Peruvian Amazon', *Economic Botany*, 62(2), pp. 109–126. doi: 10.1007/s12231-008-9010-2.
8) Qadir, M. and Oster, J. D. (2004) 'Crop and irrigation management strategies for saline-sodic soils and waters aimed at environmentally sustainable agriculture', *Science of the Total Environment*, 323(1–3), pp. 1–19. doi: 10.1016/j.scitotenv.2003.10.012.
9) Rao, M. R., Palada, M. C. and Becker, B. N. (2004) 'Medicinal and aromatic plants in agroforestry systems', *Agroforestry Systems*, 61–62(1–3), pp. 107–122. doi: 10.1023/B:AGFO.0000028993.83007.4b.
10) Chakravarty, S. *et al.* (2018) 'Homegardens: Drops to sustainability', *Agroforestry: Anecdotal to Modern Science*, (April), pp. 517–527. doi: 10.1007/978-981-10-7650-3_20.
11) Das, T. and Das, A. K. (2005) 'Inventorying plant biodiversity in homegardens: A case study in Barak Valley, Assam, North East India', *Current Science*, 89(1), pp. 155–163.
12) Galluzzi, G., Eyzaguirre, P. and Negri, V. (2010) 'Home gardens: Neglected hotspots of agro-biodiversity and cultural diversity', *Biodiversity and Conservation*, 19(13), pp. 3635–3654. doi: 10.1007/s10531-010-9919-5.
13) Hammer, K., Arrowsmith, N. and Gladis, T. (2003) 'Agrobiodiversity with emphasis on plant genetic resources', *Naturwissenschaften*, 90(6), pp. 241–250. doi: 10.1007/s00114-003-0433-4.
14) Méndez, V. E., Lok, R. and Somarriba, E. (2001) 'Interdisciplinary analysis of homegardens in Nicaragua: Micro-zonation, plant use and socioeconomic importance', *Agroforestry Systems*, 51(2), pp. 85–96. doi:

10.1023/A:1010622430223.

15) Nuberg, I. K., Evans, D. G. and Senanayake, R. (1994) 'Future of forest gardens in the Uvan uplands of Sri Lanka', *Environmental Management*, 18(6), pp. 797–814. doi: 10.1007/BF02393611.

16) Perrault-Archambault, M. and Coomes, O. T. (2008) 'Distribution of agrobiodiversity in home gardens along the Corrientes River, Peruvian Amazon', *Economic Botany*, 62(2), pp. 109–126. doi: 10.1007/s12231-008-9010-2.

17) Qadir, M. and Oster, J. D. (2004) 'Crop and irrigation management strategies for saline-sodic soils and waters aimed at environmentally sustainable agriculture', *Science of the Total Environment*, 323(1–3), pp. 1–19. doi: 10.1016/j.scitotenv.2003.10.012.

18) Rao, M. R., Palada, M. C. and Becker, B. N. (2004) 'Medicinal and aromatic plants in agroforestry systems', *Agroforestry Systems*, 61–62(1–3), pp. 107–122. doi: 10.1023/B:AGFO.0000028993.83007.4b.

Vivek Kumar
Ram Prasad
Manoj Kumar *Editors*

Rhizobiont in Bioremediation of Hazardous Waste

Springer

Rhizobiont in Bioremediation of Hazardous Waste

Vivek Kumar • Ram Prasad • Manoj Kumar
Editors

Rhizobiont in Bioremediation of Hazardous Waste

Springer

Editors
Vivek Kumar
Himalayan School of Biosciences
Swami Rama Himalayan University
Dehradun, Uttarakhand, India

Ram Prasad
Department of Botany
Mahatma Gandhi Central University
Motihari, Bihar, India

Manoj Kumar
Centre for Life Sciences
Central University of Jharkhand
Ranchi, Jharkhand, India

ISBN 978-981-16-0601-4 ISBN 978-981-16-0602-1 (eBook)
https://doi.org/10.1007/978-981-16-0602-1

© The Editor(s) (if applicable) and The Author(s), under exclusive license to Springer Nature Singapore Pte Ltd. 2021
This work is subject to copyright. All rights are solely and exclusively licensed by the Publisher, whether the whole or part of the material is concerned, specifically the rights of translation, reprinting, reuse of illustrations, recitation, broadcasting, reproduction on microfilms or in any other physical way, and transmission or information storage and retrieval, electronic adaptation, computer software, or by similar or dissimilar methodology now known or hereafter developed.
The use of general descriptive names, registered names, trademarks, service marks, etc. in this publication does not imply, even in the absence of a specific statement, that such names are exempt from the relevant protective laws and regulations and therefore free for general use.
The publisher, the authors, and the editors are safe to assume that the advice and information in this book are believed to be true and accurate at the date of publication. Neither the publisher nor the authors or the editors give a warranty, expressed or implied, with respect to the material contained herein or for any errors or omissions that may have been made. The publisher remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

This Springer imprint is published by the registered company Springer Nature Singapore Pte Ltd.
The registered company address is: 152 Beach Road, #21-01/04 Gateway East, Singapore 189721, Singapore

Preface

Owing to the speedy development and sprouting anthropogenic activities and accomplishments, the native biological diversity or our natural ecosystem is being disrupted. Development of technology, unwarranted application of chemicals in agriculture, and unwanted human activities have caused a huge burden on our ecosystem. This has resulted in probably intimidating nature's dynamics by making particular undesirable compounds. Application of microorganisms to bioremediate hazardous contaminants in an environment is a state-of-the-art approach and also a field of passionate curiosity. Though biological know-how has been employed for years in treating contaminants in soil and water system. The success and cost-efficacy of this technology has led to its application in remediating perilous chemicals at contaminated sites. Achievements attained by exploiting the inherent metabolic potentials of microbes to detoxify the soils, sediments, and aquatic systems have reinvigorated continued research interest in biological remediation.

Within the last couple of years, the flora-based bioremediation tactic has evolved into a significant, feasible option for cleansing of polluted sites. This tactic now has earned the novel tag 'phyto-remediation' and has been documented for some specifically interesting features, such as its eco-friendly nature and importantly its cost-effectiveness. Later on, it was felt that this technology is slow and it can be converted into better approach for decontamination of environment. This strategy can be made more efficacious by employing potential and synergistically capable pollutant bioremediating microbiome, which is also quite popular, cost-effective, and environmentally feasible approach. The application of 'rhizobiont' or rhizo-microbiomes in remediation approach will clearly and certainly ascertain an advantage and will be known as 'natural attenuation'.

In this compilation, we also try to encapsulate contemporary and current knowledge about contaminates biodegradation in rhizospheric zone by plant (rhizo)-microbiome interfaces and communications based on evolving techniques and nanotechnology. This will help us in better understanding the process of synergism between the 'plant-rhizo-microbiome' to further exploit rhizo-bioremediation pursuit in a better way. Additionally, a better perception and knowledge of the collaborations might lead to techniques development to bioengineer rhizospheric microbes for better contaminants biodegradation.

The book 'Rhizobiont in Bioremediation of Hazardous Waste' attempts to undertake biological remediation issues of contaminated environment and also showcases the explicit know-hows realistic in bioremediation of foremost interest for research in the field, with special attention on advancement in conventional biological approaches. We have paid focus on the role of efficient microbes or exploiting the synergism of plant and microbes towards effective process of bioremediation. We have also discussed management approaches, such as composting technology for managing pretentious environment in an eco-friendly way. Examples of successful bioremediation applications are illustrated in pesticides, heavy metals, wastewater, hydrocarbons, mangrove forest pollution, antibiotics in aquatic system, and many more. For an effective bioremediation process, microbes must attack enzymatically on the contaminants and transform them to innocuous outcomes. Moreover, the bioremediation approach can only be effectual when environmental conditions favour microbial survival, proliferation, and action. In field conditions, managing the ecological factors favouring the microbial growth will certainly lead to degradation of contaminants at a quicker rate, since similar to other approaches, bioremediation technology do have its own limitations.

To better understand the bioremediation process, it is also important to comprehend the particular chemical composition of original contaminant at the site and the autochthonous microbial populations. This edition also provides updated information about microbial bioremediation approaches and an understanding of the challenges in biodegradation technology. It is a beneficial resource for students, researchers, academicians, environmental professionals, and policymakers. We unreservedly thank all the contributors who have proficiency in this field of research for their innovative, interesting chapters and their help in making this book a successful attempt.

Dehradun, India — Vivek Kumar
Motihari, India — Ram Prasad
Ranchi, India — Manoj Kumar

Contents

1 **Plant–Microbe Interactions for Bioremediation of Pesticides** 1
Edson dos Anjos dos Santos, Dênis Pires de Lima, Denise Brentan Silva, Maria Rita Marques, and Amanda Dal'Ongaro Rodrigues

2 **Combined and Sustainable Techniques in Remediation of POPs-Contaminated Soil Sites** 25
Volodymyr V. Harkavenko and Sergey S. Seryy

3 **Biosurfactants: A Green and Sustainable Remediation Alternative** 49
Grazielly Maria Didier de Vasconcelos, Jéssica Mulinari, Talita Corrêa Nazareth, Éllen Francine Rodrigues, Bianca Chieregato Maniglia, and Cristiano José de Andrade

4 **Biosurfactant Mediated Remediation of Heavy Metals: A Review** 73
Ruchira Malik and Savita Kerkar

5 **Surface-Active Agents from *Pseudomonas* Emulsify *n*-Hexadecane: Past, Present, and Future Trends** 87
Sivamurugan Vajiravelu, K. C. Ramya Devi, R Rachel Veronica, and K. Mary Elizabeth Gnanambal

6 **Application of Bio-Nanoparticles in Biotechnological Process Focusing in Bioremediation** 115
Paula Paterlini, Cintia Mariana Romero, and Analía Alvarez

7 **Plant–Microbe Interactions in Attenuation of Toxic Waste in Ecosystem** 131
Monday Ubogu and Ejiro Akponah

8 **Biotransformation of Pollutants: A Microbiological Perspective** . . . 151
Jupinder Kaur and S. K. Gosal

9 Plant–Microbe Interactions in Bioremediation of Toxic Wastes in Tropical Environment 163
Angela Chika Udebuani, Chidinma Ogochukwu Ukachukwu, Emmanuel Uzoma Onweremadu, and Ifeanyi Charles Okoli

10 Advanced Bioremediation Strategies for Mitigation of Chromium and Organics Pollution in Tannery 195
Manikant Tripathi, Durgesh Narain Singh, Nivedita Prasad, and Rajeeva Gaur

11 Current Approaches in Bioremediation of Toxic Contaminants by Application of Microbial Cells; Biosurfactants and Bioemulsifiers of Microbial Origin 217
Amrita Kharangate-Lad and Nezlyn Cressida D'Souza

12 Microbial Scavenging of Heavy Metals Using Bioremediation Strategies 265
Ghada Abd-Elmonsef Mahmoud

13 Plant–Microbe Interaction in Attenuation of Toxic Wastes in Ecosystem 291
Kingsley Erhons Enerijiofi and Beckley Ikhajiagbe

14 PGPR in Management of Soil Toxicity 317
Jupinder Kaur

15 Earthworms, Plants, and GMO's Towards Natural Bioremediation 345
Rajalakshmi Sridharan and Veena Gayathri Krishnaswamy

16 Mitigation of Hazardous Contaminants: A Phyto-Microbiome Approach 363
Sandra Pérez Álvarez, Eduardo Fidel Héctor Ardisana, Sergio Guerrero Morales, and Abdon Palacios Monarez

17 Microbes: A Potential Tool for Bioremediation 391
Nilesh Sonune

18 Physical, Chemical, and Biological Remediation Techniques for Textile Effluents in Context with Developed and Developing Countries 409
Anum Mahmood, Barira Bilal, Zainab Naeem, and Shazia Iram

19 Remediation of Toxic Environmental Pollutants Using Nanoparticles and Integrated Nano-Bio Systems 443
Amrita Kharangate-Lad and Nezlyn Cressida D'Souza

20 Bioremediation of Wastewaters 483
Oluwadara O. Alegbeleye

21 Occurrence and Attenuation of Antibiotics in Water Using Biomass-Derived Materials 511
Nhamo Chaukura, Courtie Mahamadi, Edmore Muzawazi, and Tendai Sveera

22 Mangrove Forest Pollution and Remediation in the Rhizosphere . . . 531
Ali Ranjbar Jafarabadi, Elham Lashani, and Hamid Moghimi

23 Biotherapeutic Approaches: Bioremediation of Industrial Heavy Metals from Ecosphere 565
Reyed M Reyed

About the Editors

Vivek Kumar is an Associate Professor at the Himalayan School of Biosciences, Swami Rama Himalayan University, Jolly Grant, Dehradun, India. He leads the plant-microbe-interaction and microbial ecology research group at his institute. He serves as an editor and reviewer of several reputed international journals and research projects. He has more than hundred publications to his credit including research papers, book chapters and review articles. He has also authored one practical manual book and edited several books with Springer Nature. Dr. Kumar also served as Microbiologist for eight years in Department of Soil and Water Research, Public Authority of Agricultural Affairs & Fish Resources, Kuwait, where he was involved in policy research, advisory services and projects formulation related to sustainable agriculture and environment in Kuwait. He has been credited with first time reporting and identification of Pink Rot inflorescence disease of Date palm in Kuwait caused by Serratia marcescens. He has also organized number of conferences/workshops as convener/ organizing secretary. He has been awarded 'Young Scientist Award' for the year 2002 in 'Agricultural Microbiology' by the Association of Microbiologists of India (AMI). He has been principle investigator of several projects of national fundings.

Ram Prasad is an Associate Professor at the Department of Botany, Mahatma Gandhi Central University, Motihari, Bihar, India. His research interest includes applied microbiology, plant-microbe interactions, sustainable agriculture, and nanobiotechnology. Dr. Prasad has more than 150 publications to his credit, including research papers, review articles & book chapters and five patents issued or pending. He has also edited and authored several books. Dr. Prasad has twelve years of teaching experience and has been awarded the Young Scientist Award & Prof. J.S. Datta Munshi Gold Medal by the International Society for Ecological Communications; FSAB fellowship by the Society for Applied Biotechnology; the American Cancer Society UICC International Fellowship for Beginning Investigators, USA; Outstanding Scientist Award in the field of Microbiology by Venus International Foundation; BRICPL Science Investigator Award and Research Excellence Award. He serves as an editorial board member in Frontiers in Microbiology, Frontiers in Nutrition, Academia Journal of Biotechnology, Phyton, International Journal of Experimental Botany including Series editor of Nanotechnology in

the Life Sciences, Springer Nature, USA. Previously, Dr. Prasad served as Assistant Professor Amity University Uttar Pradesh, India; Visiting Assistant Professor, Whiting School of Engineering, Department of Mechanical Engineering at Johns Hopkins University, United States and Research Associate Professor at School of Environmental Science and Engineering, Sun Yat-sen University, Guangzhou, China.

Manoj Kumar is an Associate Professor and Head, Centre for Life Sciences, Central University of Jharkhand, Ranchi, Jharkhand. Dr. Kumar has 16 years of research and teaching experience in the field of plant developmental biology. He has been associated with Bhagalpur University, Jawaharlal Nehru University, University of Pretoria, University of Melbourne, University of Ton Duc Thang for doctoral, postdoctoral research as well as visiting scientist. He has published valuable research in reputed journals and edited books. He has guided several students at master, M. Phil., doctorate and post-doctorate levels. He has been principle investigator of several projects of national funding agencies—DBT, DRDO etc. He is associated as editor and reviewer with several research journals and offering consultancy to several biotechnology firms at international level.

Plant–Microbe Interactions for Bioremediation of Pesticides

1

Edson dos Anjos dos Santos, Dênis Pires de Lima, Denise Brentan Silva, Maria Rita Marques, and Amanda Dal'Ongaro Rodrigues

Abstract

This chapter is dedicated to examining recent works about pesticides bioremediation by plant–microbe interaction, making them nontoxic, along with metabolite analyses resulting from enzymatic reactions. The worldwide constant progress of farming is directly associated with pesticide consumption. However, the increasing amount in its use is alarming considering its adverse outcomes in humans and other organisms. The over pesticide application causes the formation of non-biodegradable deposit in groundwater and soil. Environmental cleaning requests a cheaper and environmentally friendly bioremediation. Partnerships between microorganisms and plants (called bioremediation of phyto–microbes) are rather important in pesticides remediation by accumulation, degradation, adsorption, and volatilization. This process is able to transform pesticides into nontoxic or inactive compounds. In order to better approach these strategies, it is also important to deal with methodologies applied for analyses and identification of metabolites resulting from bioremediation, such as techniques of chromatography, mass spectrometry, and hyphenated techniques.

E. dos Anjos dos Santos (✉) · M. R. Marques · A. Dal'Ongaro Rodrigues
Laboratório de Bioquímica Geral e de Microrganismos (LBq), Instituto de Biociências, Universidade Federal de Mato Grosso do Sul (UFMS), Campo Grande, MS, Brazil

D. P. de Lima
Laboratório de Pesquisa 4 (LP4), Instituto de Química, Universidade Federal de Mato Grosso do Sul (UFMS), Campo Grande, MS, Brazil

D. B. Silva
Laboratório de Produtos Naturais e Espectrometria de Massas (LAPNEM), Faculdade de Ciências Farmacêuticas, Alimentos e Nutrição, Universidade Federal de Mato Grosso do Sul (UFMS), Campo Grande, MS, Brazil

© The Author(s), under exclusive licence to Springer Nature Singapore Pte Ltd. 2021

V. Kumar et al. (eds.), *Rhizobiont in Bioremediation of Hazardous Waste*,
https://doi.org/10.1007/978-981-16-0602-1_1

Keywords

Bioremediation · Microbes · Pesticides · Plant

1.1 Introduction

Environmental pollution is increasing with industrial growth and it is affecting soil, air, continental groundwater, and oceans (Azubuike et al. 2016). Annually, polluted air and contaminated water is killing more people than many diseases, such as AIDS, tuberculosis, and malaria, as well as natural disasters, hunger, smoking, and war combined (Langrigan et al. 2018). The application of pesticides has raised the impact to human health. A fraction of applied pesticides generate residue, which can be found in the atmosphere, soil, water, and food. They are even detected in the most southern regions, such as Antarctica (Maggi et al. 2019).

In fact, pesticides are considered indispensable for large agricultural producers to grow more food on less land, controlling diseases in crops, pests, and weeds (Gill and Garg 2014). However, these chemicals act not only on the target organisms but also on pollinizer insects, causing economic loss to other types of food production (DiBartolomeis et al. 2019).

An alternative to reduce harmful impacts to the environment is bioremediation. This technique has been presenting a sustainable alternative for the degradation and detoxification of contaminated sites. This method uses processes or biological activities employing living organisms (microorganism and plants) capable to modify or decompose pollutants, turning them into inert products. The process can be ex situ when the techniques involve removal of contaminants from sites and, transferring to a treatment area. In another way, in situ methods imply that contaminants are treated at the same area where they are present. The choice of any of the techniques is related to the cost, region, nature, and concentration of pollutants (Azubuike et al. 2016; de Lima et al. 2018).

Several different studies of bioremediation of organic compounds are described as, for example, tolerance to toxicity (Cocaign et al. 2013), biotransformation (de Lima et al. 2017), biosorption (Adnan et al. 2017), biodegradation (Perissini-Lopes et al. 2016), or mineralization (Khan and Fulekar 2017). All of them aim to decrease the toxicity of xenobiotic or their complete extinction.

1.2 Pesticides Characteristics and Residue Risks

The definition of pesticide may be "any substance or mixture of chemical substances or biological ingredients intended to repel, destroy or control any pest or regulate plant growth" (FAO 2020). Pesticides comprise many chemicals used for control insects, weeds, pathogenic fungi, rats, etc.; and other substances designed to combat microorganisms, algae, etc. (US Environmental Protection Agency 2010).

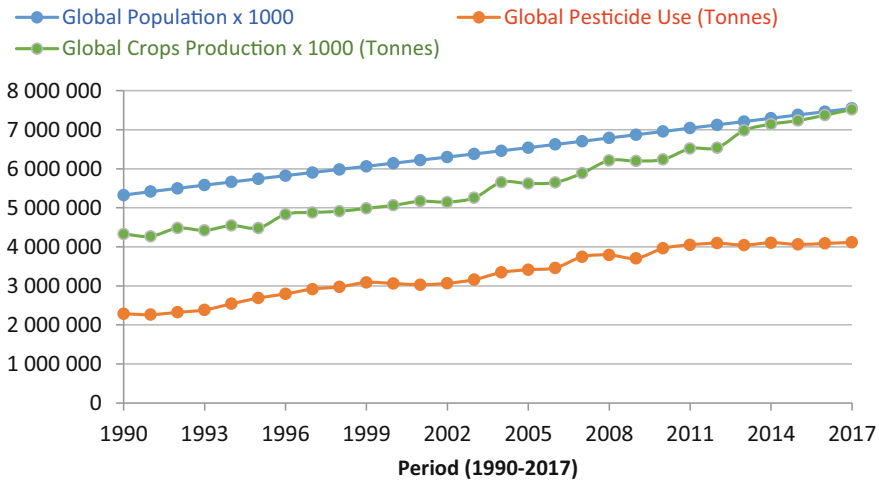


Fig. 1.1 Global population. Source: UN (2019). Global crops production, considering cereals, citrus fruit, coarse grain, primary fruit, legumes, tree nuts, primary vegetables, roots, and tubers; and global pesticide use and global crops production. Source: Food and Agriculture Organization of the United Nations—FAOSTAT (2020). Reproduced with permission

According to data of population growth in the world (Fig. 1.1), obtained from United Nations (UN), between the years 1990 and 2017 there was an exponential increase in the world population, reaching an approximate number of 7.547 billion people (UN 2019). The Food and Agriculture Organization of the United Nations (FAO) on farming statistics for the same period showed an expanding demand for world crop production, which reached an approximate value of 7.524 billion tons in the food production. This value considered only cereals, citrus fruit, coarse grain, primary fruit, legumes, tree nuts, primary vegetables, roots, and tubers (FAOSTAT 2020). If these trends continue, estimates of UN indicate that for the year 2050 the world food production has to duplicate (UN 2009).

In the same period (Fig. 1.1), it was observed that between the years 1990 and 2010 there was also a significant increase of pesticide application and, between 2010 and 2017, there was an apparent stagnation. However, in the year 2017 the value of 4,113,591.25 ton was the highest recorded until today (FAO). This can also be seen from FAO data in relation to the use of pesticides by area in the world (Fig. 1.2), maintaining an average of approximately 2.6 kg/ha (FAOSTAT 2020).

The countries of Asia and the Americas are among the largest producers and also consumers of herbicide by cultivation area (Fig. 1.2). Highlighting 2017, China and Japan used 13.07 and 11.76 kg/ha, respectively, and Brazil and USA used 5.95 and 2.54 kg/ha, respectively (FAOSTAT 2020). Although Brazil and the USA have a lower average use per area, they are considered major world consumers of herbicides. Only Brazil imported more than $ 2.46 billion in 2017 and USA $ 1.25 billion (FAOSTAT 2020).

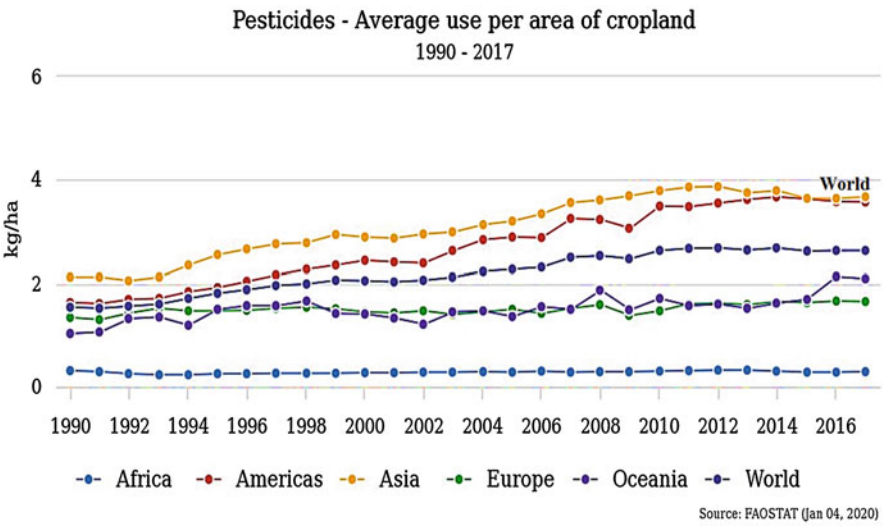


Fig. 1.2 Average amount of pesticides used per area (kg/ha) on continents and worldwide from 1990 to 2017. Source: Food and Agriculture Organization of the United Nations (http://www.fao.org/faostat/en/#data). Reproduced with permission

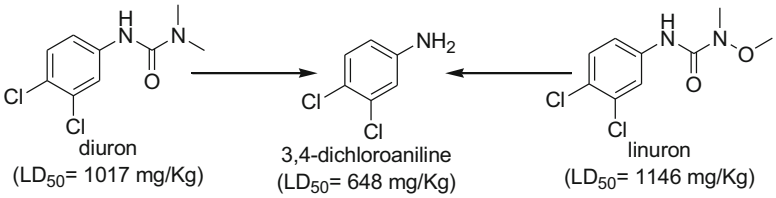


Fig. 1.3 Molecular structure and LD_{50} in rats of the diuron and linuron herbicides and the residue 3,4-dichloroaniline (3,4-D)

Nonetheless, pesticide residues are the main pollutants in agricultural areas, but the contamination can be spread by rain, rivers, and hydric basins (Wilkinson et al. 2017). A few decades ago, a significant increase in the use of more toxic pesticides to the environment and humans was reported (DiBartolomeis et al. 2019; Bilal et al. 2019; Morillo and Villaverde 2017). In addition, the indiscriminate and frequent usage of these compounds can increase the disorders caused by their toxicities, this happens because a large part of them end up accumulating in the soil and reaching groundwater (Gill and Garg 2014). Many of these compounds persist in the environment (Lushchak et al. 2018) and, they can generate more toxic products. For example, the diuron (Fig. 1.3, LD_{50} oral rat 1017 mg/kg) (Lewis 2004) and linuron (Fig. 1.3, LD_{50} rat oral 1146 mg/kg) (Lewis 1996), when deposited in soil or water become 3,4-dichloroaniline (3,4-D) (Fig. 1.3, LD_{50} rat oral 648 mg/kg) (Lewis 1996). 3,4-D is an extremely toxic and persistent substance (Castillo et al. 2014; de Lima et al. 2018).

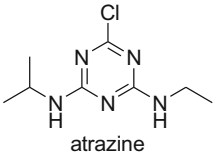


Fig. 1.4 Molecular structure of atrazine

Pesticides affect various organisms, causing harmful effects on the nervous, endocrine, respiratory, reproductive, circulatory, energetic, and hormonal regulation systems (Bilal et al. 2019). As an example of some of these effects, linuron can damage the production and function of male androgen hormones, causing changes in genes that encode testosterone synthesis, consequently, leading to dysfunctions in male reproduction (Bai et al. 2017). The atrazine herbicide (Fig. 1.4) causes endocrine disrupting effects on female and male in vertebrate species. These effects cause interferences in animal reproduction (Gely-Pernot et al. 2017).

In addition, studies with fish larvae have shown that atrazine was responsible for neurotoxic outcomes as the inhibition of the activity of the enzyme acetylcholinesterase (AChE) and disruption of the neuroendocrine system (Liu et al. 2016).

The bioremediation by microorganisms or plants, mainly via enzymes, can treat and recover polluted areas to their original condition (de Lima et al. 2018). More economically attractive, efficient, and scalable bioremediation processes have been used for years to minimize environmental impacts to remove contaminants than physical and chemical techniques (Bamforth and Singleton 2005; Megharaj et al. 2011; Azubuike et al. 2016).

Microorganisms and plants; alone or in association, present important benefits for the reduction of harmful effects of these pesticides, helping in the recovery of degraded or contaminated environments and contributing to the increasing demand for cultivation of food and renewable energy sources (Abhilash et al. 2012).

1.3 Phyto and Microbe Bioremediation

1.3.1 General Characteristics of Uptake and Translocation of Contaminants by Plants

Soil is a primary drain for chemical residues. In this sense, it can represent some risks; it can cause some type of intoxication, or it can be beneficial for live forms (Teng et al. 2014). Origin of the residues is medicines, hygiene products, agronomic products (pesticides and fertilizers in general), and industrial products (nanomaterials, polycyclic aromatic hydrocarbons—PAHs) among others (Qing et al. 2015; Pullagurala et al. 2018). The careless or accidental release of these wastes can endanger soil and biota. It is worth to mention that plants form the base of the food chain (Pullagurala et al. 2018). Consequently, environmental disorders affect the development of plants and, obviously, their consumers (Zhuang et al. 2009).

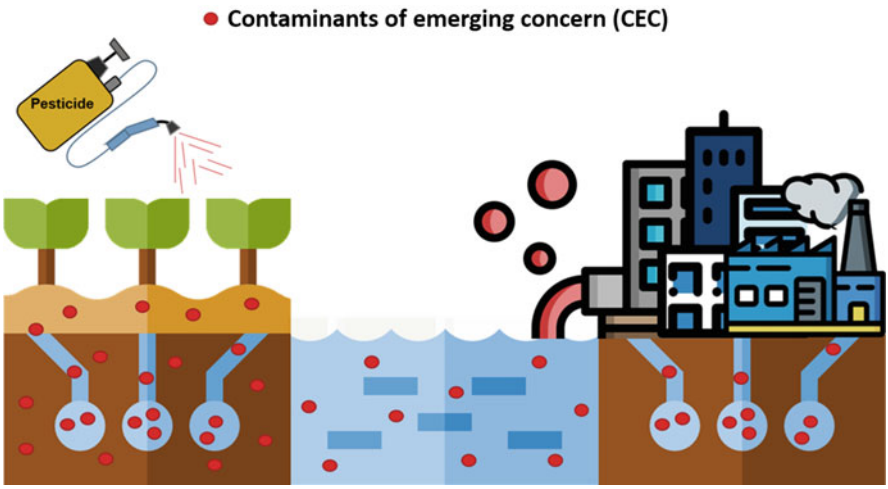


Fig. 1.5 Representation of environmental contamination by CEC

Plants are prone to absorb humic substances present in the soil and are applied for the bioremediation of heavy metals. Plants are able to absorb great amounts of metals in the soil and aquatic environments (Dixit et al. 2015). Phytoremediation has been important to remove heavy metals, such as Pb and Zn, from the soil for more than three centuries in some cultures worldwide (Cunningham and Berti 1993). However, these processes attracted attention nearly three decades ago (Sharma and Pandey 2014). Encompassing industrial progress, new types of chemical compounds were discovered and, most of them causing environmental damages (Pullagurala et al. 2018; Salimi et al. 2017). These residues are the main source of Contaminants of Emerging Concern (CEC), which includes several products, such as pharmaceuticals products, personal hygiene products, plasticizers and flame retardants, industrial dyes, chemical residues and mainly pesticides (Nilsen et al. 2019; de Lima et al. 2018; Salimi et al. 2017) (Fig. 1.5).

CECs fate in edaphic area is unpredictable, as they are subject to several environmental and climatic factors, such as runoff, air currents, and soil erosion (O'Conner et al. 2019; Marquès et al. 2016). Many plants are able to absorb CECs from the soil, changing their growth, development, metabolic pathways, among others (Morillo and Villaverde 2017).

In general, the CECs physical-chemistry properties play a central role since they are absorbed and translocated from the soil to the plant. The stability of some CECs allows them to remain in their original form within the plant. Absorption, in turn, will depend on the degree of hydrophilicity or hydrophobicity of CEC molecules, which Shone and Wood (1974) named "the ratio of chemical concentration in the transpiration stream to the concentration found in an external solution," or "Transpiration Stream Concentration Factor" (TSCF). For example, Garvin et al. (2015) showed that caffeine TSCF values were relatively higher than for endosulfans and

trichlorocarbons in soybeans, zucchini, and pumpkin plants. These compounds are more neutral or hydrophobic compounds than caffeine (a more hydrophilic compound), proving that hydrophilic compounds are translocated faster than hydrophobic ones.

Abiotic factors can greatly influence the absorption of CECs by plants. The concentration of humic acid; one of the main components of the soil, is important in the retention of CECs, mainly PAHs. Other factors such as clay crystal content, pH, soil mobility and age, hydraulic conductivity, water absorption capacity and wettability of soil are also parameters that have a major impact on the CECs absorption capacity (Ávila et al. 2014).

Additionally, chelating agents, whether added to soils artificially or secreted by the roots into the rhizosphere, can affect the absorption of contaminants by plants. The literature reports that air contaminants can be exchanged with the soil, forming residues or, they can be deposited on the leaves (Masih et al. 2012). Exchanges between air and leaves are often the main route of entry for some CECs, such as PAHs, phthalates, and polybrominated diphenyl ethers (Pullagurala et al. 2018).

The geospatial distribution of CECs also appears to be trending. The higher proportion of CECs are encountered at tropics and subtropic than temperate zones, due to the higher temperatures and the low concentration of organic matter in the soil (St-Amand et al. 2009). In addition, as expected, CECs are most found in urban than rural areas (Ligaray et al. 2016). Global climate change has a remarkable impact on the elimination of contaminants by photolysis, photodegradation, or biotransformation of PAHs (Marquès et al. 2016).

1.3.2 Phytoremediation

This methodology is associated with plant ability to deposit metals in vacuoles. After that, metals can be transported from the root to other parts through xylem vessels or in the use of complexing proteins or peptides known as phytochelatin and metallothionein. Both of them are rich cysteine residues, whose sulfhydryl group (-SH) is able to form stables complexes with heavy metal ions (Ali et al. 2013). Enzymes from plants play key roles in the metabolism of CECs. For instance, *N*-malonyltransferases, carboxylesterases, cytochromes P450, and glutathione transferases. Lipophilic contaminants can be absorbed and translocated throughout the plant tissue and, subsequently suffer enzyme transformations. The whole process comprises three phases. Phase I: reactive groups participate in hydrolysis and redox reactions of contaminants. Phase II: conjugations of glutathione, sugars, or amino acids to metabolites. Phase III: certain metabolites are either kept into vacuoles or are incorporated into the cell wall. In the absence of a secretory system, phases I, II, and II are of crucial importance for plants (Sandermann Junior 1992; Ohkawa et al. 1999; Dietz and Schnoor 2001).

In terrestrial ecosystems, trunks and branches provide a large part of the plant's visible biomass, which can act in storage or as a source for agrochemicals. Aquatic plants have higher biosource capacity or as in situ biofilter for water pollutants due to

their numerosity and low mobility. Additionally, they present a large surface area covered by a lipid-rich layer, providing them the capacity to absorb lipophilic pesticides. (Karthikeyan et al. 2014).

With regard to the bioremediation capacity of large trees, pesticides have been detected in pine and mango leaves in the classes of hexachlorocyclohexanes (HCHs) and hexachlorobenzenes (HCBs) (Calamari et al. 1995). Trees are able to remove pesticides from the soil and retain in their trunks, or storing them in bark, or even biotransform them as observed by Simonich and Hites (1995). In this case, 200 samples of bark from 32 countries were collected and 22 pesticides were identified, including degradation products and active ingredients, such as endosulfans, dichlorodiphenyltrichloroethane (DDT), HCHs, HCBs, dieldrin, aldrin, chlordane, and endrin.

Large trees have high retention capacity of soil xenobiotics such as agrochemicals in extensive areas. One of the most commonly used transformation processes is the use of xenobiotics for the synthesis of lignin (McCutcheon and Schnoor 2003). For bioremediation of contaminated groundwater, an alternative is the cultivation of trees with deep roots at the edge of the aimed areas, which will function as "solar pumps", in order to absorb contaminated water and eliminate contaminants through transpiration or bioaccumulation (Ferro et al. 2003).

1.3.3 Microbial Remediation

In 1991, Lynn Margulis and René Fester devised the term "holobiont" referring to an assemblage of a host and the many other species living in or around it. The term was later expanded and today, it defines the associations between communities of microorganisms—or microbiota—that interact with a given host. This interaction can vary from mutualistic to parasitic. Thus, the term holobiont is currently used for all metazoans, indicating the constitutive interactions between hosts and their associated microbiota, focusing on humans, animals, and plants (Simon et al. 2019). Therefore, when discussing phytoremediation, all communities associated with the plant species under study should be considered, including soil microorganisms, endophytic microorganisms, epiphytes, which are present not only in the roots, but in all plant tissues. It is necessary to include virus, fungi, actinomycetes, bacteria, and archaea.

When the microorganisms are fungi, the bioremediation performed by them can be defined as mycoremediation, that is, the ability of soil fungi, mycorrhizae, and endophytic fungi in bioremediation of contaminated areas. The fungi metabolic pathways for biotransformation of toxic and recalcitrant compounds are shown in Fig. 1.6. Including the intra and extracellular enzymatic processes made by peroxidases, laccases, transferases, and cytochrome P450 for detoxification and biodegradation or mineralization and a type of biodegradation, in which organic compounds are converted to inorganic constituents (Deshmukh et al. 2016; Olicón-Hernández et al. 2017; de Lima et al. 2018). Fungi can also accumulate xenobiotics and intermediate metabolites by organelles such

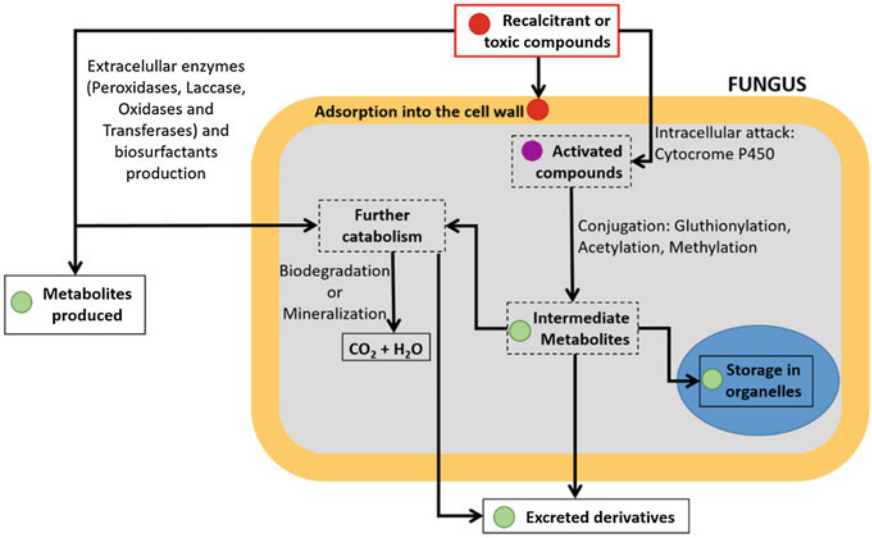


Fig. 1.6 Fungi bioremediation mechanisms of toxic and recalcitrant compounds

as intracellular lipid droplets (Verdin et al. 2005; Chang et al. 2015; Olicón-Hernández et al. 2017). Biosurfactants such as complex primary metabolites can also be excreted by fungi. These molecules have amphiphilic characteristics leading to the increase of molecular interactions (Cicatiello et al. 2016; Günther et al. 2017).

Some process exerted by fungi in the bioremediation of xenobiotics are shared by bacteria (Ijoma and Teker 2017). However, some process carried out by bacteria, such as bioaccumulation and biosorption are more limited to bioremediation of heavy metals (Abbas et al. 2018).

Bacteria associated with plants include phyllospheric, rhizospheric, and endophytic bacteria. The interactions between these microorganisms and their host plants augment plant survival, showing significant performance in the treatment of contaminated sites (Gkorezis et al. 2016).

1.4 Rhizosphere Systems and Plant–Microbe Interactions

Plants associated with bacteria (Zhang et al. 2014) and fungi (Asemoloye et al. 2017) perform an important function in the organic pesticides bioremediation. In these cases, the plants also function as buffer zones, capable of reducing the flow of pesticides, through bioaccumulation and/or metabolization (Morillo and Villaverde 2017).

Plant–microbe partnerships are related as a two-way road, mainly through associations between the rhizosphere and the plant root, aiming at survival in contaminate and nutrient deficient environments (Begum et al. 2019, Abhilash

et al. 2012). The rhizosphere comprising the area near to the plant roots supports microorganisms capable of degrading pesticides (Morillo and Villaverde 2017). The number of bacteria in the rhizosphere generally exceeds 10–100 times the volume of the soil itself (Erickson et al. 1995). Most of the soil microbiota are organotrophic and the main source of carbon for edaphic organisms is derived from plant roots and organic waste released during plant growth and development. The soil is enriched by plant nutrients such as simple sugars, polysaccharides, amino acids, low molecular weight exudates, mucilage that are used to microbial communities (Abhilash et al. 2012). A more specific approach to exudates from plant roots is a complex mixture of low molecular weight organic compounds, amino acids, carbohydrates, and certain enzymes during biodegradation and biotransformation of xenobiotics (Alvarez et al. 2012; Asemoloye et al. 2017; Asemoloye et al. 2019).

Angiosperms are commonly associated with fungi. Most of the time, these fungi need the plant alive to maintain their own growth and development. Some fungi form specific associations with the surface of plant roots; called ectomycorrhizae, while the endomycorrhizae grow internally in the roots (Davis et al. 2002).

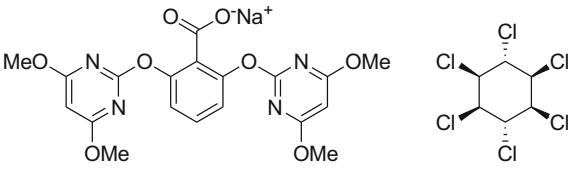
There is yet another type of interaction between microorganisms and plants called endophytism. Endophytic are fungi or bacteria that live their whole life cycle inside plants, intra or intercellularly without triggering any apparent damage or disease (Wilson 1995). They have been isolated from all the plants analyzed so far. They make complex interactions with their hosts, involving various biosignalization processes that generally end up with mutualistic interactions (Carroll 1988; Parker 1995). Endophytes benefit from the host by receiving protection and nutrition. Besides the production of antibiotics, they act in the protection from diseases in a dispute for colonization and nutrients against phytopathogens (Lee et al. 2004; Das and Varma 2009).

Plant roots have a major positive effect on the remediation of soil contaminants. Walton and Anderson (1990) analyzed a contaminated area by trichloroethylene (TCE) and they observed that the rhizosphere had a much greater capacity to degrade the contaminant than regions without rhizosphere. Subsequently, Anderson and Walton (1995) analyzed the properties of the rhizosphere microbial communities of five plant species associated with TCE degradation. They observed that about 70% was processed by mineralization, incorporation, and volatilization through the plant.

Eventually, in the future, these processes can be used for sustainable production of biomass used in the production of energy such as oilseeds for biodiesel and saccharide for alcohol.

1.5 Plant–Microbial Remediation

If the bioremediation of pesticides was performed solely by the plant, it would be affected by several factors, such as bioavailability in the soil and preclude the efficiency of the process (Morillo and Villaverde 2017). However, microorganisms increase the desorption of pesticides and assist in absorption and biodegradation



bispyribac sodium lindane

Fig. 1.7 Molecular structures of pesticides that have undergone plant–microbe bioremediation processes

processes while associate with plants by excreting organic acids through their roots (Morillo and Villaverde 2017).

Microorganisms themselves are great for bioremediation of pesticides, this is due to the diversity of enzymes they have, in addition to their expression capacity (de Lima et al. 2018; Huang et al. 2018; Spina et al. 2018). However, association of microorganisms with plants can increase the mechanisms by which biodegradation, absorption, bioaccumulation, and biotransformation of xenobiotics (Pereira et al. 2006; Alvarez et al. 2012; Asemoloye et al. 2017). In situ bioremediation with native microorganisms can be influenced by the unavailability of adequate levels of nutrients and/or environment in the polluted site (Smith et al. 2015).

Alternatively, the complementation with plants can significantly improve bioremediation efficiency, as plants assist in the formation of microbial habitats, such as increasing soil porosity and the transfer of mass of substrates and electron. In return, the plants receive nutrients of microorganisms. However, microorganisms associated with plant also improve plant growth through different processes and, reducing soil toxicity by removing contaminants (Gkorezis et al. 2016).

The phyto–microbe bioremediation strategy of contaminated environments is increasing, especially in the case of toxic pesticides (Asemoloye et al. 2017). As examples, the plant *Triticum aestivum* together with bacterial consortium. This association was able to carry out the degradation of the herbicide sodium bispyribac (Fig. 1.7). It was evidenced that only one bacterial consortium was able to remove the herbicide from the soil and provided the plant growth, increasing of its biomass. In contrast, the plant improved the action of the bacterial consortium to detoxify the soil and in this mutualism (Ahmad et al. 2019).

Another example is the bioremediation of environments containing the herbicide lindane (Fig. 1.7) or hexachlorocyclohexanes, this is an organochlorine pesticide (OP), where all the isomers are highly toxic to mammals (Álvarez et al. 2012). A synergistic association of grown *Megathyrsus maximus* (Jacq.) with rhizospheric fungi was able to remove lindane in the soil in 3 months. The study also highlighted the expression of enzymes, such as phosphoesterases and 1,2-dioxigenase catechol, in strains of rhizospheric fungi species (Asemoloye et al. 2017). The synergistic association was successful between plants and microorganisms and was also observed when plant root exudates are applied in association with microorganisms in bioremediation (Alvarez et al. 2012).

Interaction of plant and microorganisms depends on the climatic conditions in which they are adapted. Changes in the pattern of precipitation and temperature can

cause severe impacts, beneficial or not, on the interactions between plants and their symbionts (Rasmussen et al. 2019). This pattern becomes progressively special with current climate changes (Begum et al. 2019), creating ecological and evolutive uncertainties interactions (Rasmussen et al. 2019).

1.6 Metabolite Identification and Analyses of Bioremediation Reactions

The analyses of products and toxic compounds from bioremediation studies can be performed by analytical techniques coupled to detectors capable of responding to the presence of compounds by analytical analyses. Metabolites identification can also be performed when techniques that produce structural characterization information are applied. The main methodologies applied for analyses and identification of metabolites from bioremediation approaches are gas chromatography coupled to mass spectrometry (GC-MS) and high performance liquid chromatography coupled to mass spectrometry (HPLC-MS). Therefore, here it is focused in discussion about these methodologies; GC-MS and HPLC-MS, highlighting issues and application of mass spectrometry (MS).

GC-MS is a widely used trustable methodology to analyze non-polar, volatile, and thermostable compounds in scientific, technological, and industrial applications. It has been used for environmental monitoring, flavor and fragrance analyses (food and beverage), forensic analyses, detection and quantification of pesticides, pharmaceutical and petrochemical analyses, and others (Chauhan et al. 2014). Gas chromatography (GC) is an analytical methodology for separating compounds that use an inert gas as a mobile phase (usually helium) and commonly long capillary chromatographic columns. They are classified as long, medium, and short. Long columns (60–100 m) show higher resolution, but slow speed for the analyses. The most used columns are capillary, they are often fused silica coated with the liquid/polymer stationary phase internal surface (Zoccali et al. 2019; Rahman et al. 2015). This characteristic (different internal diameter) directly impacts in resolution, speed analysis, and capacity. Columns with 0.1 mm internal diameters have showed better results that are related to these properties (resolution and speed) (Rahman et al. 2015).

There are different stationary phases for GC columns and their choice is essential to develop efficient methods for separation of metabolites. In this sense, it should be considered the physical and chemistry properties of analytes (compounds). Different chromatographic columns can be purchased by several manufactures. Non-polar to polar columns can be founded and their applications depend on the chemical properties of analytes. Basically, the non-polar column (e.g., 100% dimethylpolysiloxane) is used for non-polar compound analyses, while for polar compounds it is recommended polar columns (e.g., 90% (cyanopropylphenyl)-10%-methylpolysiloxane) (Rahman et al. 2015). The most applied chromatographic columns for pesticide analyses are 5%-phenyl-95%-dimethylpolysiloxane, which separates the pesticides due to their volatility. Currently, pesticides are being also

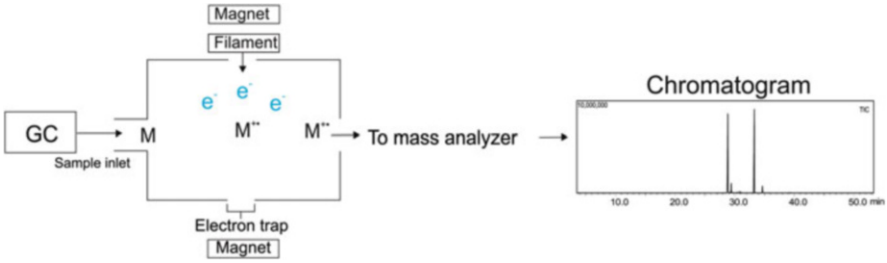


Fig. 1.8 Representation of electron ionization (EI) source that is coupled to gas chromatography (GC) producing chromatogram

analyzed by using two-dimensional gas chromatography, improving the analytical separation and results. In this case, it can be used a column 5%-phenyl-95%-dimethylpolysiloxane in the first dimension and a more polar column in the second dimension (e.g., 50%-phenyl-50%-dimethylpolysiloxane) to add another factor in the separation like as polarity (Pico et al. 2020).

GC has been applied in pesticide residues from several matrixes, as well as to analyze products and metabolites obtained by bioremediation studies, mainly GC-MS because its applicability for qualitative and quantitative analyses, including structural characterization of their products (Sidhu et al. 2019) such as for pyrethroids (Castellarnau et al. 2016) and polychlorinated biphenyls (Guo et al. 2019).

GC-MS uses electron ionization (EI) source, since the analytes are ionized from gas phase state in this MS technique and thus its coupling to GC is easy and possible (Fig. 1.8). In EI, the analyte is volatilized, and the electron is a cross molecule. This disrupts the analyte's energy and one or more electrons are detached, producing radical ions and subsequently, fragment ions are formed. Therefore, EI is named a hard method (Meyer 2016).

Although GC-MS is a robust method, the LC-MS has been widely used for pesticide analyses. It has demonstrating to be valuable for pesticides in qualitative and quantitative studies (Pico et al. 2020; Van Der Hoff and Van Zoonen 1999). Comparison between GC-MS and LC-MS for analyses of several pesticides demonstrated that LC-MS was better and more sensitive, and GC-MS was the best only for pyrethrins and organochlorines (Alder et al. 2006). From 2003 until now, the number of articles that applied LC-MS for pesticides is higher than GC-MS (Pico et al. 2020). Thus, LC-MS is applicable to analyze polar pesticides, for example, quaternary ammonium salts, urea derivatives, and others. The non-polar pesticides are recommended to analyze by GC-MS. In addition, polar analytes can be performed derivatization reactions and analyzed by GC-MS, but the structural characterization can be difficult, as the mass of compounds will be altered and will need to be considered to propose the metabolites (Samsidar et al. 2018; Sidhu et al. 2019).

Bioremediation reactions have been monitored and their metabolites identified by GC-MS, such as for endosulfan and petroleum biotransformation by

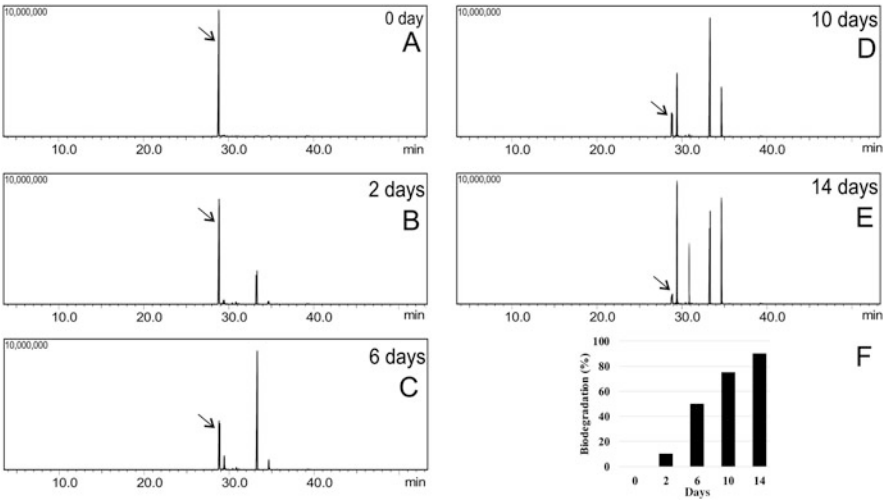


Fig. 1.9 Total ion chromatograms obtained by GC-MS from biodegradation of a pesticide after 0 (**a**), 2 (**b**), 6 (**c**), 10 (**d**), and 14 days (**e**). Graphic of biodegradation percentage (%) by microorganism (**f**)

microorganisms (Wang et al. 2019; Kumar et al. 2008). Their biodegradation was determined by GC-MS, but the structural identifications of products were not performed. Thus, GC-MS analyses are also applied for the determination of degradation percentage, performed from the different time reactions (Fig. 1.9).

EI-MS produces mass spectra highly similar to the possible databases used to identify the compounds, making it possible to compare with more than 240,000 spectra from databases. Although there are databases with EI-MS spectra, the identification by these spectral comparisons is not widely explored in bioremediation studies (Steckel and Schlosser 2019; Cook et al. 1999), since these biodegradation products were not frequently included in the commercial libraries. Therefore, the analyst, using the information about the molecular ion and its fragment ions, realizes the structural identification and this is a bottleneck, because it depends on the experience of the MS analyst.

Although few studies report the fragmentation pathways of biodegradation products. The fragmentation mechanism can be suggested from the fragmentation of molecular ion, the addition or losses of mass from initial compound (pesticide) and the comparison with classical losses described for EI reactions (Steckel and Schlosser 2019). These reactions are studied for a long time and it can be founded in good textbooks and materials about the classical fragmentation reactions on EI-MS (McLafferty and Turecek 1993).

Compared to GC-MS, HPLC-MS has been more widely useful to pesticide analyses. In addition, it can be applied as multi-residues method (Alder et al. 2006).

There are several types of commercial stationary phases for HPLC, such as C8, C18, hydrophilic interaction chromatography (HILIC), pentafluorophenyl (PFP),

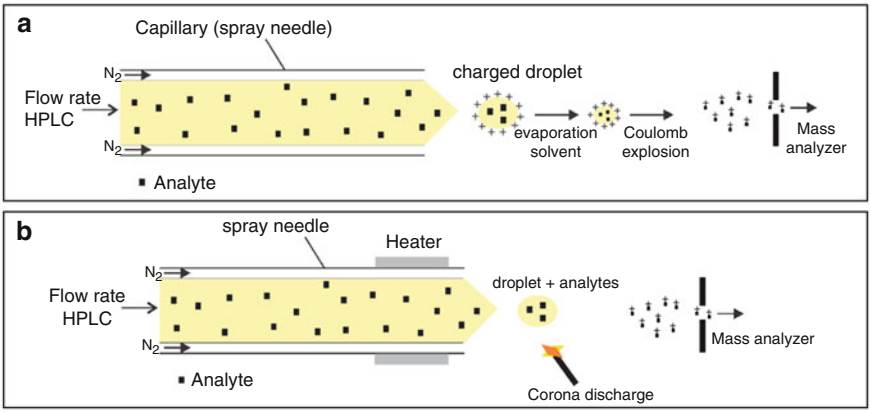


Fig. 1.10 Scheme of ESI and APCI sources

pentafluorophenyl propyl (PFPP), and others, as well as different particle types, including porous, monolithic, and fused core. Several materials can be found in the literature that explain about the differences of these chromatographic columns (Silva et al. 2019; Chester 2012), but C18 columns are the most used for pesticide analyses, showing efficient separation of them (LeDoux 2011; Primel et al. 2012; Alder et al. 2006).

Electrospray ionization (ESI) or atmospheric pressure chemical ionization (APCI) is normally applied in HPLC analyses. These techniques have shown better sensitivity and applicability. In addition, they are soft techniques, making easer the molecular weight determination and they are recommended for thermostable analytes. A mass spectrometer can be divided into three parts: ionization source (such as ESI, APCI), analyzers, and detector (Kebarle and Verkerk 2010). In ionization source, the molecules are transformed into ions, subsequently, the ions are separated based on *m/z* values (and fragmented when is required) in the analyzers, and finally they are tracked in the detector (Kebarle and Verkerk 2010; Ernst et al. 2014; El-Aneed et al. 2009).

Using ESI source, an analyte solution, when into the capillary, receives an electric potential (2–5 kV) and charged droplets are produced. The evaporation process with nitrogen reduces these charged droplets, increasing the repulsive forces until rupture of droplets (named Coulomb explosion) transferring the charges to analytes and liberating them into the gas phase (Fig. 1.10) (Fenn 2000; El-Aneed et al. 2009). The main reactions in the ESI source are acid–base and coordination reactions. Thus, the main ions observed in ESI are: $[M + H]^+$, $[M + K]^+$, $[M + Na]^+$ and $[M\text{-}H]^-$, $[M\text{-}Cl]^-$, as well as their dimeric ions (e.g., $[2\ M + H]^+$). Acid compounds are better ionized in negative ion mode, while basic compounds in positive mode (Crotti et al. 2006). Therefore, both modes can be acquired in bioremediation reactions to obtain wide chemical information (Ferrer and Thurman 2003).

APCI is also a soft technique, similarly to ESI, and to produce fragments is necessary a part in the analyzer that allow the fragmentation of parent ions, such as

collision-induced dissociation (CID). The analytes are solubilized and introduced into a heated capillary to produce a spray, but differently of ESI, the electric potential is applied by corona discharge and the ionization is transferred to analytes (Silva et al. 2019; El-Aneed et al. 2009). ESI is more widely used than APCI, including for pesticide analyses. ESI is recommended to ionize polar compounds, while APCI is applied for less polar compounds and low molecular weight (<1500 Da) (Alder et al. 2006; Ernst et al. 2014). The more widespread technique applied for pesticide analyses has been ESI, but many studies have reported APCI in analyses of trace pesticides (Alder et al. 2006; Thurman et al. 2001; Hernandez et al. 2005).

An important point in MS analyses is the low or high resolution analyzer. Resolution is defined as the ability of the analyzer to separate two ions with mass differences ΔM and the resolution is calculated by the eq. $R = M/\Delta M$. The analyzers can exhibit low-, high-, and ultra-resolution, which can separate ions with mass differences of units (e.g., Q, QIT), 0.0001 (e.g., TOF), and 0.00001 (e.g., FT-ICR, Orbitrap), respectively (Bier 1997; Cooks et al. 1992; El-Aneed et al. 2009).

High resolution (HR) analyzers can provide accurate mass of ions, that is important to define and confirm the molecular formula of an unknown analyte, beyond it provides better discrimination of background (El-Aneed et al. 2009). HR is extremely relevant in bioremediation studies, mainly to characterize the biodegradation products. In this sense, it is normally applied high resolution in the MS analyses and TOF is the most used in pesticide and bioremediation analyses (Alder et al. 2006). However, the sensitivity of HR mass spectrometers can be a problem to quantify traces residue levels and others analyzers can be better applied in determinations of quantification, such as QqQ (Alder et al. 2006; Hernández et al. 2004; Soler et al. 2006).

A post-genomics tool (metabolomic) has also been applied in bioremediation research. This is an emerging technique applied, for example, in nutrition, microbiology, pharmaceutical, chemistry, and biotechnology (Puchades-Carrasco and Pineda-Lucena 2015). Metabolomics is based on metabolome determination, which includes only metabolites of low molecular weight, their acquisition (by LC-MS, GC-MS, or other), and processing of a high amount data (Ernst et al. 2014). Some metabolomics strategies can be applied in bioremediation research which can be useful to determine biodegradation pathways by isotope distribution analysis, molecular networking, and multivariate statistical analyses (Villas-Bôas and Bruheim 2007). However, metabolomics strategies are rare to get chemical information in bioremediation nowadays. In addition, metabolomics can be associated to proteomics data, which determine a quantitative protein correlation of gene expression and thus, they can give important information for bioremediation research (Singh 2006).

There are several examples of the application of these techniques for the identification of metabolites generated in the bioremediation of environments contaminated by herbicide. Among the identification of metabolites generated in the biodegradation of the herbicide bispyribac by the bacterial consortium BDAM and the plant *Triticum aestivum*, carried out by LC-MS analyses, it was possible to detect the products showed in Fig. 1.11 (Ahmad et al. 2019). The final product was identified as 3-(carboxyamino)-2-methylpropanoic acid (iv), a derivative of beta-alanine.

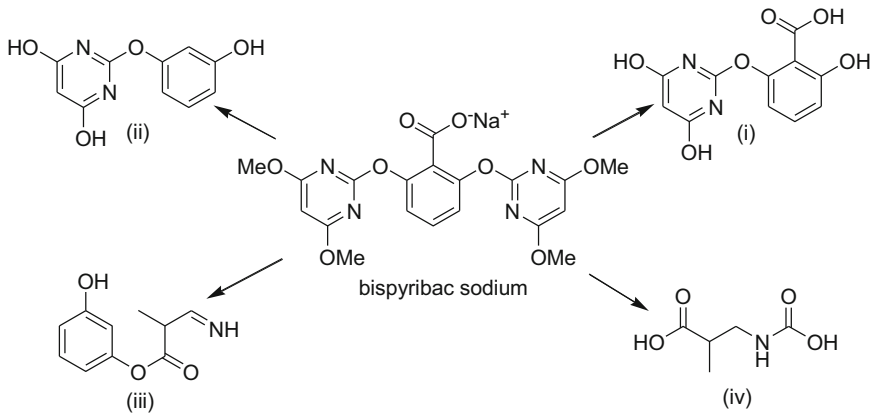


Fig. 1.11 Proposed metabolites generated by biodegradation of bispyribac sodium in contaminated wheat vegetated soil, detected by LC-MS technique (Ahmad et al. 2019)

A path of the biodegradation of the organochlorine chemical lindane by rhizospheric *M. maximus*, was depicted using GC-MS technique (Asemoloye et al. 2017). In a process of biodegradation or biotransformation for bioremediation of environments contaminated by pesticides, the identification of the generated species becomes crucial to detect possible less toxicity or even inert compounds in relation to the initial toxicity, which is intended for the processes of bioremediation and compounds that in turn have higher toxicity (de Lima et al. 2018).

1.7 Conclusion

The bioremediation of environments contaminated by pesticides is and will be increasingly important in the recovery and reduction of damage caused by them, mainly due to the growing demand and need for food in the world. From the most diverse types of processes used to remedy pesticides, the coupled application of plants and microorganisms stands out for their synergisms, increasing the expression of biodegradable enzymes, which provide more favorable environments for bioremediation. Although works in this direction are still scarce, the discovery of bacteria and fungi endophytic or found in the rhizosphere could be a pivotal tool in association with plants for bioremediation. The study of the influence of plant exudates, mainly from their roots, on strains of fungi and bacteria that are known for their potential for bioremediation of environment contaminated by pesticides, seems to be the best way to potentiate their action and evaluate the behavior of these microorganisms in the application environment, mainly in the soil. LC-MS and GC-MS techniques are helpful in detecting metabolites formed during the biodegradation or biotransformation process of the pesticides. In addition, these techniques assisting in the elucidation of the biodegradation route. The identification of

intermediates and products allows the classification of the bioremediation process and the success of its application.

References

Abbas SZ, Rafatullah M, Hossain K, Ismail N, Tajarudin HA, Abdul Khalil HPS (2018) A review on mechanism and future perspectives of cadmium-resistant bacteria. Int J Environ Sci Technol 15:243–262

Abhilash PC, Powell JR, Singh HB, Singh BK (2012) Plant-microbe interactions: novel applications for exploitation in multipurpose remediation technologies. Trends Biotechnol 30:416–420

Adnan LA, Sathishkumar P, Yusoff ARM, Hadibarata T, Ameen F (2017) Rapid bioremediation of alizarin red S and Quinizarine green SS dyes using *Trichoderma lixii* F21 mediated by biosorption and enzymatic processes. Bioprocess Biosyst Eng 40:85–97

Ahmad F, Ashraf N, Zhou R-B, Da-Chuan Y (2019) Enhanced remediation of bispyribac sodium by wheat (*Triticum aestivum*) and a bispyribac sodium degrading bacterial consortium (BDAM). J Environ Manage 244:383–390

Alder L, Greulich K, Kempe G, Vieth B (2006) Residue analysis of 500 high priority pesticides: better by GC-MS or LC-MS/MS? Mass Spectrom Rev 25:838–865

Ali H, Khan E, Sajad MA (2013) Phytoremediation of heavy metals-concepts and applications. Chemosphere 91:869–881

Alvarez A, Benimeli CS, Saez JM, Fuentes MS, Cuozzo AS, Polti MA, Amoroso MJ (2012) Bacterial bio-resources for remediation of hexachlorocyclohexane. Int J Mol Sci 13:15086–15106

Álvarez A, Yañez ML, Benimeli CS, Amoroso MJ (2012) Maize plants (*Zea mays*) root exudates enhance lindane removal by native Streptomyces strains. Int Biodeter Biodegr 66:14–18

Anderson TA, Walton BT (1995) Comparative fate of [^{14}C] trichloroethylene in the root zone of plants from a former solvent disposal site. Environ Toxicol Chem 14:2041–2047

Asemoloye MD, Ahmad R, Jonathan SG (2017) Synergistic rhizosphere degradation of γ-hexachlorocyclohexane (lindane) through the combinatorial plant-fungal action. PLoS One 12:e0183373

Asemoloye MD, Jonathan SG, Ahmad R (2019) Synergistic plant-microbes interactions in the rhizosphere: a potential headway for the remediation of hydrocarbon polluted soils. Int J Phytoremediation 21:71–83

Ávila C, Nivala J, Olsson L, Kassa K, Headley T, Mueller RA, Bayona JM, García J (2014) Emerging organic contaminants in vertical subsurface flow constructed wetlands: influence of media size, loading frequency and use of active aeration. Sci Total Environ 494:211–217

Azubuike CC, Chikere CB, Okpokwasili GC (2016) Bioremediation techniques-classification based on site of application: principles, advantages, limitations and prospects. World J Microbiol Biotechnol 32:180

Bai J, Han H, Wang F, Su L, Ding H, Hu X, Hu B, Li H, Zheng W, Li Y (2017) Maternal linuron exposure alters testicular development in male offspring rats at the whole genome level. Toxicology 389:13–20

Bamforth S, Singleton I (2005) Bioremediation of polycyclic aromatic hydrocarbons: current knowledge and future directions. J Chem Technol Biotechnol 80:723–736

Begum N, Qin C, Ahanger MA, Raza S, Khan MI, Ashraf M, Ahmed N, Zhang L (2019) Role of arbuscular mycorrhizal fungi in plant growth regulation: implications in abiotic stress tolerance. Front Plant Sci 10:1068

Bier ME (1997) Coupling ESI and MALDI sources to the quadrupole mass filter, quadrupole ion trap, linear quadrupole ion trap, and orbitrap mass analyzers. In: Cole RB (ed) Electrospray and

MALDI mass spectrometry fundamentals, instrumentation, practicalities, and biological applications, 2nd edn. Wiley, New York
Bilal M, Iqbal HMN, Barceló D (2019) Persistence of pesticides-based contaminants in the environment and their effective degradation using laccase-assisted biocatalytic systems. Sci Total Environ 695:133896
Calamari D, Tremolada P, Notarianni V (1995) Relationship between chlorinated hydrocarbons in vegetation and socioeconomic indices on a global scale. Environ Sci Technol 29:2267–2272
Carroll GC (1988) Fungal endophytes in stems and leaves: from latent pathogen to mutualistic symbiont. Ecology 69:1–9
Castellarnau M, Azcon JR, Lopez JF, Grimalt JO, Marco MP, Nieuwenhuijsen M, Picado A (2016) Assessment of analytical methods to determine pyrethroids content of bednets. Trop Med Int Health 22:41–51
Castillo JM, Nogales R, Romero E (2014) Biodegradation of 3,4 dichloroaniline by fungal isolated from the preconditioning phase of winery wastes subjected to vermicomposting. J Hazard Mater 267:119–127
Chang W, Zhang M, Zheng S, Li Y, Li X, Li W, Li G, Lin Z, Xie Z, Zhao Z, Lou H (2015) Trapping toxins within lipid droplets is a resistance mechanism in fungi. Sci Rep 5:15133
Chauhan A, Goyal MK, Chauhan P (2014) GC-MS technique and its analytical applications in science and technology. J Anal Bioanal Tech 5:222
Chester TL (2012) Recent developments in high-performance liquid chromatography stationary phases. Anal Chem 85:579–589
Cicatiello P, Gravagnuolo AM, Gnavi G, Varese GC, Giardina P (2016) Marine fungi as source of new hydrophobins. Int J Biol Macromol 92:1229–1233
Cocaign A, Bui L-C, Silar P, Tong LCH, Busi F, Lamouri A, Mougin C, Rodrigues-Lima F, Dupret J-M, Dairou J (2013) Biotransformation of *Trichoderma* spp. and their tolerance to aromatic amines, a major class of pollutants. Appl Environ Microbiol 79:4719–4726
Cook J, Engel M, Wylie P, Quimby B (1999) Multiresidue screening of pesticides in foods using retention time locking, GC-AED, database search, and GC/MS identification. J AOAC Int 82:313–326
Cooks RG, Hoke SH, Morand KL, Lammert SA (1992) Mass spectrometers: instrumentation. Int J Mass Spectrom Ion Proc 118:1–36
Crotti AEM (2006) Espectrometria de massas com ionização por "electrospray": processos químicos envolvidos na formação de íons de substâncias orgânicas de baixo peso molecular. Quim Nova 29:287–292
Cunningham SD, Berti WR (1993) Remediation of contaminated soils with green plants: an overview. In Vitro Cell Dev Biol Plant 29:207–212
Das A, Varma A (2009) Symbiosis: the art of living. In: Varma A, Kharkwal AC (eds) Symbiotic fungi principles and practice. Springer, Berlin, pp 1–28
Davis LC, Castro-Diaz S, Zhang Q, Erickson LE (2002) Benefits of vegetation for soils with organic contaminants. Crit Rev Plant Sci 21:457–491
de Lima DP, Giannesi GC, dos Santos EA, Freitas TSE, Lopes RS, Lôpo MN, Beatriz A, Marques MR, Marchetti CR (2017) *N*-acetylation of aromatic amines by the soil fungus *Aspergillus japonicus* (UFMS 48.136). Lett Org Chem 14:227–230
de Lima DP, dos Santos EA, Marques MR, Giannesi GC, Beatriz A, Yonekawa MKA, Montanholi AS (2018) Fungal bioremediation of pollutant aromatic amines. Curr Opin Green Sustain Chem 11:34–44
Deshmukh R, Khardenavis AA, Purohit HJ (2016) Diverse metabolic capacities of fungi for bioremediation. Indian J Microbiol 56:247–264
DiBartolomeis M, Kegley S, Mineau P, Radford R, Klein K (2019) An assessment of acute insecticide toxicity loading (AITL) of chemical pesticides used on agricultural land in the United States. PLoS One 14:e0220029
Dietz AC, Schnoor JL (2001) Advances in phytoremediation. Environ Health Perspect 109:163–168

Dixit R, Wasiullah MD, Pandiyan K, Singh UB, Sahu A, Shukla R, Singh BP, Rai JP, Sharma PK, Lade H, Paul D (2015) Bioremediation of heavy metals from soil and aquatic environment: an overview of principles and criteria of fundamental processes. Sustainability 7:2189–2212

El-Aneed A, Cohen A, Banoub J (2009) Mass spectrometry, review of the basics: electrospray, MALDI, and commonly used mass analyzers. Appl Spectrosc Rev 44:210–230

Erickson LE, Davis LC, Narayanan M (1995) Bioenergetics and bioremediation of contaminated soil. Thermochim Acta 250:353–358

Ernst M, Silva DB, Silva RR, Vêncio RZN, Lopes NP (2014) Mass spectrometry in plant metabolomics strategies: from analytical platforms to data acquisition and processing. Nat Prod Rep 31:784–806

FAO (2020) Food and Agriculture Organization of the United Nations, Pesticide registration toolkit. http://www.fao.org/pesticide-registration-toolkit/information-sources/terms-and-definitions/terms-and-definitions-p. Accessed 14 Nov 2020

FAOSTAT (2020) Statistics division. Data of pesticide use and trade latest update: September 14, 2020. http://www.fao.org/faostat/en/#data. Accessed 14 Nov 2020

Fenn JB (2000) Mass spectrometric implications of high-pressure ion sources. Int J Mass Spectrom 200:459–478

Ferrer I, Thurman EM (2003) Liquid chromatography/time-of-flight/mass spectrometry (LC/TOF/MS) for the analysis of emerging contaminants. Trends Anal Chem 22:750–756

Ferro A, Gefell M, Kjelgren R, Lipson DS, Zollinger N, Jackson S (2003) Maintaining hydraulic control using deep rooted tree systems. In: Scheper T, Tsao DT (eds) Advances in biochemical engineering/biotechnology. Springer, Berlin, pp 125–156

Garvin N, Doucette WJ, White JC (2015) Investigating differences in the root to shoot transfer and xylem sap solubility of organic compounds between zucchini, squash and soybean using a pressure chamber method. Chemosphere 130:98–102

Gely-Pernot A, Saci S, Kernanec P-Y, Hao C, Giton F, Kervarrec C, Tevosian S, Mazaud-Guittot S, Smagulova F (2017) Embryonic exposure to the widely-used herbicide atrazine disrupts meiosis and normal follicle formation in female mice. Sci Rep 7:3526

Gill HK, Garg H (2014) Pesticides: environmental impacts and management strategies. In: Larramendy ML, Soloneski S (eds) Pesticides—toxic aspects. IntechOpen, London, pp 117–230. https://www.intechopen.com/books/pesticides-toxic-aspects/pesticides-environmental-impacts-and-management-strategies. Accessed 12 Dec 2019

Gkorezis P, Daghio M, Franzetti A, Van Hamme JD, Sillen W, Vangronsveld J (2016) The interaction between plants and bacteria in the remediation of petroleum hydrocarbons: an environmental perspective. Front Microbiol 7:1836

Günther M, Zibek S, Rupp S (2017) Fungal glycolipids as biosurfactants. Curr Biotechnol 6:205–218

Guo F, Wang Z, Zhao L, Liu W (2019) A proposed method of enantioselectivity analysis for residual chiral PCBs in gas chromatography. Chemosphere 229:401–408

Hernández F, Ibáñez M, Sancho JV, Pozo OJ (2004) Comparison of different mass spectrometric techniques combined with liquid chromatography for confirmation of pesticides in environmental water based on the use of identification points. Anal Chem 76:4349–4357

Hernandez F, Sancho JV, Pozo OJ (2005) Critical review of the application of liquid chromatography/mass spectrometry to the determination of pesticide residues in biological samples. Anal Bioanal Chem 382:934–946

Huang Y, Xiao L, Li F, Xiao M, Lin D, Long X, Wu Z (2018) Microbial degradation of pesticide residues and an emphasis on the degradation of cypermethrin and 3-phenoxy benzoic acid: a review. Molecules 23:2313

Ijoma GN, Tekere M (2017) Potential microbial applications of co-cultures involving ligninolytic fungi in the bioremediation of recalcitrant xenobiotic compounds. Int J Environ Sci Technol 14:1787–1806

Karthikeyan R, Davis LC, Erickson LE, Al-Khatib K, Kulakow PA, Barnes PL, Hutchinson SL, Nurzhanova AA (2014) Potential for plant-based remediation of pesticide-contaminated soil and water using nontarget plants such as trees, shrubs, and grasses. Crit Rev Plant Sci 23:91–101

Kebarle P, Verkerk UH (2010) In: Cole RB (ed) Electrospray and MALDI mass spectrometry, 2nd edn. Wiley, New Jersey, pp 3–48

Khan R, Fulekar MH (2017) Mineralization of a sulfonated textile dye reactive red 31 from simulated wastewater using pellets of *Aspergillus bombycis*. Bioresour Bioprocess 4:23

Kumar M, Lakshmi V, Khanna S (2008) Biodegradation and bioremediation of endosulfan contaminated soil. Bioresour Technol 99:3116–3122

Landrigan PJ, Fuller R, Acosta NJR, Adeyi O, Arnold R, Basu N, Baldé AB, Bertollini R, Bose-O'Reilly S, Boufford JI, Breysse PN, Chiles T, Mahidol C, Coll-Seck AM, Cropper ML, Fobil J, Fuster V, Greenstone M, Haines A, Hanrahan D, Hunter D, Khare M, Krupnick A, Lanphear B, Lohani B, Martin K, Mathiasen KV, McTeer MA, Murray CJL, Ndahimananjara JD, Perera F, Potočnik J, Preker AS, Ramesh J, Rockström J, Salinas C, Samson LD, Sandilya D, Sly PD, Smith KR, Steiner A, Stewart RB, Suk WA, van Schayck OCP, Yadama GN, Yumkella K, Zhong M (2018) The lancet commission on pollution and health. Lancet 391:462–512

LeDoux M (2011) Analytical methods applied to the determination of pesticide residues in foods of animal origin. A review of the past two decades. J Chromatogr A 1218:1021–1036

Lee S, Flores-Encarnacíon M, Contreras-Zentella M, Garcia-Flores L, Escamilla JE, Kennedy C (2004) Indole-3-acetic acid biosynthesis is deficient in *Gluconacetobacter diazotrophicus* strains with mutations in Cytochrome c biogenesis genes. J Bacteriol 186:5384–5391

Lewis RJ (1996) Sax's dangerous properties of industrial materials, 9th edn. Van Nostrand Reinhold, New York, pp 1088–1122

Lewis RJ (2004) Sax' dangerous properties of industrial materials, 11th edn. Wiley, Hoboken, p 1542

Ligaray M, Baek SS, Kwon H, Choi S, Cho KH (2016) Watershed-scale modeling on the fate and transport of polycyclic aromatic hydrocarbons (PAHs). J Hazard Mater 320:442–457

Liu Z, Wang Y, Zhu Z, Yang E, Feng X, Fu Z, Jin Y (2016) Atrazine and its main metabolites alter the locomotor activity of larval zebrafish (*Danio rerio*). Chemosphere 148:163–170

Lushchak VI, Matviishyn TM, Husak VV, Storey JM, Storey KB (2018) Pesticide toxicity: a mechanistic approach. EXCLI J 17:1101–1136

Maggi F, Tang FHM, la Cecilia D, McBratney A (2019) PEST-CHEMGRIDS, global gridded maps of the top 20 crop-specific pesticide application rates from 2015 to 2025. Sci Data 6:170

Margulis L, Fester R (1991) Symbiosis as a source of evolutionary innovation: speciation and morphogenesis. MIT Press, Cambridge

Marquès M, Mari M, Audí-Miró C, Sierra J, Soler A, Nadal M, Domingo JL (2016) Climate change impact on the PAH photodegradation in soils: characterization and metabolites identification. Environ Int 89:155–165

Masih A, Masih J, Taneja A (2012) Study of air-soil exchange of polycyclic aromatic hydrocarbons (PAHs) in the north-central part of India-a semi-arid region. J Environ Monit 14:172–180

McCutcheon SC, Schnoor JL (eds) (2003) Phytoremediation: transformation and control of contaminants. Wiley, New York

McLafferty FW, Turecek F (1993) Interpretation of mass spectra, 4th edn. University Science Books, Sausalito

Megharaj M, Ramakrishnan B, Venkateswarlu K, Sethunathan N, Naidu R (2011) Bioremediation approaches for organic pollutants: a critical perspective. Environ Int 37:1362–1375

Meyer MR (2016) Handbook of GC-MS: fundamentals and applications. Anal Bioanal Chem 408:1535

Morillo E, Villaverde J (2017) Advanced technologies for the remediation of pesticide-contaminated soils. Sci Total Environ 586:576–597

Nilsen E, Smalling KL, Ahrens L, Gros M, Miglioranza KSB, Picó Y, Schoenfuss HL (2019) Critical review: grand challenges in assessing the adverse effects of contaminants of emerging concern on aquatic food webs. Environ Toxicol Chem 38:46–60

O'Connor D, Zheng X, Hou D, Shen Z, Li G, Miao G, O'Connell S, Guo M (2019) Phytoremediation: climate change resilience and sustainability assessment at a coastal brownfield redevelopment. Environ Int 30:104945

Ohkawa H, Imaishi H, Shiota N, Yamada T, Inui H (1999) Cytochrome P450s and other xenobiotic metabolizing enzymes in plants. In: Brooks JT, Roberts TR (eds) Pesticide chemistry and biosciences: the food-environment challenge. Royal Society of Chemistry, Cambridge, pp 259–264

Olicón-Hernández DR, González-López J, Aranda E (2017) Overview on the biochemical potential of filamentous fungi to degrade pharmaceutical compounds. Front Microbiol 8:1792

Parker MA (1995) Plant fitness variation caused by different mutualist genotypes. Ecology 76:1525–1535

Pereira RC, Camps-Arbestain M, Garrido BR, Macías F, Monterroso C (2006) Behaviour of α-, β-, γ-, and δ-hexachlorocyclohexane in the soil-plant system of a contaminated site. Environ Pollut 144:210–217

Perissini-Lopes B, Egea TC, Monteiro DA, Vici AC, Da Silva DGH, Lisboa DCO, De Almeida EA, Parsons JR, Da Silva R, Gomes E (2016) Evaluation of diuron tolerance and biotransformation by fungi from a sugar cane plantation sandy-loam soil. J Agric Food Chem 64:9268–9275

Pico Y, Alfarhan AH, Barcelo D (2020) How recent innovations in gas chromatography-mass spectrometry have improved pesticide residue determination: an alternative technique to be in your radar. Trends Anal Chem 122:115720

Primel EG, Caldas SS, Escarrone ALV (2012) Multi-residue analytical methods for the determination of pesticides and PPCPs in water by LC-MS/MS: a review. Cent Eur J Chem 10:876–899

Puchades-Carrasco L, Pineda-Lucena A (2015) Metabolomics in pharmaceutical research and development. Curr Opin Biotechnol 35:73–77

Pullagurala VLR, Rawat S, Adisa IO, Hernandez-Viezcas JA, Peralta-Videa JR, Gardea-Torresdey JL (2018) Uptake and translocation of contaminants of emerging concern in soil. Sci Total Environ 636:1585–1596

Qing X, Yutong Z, Shenggao L (2015) Assessment of heavy metal pollution and human health risk in urban soils of steel industrial city (Anshan), Liaoning, Northeast China. Ecotoxicol Environ Saf 120:377–385

Rahman MM, Abd El-Aty AM, Choi J, Shin H, Shin SC (2015) Basic overview on gas chromatography columns. In: Anderson JL, Berthod A, Estevez VP, Stalcup AM (eds) Analytical separation science, 3rd edn. Wiley, Hoboken, pp 823–834

Rasmussen PU, Bennett AE, Tack AJM (2019) The impact of elevated temperature and drought on the ecology and evolution of plant–soil microbe interactions. J Ecol 00:1–16

Salimi M, Esrafili A, Gholami M, Jafari AJ, Kalantary RR, Farzadkia M, Kermani M, Sobhi HR (2017) Contaminants of emerging concern: a review of new approach in AOP technologies. Environ Monit Assess 189:414

Samsidar A, Siddiquee S, Shaarani SM (2018) A review of extraction, analytical and advanced methods for determination of pesticides in environment and foodstuffs. Trends Food Sci Technol 71:188–201

Sandermann Junior H (1992) Plant metabolism of xenobiotics. Trends Biochem Sci 17:82–84

Sharma P, Pandey S (2014) Status of phytoremediation in world scenario. Int J Environ Biorem Biodegrad 2:178–191

Shone MGT, Wood AV (1974) A comparison of the uptake and translocation of some organic herbicides and a systemic fungicide by barley I. Absorption in relation to physico-chemical properties. J Exp Bot 25:390–400

Sidhu GK, Singh S, Kumar V, Dhanjal DS, Datta S, Sing J (2019) Toxicity, monitoring and biodegradation of organophosphate pesticides: a review. Crit Rev Environ Sci Technol 49:1135–1187

Silva DB, Nocchi SR, Borges KB, Lopes NP (2019) Liquid chromatography coupled to mass spectrometry for quantitative analyses of medicinal plants and natural products. In: Diniz

MFMF, Scotti L, Scotti MT, Alves MF (eds) Natural products and drug discovery, 1st edn. Elsevier, Amsterdam, p 143
Simon JC, Marchesi JR, Mouge C, Selosse MA (2019) Host-microbiota interactions: from holobiont theory to analysis. Microbiome 7:1–5
Simonich SL, Hites RA (1995) Organic pollutant accumulation in vegetation. Environ Sci Technol 29:2905–2914
Singh OV (2006) Proteomics and metabolomics: the molecular make-up of toxic aromatic pollutant bioremediation. Proteomics 6:5481–5492
Smith E, Thavamani P, Ramadass K, Naidu R, Srivastava P, Megharaj M (2015) Remediation trials for hydrocarbon-contaminated soils in arid environments: evaluation of bioslurry and biopiling techniques. Int Biodeter Biodegr 101:56–65
Soler C, Hamilton B, Furey A, James KJ, Mañes J, Picó Y (2006) Comparison of four mass analyzers for determining carbosulfan and its metabolites in citrus by liquid chromatography/mass spectrometry. Rapid Commun Mass Spectrom 20:2151–2164
Spina F, Cecchi G, Landinez-Torres A, Pecoraro L, Russo F, Wu B, Cai L, Liu XZ, Tosi S, Varese GC, Zotti M, Persiani AM (2018) Fungi as a toolbox for sustainable bioremediation of pesticides in soil and water. Plant Biosyst 152:474–488
St-Amand AD, Mayer PM, Blais JM (2009) Prediction of SVOC vegetation and atmospheric concentrations using calculated deposition velocities. Environ Int 35:851–855
Steckel A, Schlosser G (2019) An organic chemist's guide to electrospray mass spectrometric structure elucidation. Molecules 24:611
Teng Y, Wu J, Lu S, Wang Y, Jiao X, Song L (2014) Soil and soil environmental quality monitoring in China: a review. Environ Int 69:177–199
Thurman EM, Ferrer I, Barcelo D (2001) Choosing between atmospheric pressure chemical ionization and electrospray ionization interfaces for the HPLC/MS analysis of pesticides. Anal Chem 73:5441–5449
UN (2009) Food production must double by 2050 to meet demand from world's growing population, innovative strategies needed to combat hunger, experts tell second committee, sixty-fourth general assembly, second committee. Last update: October 9, 2009. https://www.un.org/press/en/2009/gaef3242.doc.htm. Accessed 14 Nov 2020
UN (2019) Department of Economic and Social Affairs, Population Dynamics, World Population Prospects 2019. https://population.un.org/wpp/
US Environmental Protection Agency (2010) Aquatic biodiversity glossary. Terminology services - vocabulary catalog list detail report. Last update: 8 Dec 8 2010. https://ofmpub.epa.gov/sor_internet/registry/termreg/searchandretrieve/glossariesandkeywordlists/search.do?details=&glossaryName=Aquatic%20Biodiversity%20Glossary. Accessed 12 Jan 2020
Van Der Hoff GR, Van Zoonen P (1999) Trace analysis of pesticides by gas chromatography. J Chromatogr A 843:301–322
Verdin A, Sahraoui AL-H, Newsam R, Robinson G, Duran R (2005) Polycyclic aromatic hydrocarbons storage by *Fusarium solani* in intracellular lipid vesicles. Environ Pollut 133:283–291
Villas-Bôas SG, Bruheim P (2007) The potential of metabolomics tools in bioremediation studies. OMICS 11:305–313
Walton BT, Anderson TA (1990) Microbial degradation of trichloroethylene in the rhizosphere: potential application to biological remediation of waste sites. Appl Environ Microbiol 56:1012–1016
Wang D, Lin J, Lin J, Wang W, Li S (2019) Biodegradation of petroleum hydrocarbons by *Bacillus subtilis* BL-27, a strain with weak hydrophobicity. Molecules 24:3021
Wilkinson AD, Collier CJ, Flores F, Langlois L, Ralph PJ, Negri AP (2017) Combined effects of temperature and the herbicide diuron on photosystem II activity of the tropical seagrass *Halophila ovalis*. Sci Rep 7:45404
Wilson D (1995) Endophyte: the evolution of a term, and clarification of its use and definition. Oikos 73:274–276

Zhang Y, Ge S, Jiang M, Jiang Z, Wang Z, Ma B (2014) Combined bioremediation of atrazine-contaminated soil by *Pennisetum* and *Arthrobacter* sp. strain DNS10. Environ Sci Pollut Res 21:6234–6238

Zhuang P, Huiling Z, Wensheng S (2009) Biotransfer of heavy metals along a soil-plant-insect-chicken food chain: field study. J Environ Sci 21:849–853

Zoccali M, Tranchida PQ, Mondello L (2019) Fast gas chromatography-mass spectrometry: a review of the last decade. Trends Anal Chem 118:444–452

Combined and Sustainable Techniques in Remediation of POPs-Contaminated Soil Sites

2

Volodymyr V. Harkavenko and Sergey S. Seryy

Abstract

Modern environmental technologies face massive challenges in dealing with persistent organic pollutants (POPs). The storage and disposal of POPs is now strictly controlled in most countries. However, sustainable techniques for POPs disposal are still lacking. Here we are going to raise a discussion on new approaches in hazardous waste management. Moreover, it is appropriate to discuss what is meant by the modern "POPs" concept. It is obvious that POPs comprehension has widened significantly from the times this group of substances was first determined by the Stockholm convention. Now the modern understanding of contaminant persistency requires new determinations and, therefore, new treatment approaches.

Keywords

POPs · CHC · PCB · DDT · Oil pollution · Sustainable remediation

V. V. Harkavenko (✉)
Institute of Biology, V.N. Karazin Kharkiv National University, Kharkiv, Ukraine

Arva Greentech GmbH, Berlin, Germany
e-mail: vladimir_garkavenko@ukr.net

S. S. Seryy
Arva Greentech GmbH, Berlin, Germany

UNIDO International Expert on Mission in Hazardous Waste Management, Vienna, Austria
e-mail: seryy@arva-green.tech

© The Author(s), under exclusive licence to Springer Nature Singapore Pte Ltd. 2021

V. Kumar et al. (eds.), *Rhizobiont in Bioremediation of Hazardous Waste*,
https://doi.org/10.1007/978-981-16-0602-1_2

2.1 Introduction

In this article, we present our insight into the problem of persistent remediation of hazardous and stable organic pollutants traditionally pertaining to the group of persistent organic pollutants (POPs) prescribed in the Stockholm Convention (Stockholm Convention on Persistent Organic Pollutants (POPs) Texts and Annexes 2017). It should be pointed out here that at the time of creating documents under the Stockholm Convention, POPs meant a much narrower group of pollutants than it is conventional to consider today. "The Dirty Dozen" specified in the first version of the convention can be conditionally divided into two groups of substances: pesticides and polychlorinated hydrocarbons. After the fourth meeting of the parties to the convention, the list of pollutants was extended with nine more substances. It is currently obvious that further extension of the POP list under the Stockholm Convention is a matter of time. So what properties are most critical so far to determine a certain substance as hazardous for the environment as regarded by the international community, local regulators, and the environmental industry?

Here we want to list the criteria in turns, starting from those that are to cause the greatest concern, in our opinion:

1. Toxicity for humans or for the critical components of the ecosystem, which jeopardizes the collective health or economic interests of the society
2. Ability to bioaccumulate in critical food pyramids
3. Resistance to destruction under the influence of natural environmental conditions

It should be noted that these criteria are applicable for synthetic chemical compounds, and each of these items for a specific chemical can play an essential role and lead to far-reaching consequences in the public perception of the industry and/or regulatory control.

Thus, it can be demonstratively exemplified with the information campaign launched around microplastic pollution where the toxicity of microplastic particles itself does not seem so threatening yet, but it is the recently discovered bioaccumulation ability of microplastic that is of general concern. It has turned out unexpectedly that the propagation scales of microplastic particles are so vast that, having even a slight accumulation effect in the food chain, they will eventually get into the human diet. The emergence of such unexpected "marinade" naturally caused fierce debates, and only a few years after the problem of microplastic was publicly declared, scientific reviews already classify it as a "new persistent environmental pollutant" (Yu et al. 2018).

It must be noted that the above-mentioned characteristic, although it has been given to the contaminant only by the research community so far, is well-placed to get spread into the field of regulatory documents of the upcoming conferences of the Stockholm or some other global convention. The wording "persistent environmental pollutant" is obviously very close to the traditional term—POPs, and we are only one semantic step away from the extension of the POP list in this specific case. New

environmental threats are identified regularly and continuously, thus we are sure that the POP family is bound to be rising over time.

Understanding the global nature of the POP problematics urges the industry and the scientific community to elaborate an equally global methodological approach to solve the problems of disposal of POPs. This approach apparently should be concerted and, what is more, get enshrined in such international initiatives as SDG and the general policy for sustainable development led by the UN (Warner and Hadley 2012).

In this context, we will feature a partial vision of applying the SDG principles to POPs disposal in soils only, since, turning to the basic concept for POPs, most of which were used as pesticides, exactly soil sites were originally most susceptible to pollution. POPs further ingress into the water medium is only a consequence of natural leaching or improper irrigation. We assume that it is understanding the right methodology of POP disposal on soil sites underlies the control of the POP situation in the whole ecosystem. Moreover, water treatment, if pollutants are persistent, also finally resolves into their primary accumulation in solid phase, for instance, in sludge, with subsequent disposal of compact sludge with concentrated pollutant.

Therefore, we can postulate that the solutions applicable to the remediation of POP-contaminated soils are also basic for water treatment and POP disposal in wastewater treatment plants. It follows that the model of sustainable remediation of POPs in soil substrate is the most relevant one.

Additionally, in the text below, we encompass only the in situ remediation methods where each definite site is too extended to perform treatment in ex situ mode, and it can be treated only without moving the full volume of contaminated substrate. For reactor systems of treatment, the presented ideas and approaches can be only partially relevant.

Now we need to outline a range of technologies which we can characterize as stable in remediation of POP-contaminated sites. In general, site remediation and selection of a definite technology within the sustainability concept should be decided upon based on a comprehensive evaluation of their possible impact on the environment. In our opinion, the Net Environmental Benefit Analyses (NEBA) algorithm is best suited for it. NEBA may be thought of as elaboration of ecological risk assessment. That is, it is a risk–benefit analysis applied to environmental management actions. However, since risk assessment does not normally consider benefits, and risk assessors are not familiar with the requirements of an assessment that estimates benefits, the NEBA framework is useful to accentuate the specific features of such analyses (Efroymson et al. 2004). Thus, NEBA may help to avoid the possibility that the selected remedial or ecological restoration alternative will fail to provide any net environmental benefit (e.g. the remediation alternative causes environmental injuries greater than the damage associated with the contamination) over natural attenuation of contaminants and ecological recovery. However, we are not going to set an example of conducting the NEBA procedure in this article, since we are guided by the reference that the remediation decision has already been made, thus we discuss only the definite technology and the ways to implement it.

2.2 Sustainable Soil Remediation: Main Principles

A sustainable remediation technology may be characterized as "a remedy or combination of remedies whose net benefit on human health and the environment is maximized through the careful use of limited resources" (Mudhoo and Mohee 2012). Sustainable remediation is determined more specifically by SD. Warner, PW. Hadley: "Striving to balance the environmental, economic, and social benefits and costs associated with remediation while maintaining a resource conservative approach" (Warner and Hadley 2012). Here, three mandatory components of a sustainable process are most accurately indicated, however, we will take the liberty of asserting the following ranking of sustainability criteria for remediation in the modern environmental industry:

1. Economic
2. Social
3. Environmental

Such ranking is empirical in our case, showing the primitive importance of the economic component of the remediation process. In our industrial experience, many technologies which were environmentally optimal for a specific case were rejected due to their high cost or social concerns.

The social sustainability factor is not less important, and the social appraisal of "purity" of a technology often affects the future of its implementation. The society should be understood widely, including the scientific community. Thus, we will set an example of soil remediation by using nanoparticles and GMO (Sarkar et al. 2019; Wang and Chen 2007). We assume that it is the bias and fears of the society today that build up one of the main barriers to a wide implementation of such technologies in the industry. At the same time, it is impossible to deny that both technologies undoubtedly have a number of risks, however, we believe that they are currently evaluated too "emotionally" for calculation of actual benefits and risks of their usage for specific cases. Thus, the controversial perception of a particular technology by the scientific community obviously shapes the assessment of its sustainability over its direct environmental benefit.

It follows from the foregoing that not every advanced and progressive remediation technology in itself can be considered to be sustainable. And, turning to the POP problematics, it should be noted that the conventional techniques often fail to provide technical possibilities for disposal of persistent contaminants, which has produced POPs concerns in the international community.

So, what can be the solution for sites which are too complicated for traditional remediation methods, and are not enough high-tech or overregulated for cutting-edge methods to be applied? We believe that the only right approach is currently the combination of two or more conventional remediation techniques aimed at obtaining a synergistic result. At the same time, we are talking precisely about operating the industry's basic technologies, which, if summed up, produces high results in

restoring natural sites and, at the same time, enables preserving efficiency in economic terms.

Thus, for instance, successful model experiments on the combination of chemical oxidation and bioremediation to clean the substrate from polycyclic aromatic hydrocarbons (PAHs) (Wang et al. 2004) or pesticide derivatives are described (Arnold et al. 1996). In both cases, the Fenton reagent, which is basic for in situ oxidation, operates as a chemical oxidizing agent.

It should be noted here that oxidation is a universal principle of decomposition of a pollutant, regardless of the method chosen: burning a pollutant means quick oxidation, whereas its decomposition by chemical or biological methods is a slow oxidation process, with a rare exception of highly specific enzymatic reactions targeted at a specific substance or class of compounds.

However, since soil contamination is heterogenous in the vast majority of cases thus disabling us from using highly specific methods, we tend to generalize the modern techniques of soil decontamination as oxidation reactions. At the same time, it is obvious that chemical oxidation, being used correctly, is a good basement to start a biological oxidation process. Meanwhile, there is a range of substantial factors restricting the usability of bioremediation, which limit the chemical techniques, basically due to the nature of possible reaction products (Chang and Kikuchi 2012).

1. Toxicity
2. Unacceptable acid-alkaline medium
3. Low bioavailability of reaction products

The substrate itself must also conform to a range of requirements mandatory for growth of microbial flora (Haller 2017). For example, a suitable soil texture is needed both to sufficiently provide aeration capabilities and to retain moisture well. Such texture is characteristic of natural or reclamated soil substrates, but some chemical processes can cause excessive aggregation of substrate particles or otherwise disrupt their structure, which then will adversely affect the bioavailability of the pollutant (Ifon et al. 2019).

Among other things, such methods as high temperature acid sludge extraction, for example, for elimination of heavy metals (Stylianou et al. 2007), are capable of effective sterilization and aggregation of substrate, so it will become technically of little utility for bioremediation, although it will not manifest apparent toxic properties. Therefore, given the subsequent use of biological methods of remediation, appropriate chemical oxidation methods should be selected correctly by taking into account the final result preferred. What is more, we should also consider the intermediary nature of any technology used.

We explain this statement as follows: basically all technologies of in situ soil remediation currently available employ the waste-to-waste (European Environment Agency 2014) approach, which means that:

1. They transform more hazardous waste into less hazardous waste.

2. They reduce the amount of the target pollutant to levels below the LOC (by so doing, they often increase the collateral pollution (Saier and Trevors 2010; Surriya et al. 2015)).
3. They concentrate the pollutant in small volumes to isolate it subsequently from the substrate and to dispose it by using other methods (Mosa et al. 2016).

In a range of cases, several approaches of the above-mentioned ones are implemented simultaneously, which shows that substantially each remediation measure constitutes only one of the stages of a long pollutant disposal process, which particularly concerns POPs.

We exemplify it with the following case: having been amended in 2019, the Environmental Management Act (Environmental Management Act Pub. L. No. B.C. Reg. 375/96 2019) of British Columbia (Canada) currently limits the DDT (dichloro-diphenyl-trichloroethane) concentration for industrial sites at the level of 1000 ppm, although it did not always use to be so: as long ago as in 2013, according to the Stage 8 Amendments to the Contaminated Sites Regulation (Stage 8 Amendments to the Contaminated Sites Regulation Environmental Management Act 2013), this indicator was specified at the level of 3500 ppm. It follows that, if we had been taking measures for remediation of the DDT-contaminated industrial site in British Columbia in 2013, treatment lower than 3500 would have been a satisfactory result. POP disposal procedures are typically very costly: the price for POPs storage on a disposal site alone reaches 500$ per ton of substrate (Collins 2009), and it is logical to assume that our purpose would have been an ultimately fast and cost-effective achievement of a level substantially different from the level of concern (LOC) within the analytical evaluation method selected, namely 3000 ppm approximately. Such pollution level would have been reliably evaluated as lower than the LOC by using any standard analytical method, and its achievement through chemical oxidation would have required less reagents, resources, and working hours than for complete DDT decomposition in substrate, provided that complete decomposition is possible for this specific case in general. Thus, a compromise was reached between all stakeholders of the remediation process: the customer, the contractor, and the regulator. Based on the above criteria, the stated solution can be deemed to be sustainable. However, as new standards were adopted, repeated remediation of this site becomes a matter of time.

The environmental legislation all over the world is becoming stricter, which is particularly obvious in the growing economies, such as China where several major reforms in the field of soil protection and degraded soil restoration have been implemented over the latest decades, which have considerably reframed the attitude of the regulators to a wide range of pollutants (Li et al. 2015; Zhilin et al. 2014). Meanwhile, quite a small range of soil remediation solutions may be deemed reliably sustainable in future, therefore, in conducting site treatment works, the possibility of repeated remediation necessary some time later should always be taken into account.

It means that the industry evolution by itself urges executives to opt for remediation methods which can be successfully harmonized between themselves and potentially with other techniques.

At the same time, if several different remediation techniques are sequentially used at a site, bioremediation should be mostly preferred in selecting the final method. This is predetermined by several reasons:

1. The biological processes enable creating self-healing systems in which destructive microorganisms continue to destroy the pollutant for a long time after the works are finished (Haller 2017).
2. The biological methods improve the substrate quality and normalize its main indicators, e.g. the acid-base balance and texture (Haller 2017), which will enable subsequent selection of any convenient approach to further site treatment.
3. Bioremediation is almost always associated with prolonged decrease in toxicity of wastes, their immobilization and/or accumulation in a compact volume (as in phytoremediation or where mushroom mycelium is used) (Mosa et al. 2016).

Now it should be noted that bioremediation itself does not necessarily restrict us to use only one type of microorganisms or plants since the purpose is to restore (or even create from the scratch) an entire ecosystem. What is more, we can be confident in asserting that such system will be created eventually and naturally regardless of our endeavors: even the sites of man-made disasters are gradually overgrown by the most diversified biological species without human intervention.

What process operators should do is only to be willing to control the formation of such ecosystem, or to decide upon its spontaneous development influenced by nature.

One more important implication arises from the above: the primary treatment method which is basically chemical remediation (as we envisage it here) should not necessarily have a high degree of conversion by itself. It has been empirically displayed that the cost performance rate for chemical or physical remediation methods has non-linear dependence, and the greater amount of pollutant needs to be treated, the faster the price will be growing: essentially, the price growth depending on the case volume for physical and chemical methods is close to the exponential one (see Fig. 2.1) (De Waele 2017). Additionally, the use of such reagents as, for instance, iron oxide and permanganate in large volumes necessary to achieve effective pollutant destruction will lead to mineralization of soils and to degradation of their microbiota (Liao et al. 2019). At the same time, as shown below, even with low actual results of conversion, chemical oxidation done before bioremediation provides the whole process with a powerful systemic boost effect which finally significantly exceeds the sum of conversions of the both methods used separately. This very principle of "the integer which is higher than the sum of its parts" makes it possible to mention the holistic approach to site restoration through the use of combined techniques.

Turning to Fig. 2.1, it should be noted that the holistic approach is empirically shown to be most effective in terms of the cost/performance ratio for large volumes of contaminated substrate. Below we will describe examples of particular technological solutions which are the ones making combined chemical and biological

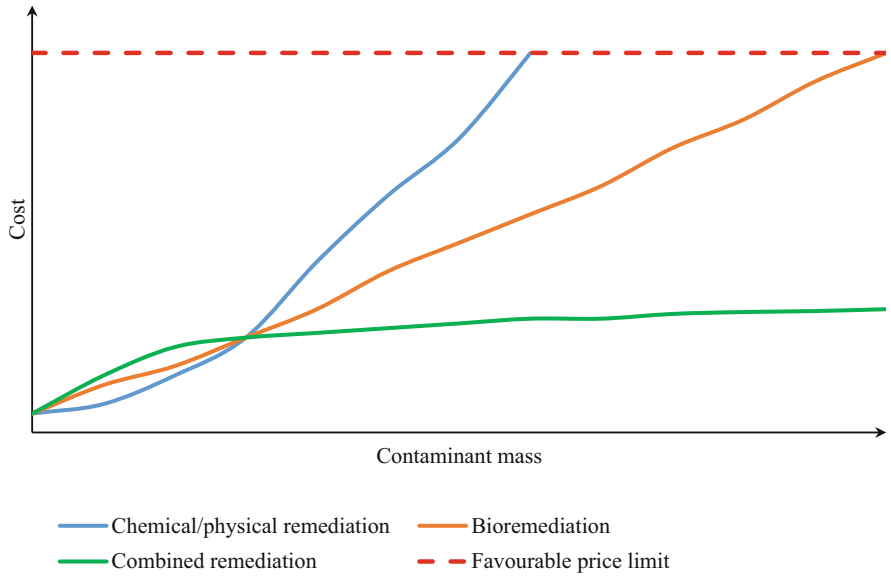


Fig. 2.1 Cost performance rate for chemical/physical, biological, and combined methods for soil remediation depending on case volume (contaminant mass). Easy to see, that in big projects combined techniques are preferable

methods progressive and increasingly demanded in the market of environmental technologies.

2.3 Chemical Remediation

So, let us consider the fundamentally possible ways of conducting chemical oxidation of contaminants in the soil in situ.

We should stipulate right now that here we primarily describe the very solutions which are successfully harmonized with bioremediation, being used before, after, and simultaneously with it. It should also be noted here that In Situ Chemical Oxidation (ISCO) in industry usually means the methods intended to destroy the pollutant in the bulk of substrate by deep injection of strong chemical oxidizers. Meanwhile, the specific features of in situ detoxification of the POPs-contaminated open grounds or wastewater sludges with similar oxidative reagents require absolutely different infrastructure solutions. Nevertheless, here we will also encompass some techniques of underground contaminant disposal, since their harmonization with biological methods is quite critical and demonstrative in a number of cases (Sutton et al. 2011). In this research, we also pay attention to the methods based on zero valent iron (ZVI) nanoparticles (Mu et al. 2017). These solutions are positioned separately, since they deoxidize the pollutant, in contrast to the overwhelming majority of the chemical remediation techniques, but in our opinion, they may be

considered in the general canvas of redox reactions. Despite the aforementioned ZVI toxicity concerns, there are also successful solutions for combined remediation, ZVI + bioremediation manifesting a decrease in the total ecotoxicity of a contaminated site (Galdames et al. 2017).

At first, we will outline the fundamentally possible technical approaches to chemical contaminant destruction in substrate which are widespread in industry:

1. By using acids (Stylianou et al. 2007)
2. Based on decomposition reactions of liquid peroxide
3. Based on dry peroxide producing compounds (De la Calle et al. 2012)
4. Based on permanganate (Huling and Pivetz 2006)
5. Based on gaseous oxidizing agents (ozone) (Huling and Pivetz 2006)
6. ZVI

All these approaches can be implemented depending on the nature of pollution and on the site infrastructure by using various catalysts and equipment improving the efficiency of the remediation process.

Moreover, potentially the most and least bio-friendly technologies should be determined at once. Thus, acids and permanganate obviously destroy the substrates' chemical composition to the greatest extent, whereas hydrogen peroxide and ozone alone do not have any prolonged harmful effects. Dry peroxide-ion producers here are positioned in between, since, on the one hand, they decompose not only into water and oxygen as peroxide and ozone, but, on the other hand, the typical products of their reaction are sodium, calcium, magnesium and other salts which in small quantities may be acceptable in soils even for agricultural purposes.

Catalytic additives and auxiliary reagents can make a certain contribution to the suitability of the substrate for bioremediation. As mentioned above, one of the most common methods of chemical remediation is the Fenton reaction based on the interaction of hydrogen peroxide with iron ions (Fenton 1894). Obviously, the use of this reaction leads to supersaturation of substrate with iron salts (an excess amount is added consciously, due to the instability of Fe II ions), which can be critical in future, for example, for higher plants (Bartakova et al. 2001). It is curious that the need for iron for the Fenton reaction can be partially covered by iron-containing minerals that are basically contained in the soil of a particular site, which eliminates the need for saturation of the substrate with exogenous iron (Santos et al. 2018). However, such approach is not applicable for soils with originally low iron content. It predetermines the necessity to add it, for clear reasons, and subsequent removal of such exogenous iron becomes rather a complex task: it is possible to change the nature of a specific chemical iron compound, but the only possibility to remove it is to wash it away with great volumes of liquid. Iron compounds are not the only additive used to increase the efficiency of Fenton reaction in particular and of peroxide decomposition reactions as a whole. The popularity of such reactions in organic contaminant decomposition in substrate in situ remains consistently high (Baldissarelli et al. 2019), and it is the new approaches for catalysis and modification of oxidative reactions that make it possible to increasingly extend the scope of

application of the solutions based on liquid peroxide. Thus, for instance, the Fenton reaction is shown as effective also for decomposition of POPs, such as DDT, as demonstrated in the research work by Cao et al. (2013). It should be noted that, to reach the best result in DDT decomposition, the authors resorted to adding EDTA, ZVI, and artificial aeration to the standard formula. EDTA and ZVI can significantly influence the substrate's condition after the first stage of remediation and on its suitability for biological treatment. Meanwhile, EDTA, due to its propensity to chelate ions, can disrupt the electrolyte balance of the substrate, and ZVI nanoparticles, as mentioned earlier, raise concerns about their potential toxicity.

However, such risks are inherent in the use of any nano-size agent (Gupta and Xie 2018), and, what is more, numerous research works show the toxicity of nanoparticles exactly for the soil microbiota. At first glance, it clearly discords with the aforementioned results of Galdames et al. (2017), but we believe that the contradiction is only imaginary: the fact is that the situation of POPs disposal always compels us to evaluate not only (and not so much) risks of a definite technological remediation solution, but primarily the benefits. Here we should note that namely the risk/benefit assessment for ZVI in soil remediation was performed in the report by Bardos et al. (2011), although we have a wider vision of the problem: apparently, knowing the specific toxicity risks of reagents in use, we should regard them not separately from the reality of a particular contaminated site, but only by taking into account the nature and level of POP contamination we are dealing with.

Obviously, the toxic effects of POPs in substrate can be so considerable that it may be expedient to use reagents whose residual toxicity will be much lower than the contaminants, where it is prone to decrease in the course of subsequent bioremediation.

In contrast, some catalysts and additives applicable for chemical remediation may turn out to be useful for subsequent biological processes. The proportion of anaerobic processes is inevitably significant in the total biological activity of microbiota at an open non-equipped site, and obviously the deeper the contamination is the greater is the proportion. Thus, in case of future anaerobic remediation, according to a number of studies (Hatzikioseyian 2010), the microbiota will use nitrogen and metal oxides as oxidizers, for instance, iron and manganese oxides (MnO_2). The latter should be emphasized, since, firstly, the Mn IV oxide is a powerful catalyst of peroxide decomposition, and, according to some research works (Dessie et al. 2020; Hooda et al. 2013; Morsi et al. 2020), manganese oxide in various forms, including the form of nanoparticles, can activate also the function of the oxidative enzymes of aerobic organisms. Thus, we can assume that the catalyst initially used to increase the efficiency of peroxide decomposition, e.g. in the composition of Fenton's modified reagent, can not only fail to damage subsequent biological processes, but it also can intensify them. Thus, in the course of the chemical phase of remediation, it is essential to use components which can be harmonized with the upcoming biological process, and which correspond to the specific nature of the substrate's mineral composition on a particular site. It also follows from the above that some catalysts or reagents can hardly be eliminated from soil upon completion of the contaminant decomposition process, and thus their use should be predetermined

only by an unconditionally high ultimate environmental or economic benefit, e.g. comply with the sustainability criteria. This is the very nature of permanganate, a reagent popular in chemical remediation, which removal from the treated sites has become the subject matter of numerous bioremediation studies. Nevertheless, sustainable use of permanganate and persulfate oxidation of contaminants in the soil followed by successful bioremediation eliminating both contamination residues and secondary substrate contamination with excess reagents are currently being exemplified with positive cases (Mora et al. 2020).

Here we should also mention three other aspects of harmonization of chemical and biological remediation methods which primarily concern exactly the chemical oxidation techniques based on liquid peroxide or dry peroxide producing compounds. Chemical oxidation can be used for the following purposes:

1. Increasing the contaminant's availability for bioremediation
2. Intensification of biological processes influenced by oxidative stress
3. To control the pattern of bioremediation (primarily aerobic/anaerobic)

2.4 Increasing Contaminant Availability for Bioremediation

Turning to Fig. 2.1, we should explain the exact way the combined methods beat the mono-technique approaches. As the illustration displays, the biological methods of treatment are generally cheaper than the chemical ones, although they grow in value over time—basically due to the necessity for repeated adding of bacterial preparations and long-term maintenance of vast waste grounds equipped with special infrastructure. Meanwhile, each new portion of substrate requires increasingly vast areas for waste ground storage for treatment, as well as increasingly extensive infrastructure the scaling of which does not always raise the price linearly. A simple conclusion follows: bioremediation can be made critically cheaper if it is accelerated, with an ultimately short cycle of using a waste ground area unit for treatment of a substrate mass unit. What is the possible way to speed up the natural biological process going in not the most favorable conditions? Several fundamental approaches may be used here:

1. Increasing the amount of destructor organisms, "hungry mouths" eating the contaminant
2. Enhancing the quality of strains, selection, "training" of biodestructors for a more effective remediation process
3. Reducing toxicity and making the contaminant more available for such destructors

The first two approaches require additional trophic factors, such as fertilizers (or prebiotics), to be added to the substrate, as well as using reactor technologies or introduced strains. In such case, a reactor is necessary either for proliferation and selection of native microflora inoculated from soil or for proliferation of an effective

introducing destructor from a stock culture (Kantachote 2001). Such measures can be fully justified, but it should be noted that the top efficiency limit for bioremediation should still be predetermined by the toxicity/availability of the target contaminant. And oxidation is one of the effective methods to make contaminants more available for destructor microorganisms (Seryy et al. 2020). At the same time, it causes a certain confusion in terminology: "bioavailability" typically means the contaminant's availability both for organisms involved in remediation and for the ecosystem in general, i.e. the contaminant's capability to ingress into food chains and to reach the top trophic levels in them. Although these concepts are obviously interrelated, the contaminant's availability for decomposition is considered to be a positive criterion, and its availability for ecosystems in general and for humans, as described above, is always a subject of concern. That is why the potential of a specific remediation method for immobilizing a pollutant at a processing site is becoming very important with parallel increase in its "edibility" for microbiota and a decrease in the toxicity of end metabolites. For POPs, e.g. for DDT, it is indicated that long staying in soil under the influence of oxidation processes reduces the contaminant's mobility in the ecosystem (bioavailability in its broad sense), but it makes it more "attractive" for the microbiota on the site (Mansouri et al. 2017; Morrison et al. 2000).

2.5 Intensification of Biological Processes Under the Influence of Oxidative Stress

The intensification of biological processes by means of oxidative stress is a complex process which is typically applicable for substrate microbiota and which predetermines both the selection of the most effective and adapted destructor organisms and activates strains already selected. Oxidative intensification is a universal process for various substrates, and it can be used both in soils and in water treatment, or in sludge activation on wastewater treatment facilities (Кузнецов et al. 2013; Листов et al. n.d.). It is curious that for multicellular organisms, such as fungal mycelium, it is indicated that oxidative stress boosts the activeness of enzymatic systems involved in the disposal of the target contaminant, as it was demonstrated on two strains of fungi by Russo et al. (2019) for DDT biodegradation in soil.

Thus, through the example of experimental remediation of a contaminated site (Fig. 2.2), we have shown that partial chemical oxidation of contaminants catalyzed by MnO_2, carried out before bioremediation, considerably intensifies biological processes. Moreover, it concerns both POPs and more trivial cases, e.g. oil pollutions (Babayev et al. 2019; Seryy et al. 2020). It is noteworthy that when DDT is destroyed in soil substrate, only 18% of contaminant was chemically destroyed, and biological remediation after oxidative treatment showed 98% of the total DDT destruction. Furthermore, the full site remediation cycle was 90 days, which is a high speed for the industry: the normal DDT biodegradation speed in soil can be equal to 6–30% for 42 days (Foght et al. 2010). At the same time, faster

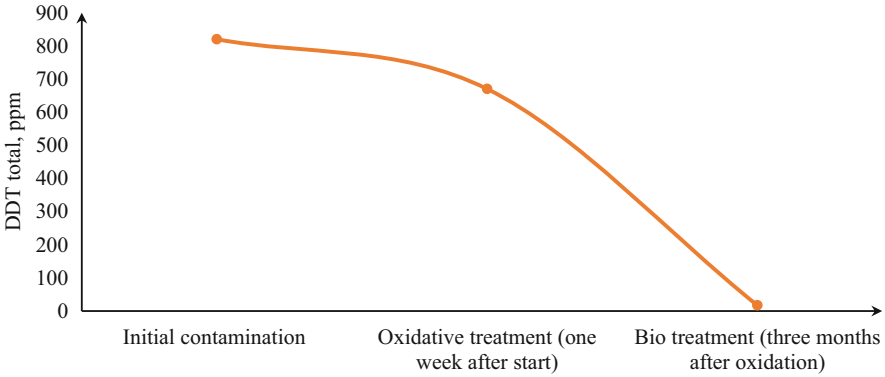


Fig. 2.2 DDT-polluted site decontamination through 90-day combined chemical-biological process, where the chemical oxidation created beneficial environment and effective booster for further bioremediation

methods of DDT bioremediation have been described (Purnomo et al. 2011); however, they require a developed infrastructure or are realized by more highly developed, multicellular organisms, which often leads to bioaccumulation.

In this context, different understanding of DDT destruction should be mentioned as a particular example of POPs in substrates. Due to a vast variety of remediation techniques, especially the biological methods, three possible outcomes of DDT-contaminated site remediation reported in the literature can be distinguished (Huang and Wang 2013; Purnomo et al. 2011):

1. Mineralization: complete decomposition of the contaminant's organic matter to CO_2
2. Degradation: decomposition of the contaminant to intermediate metabolites
3. Accumulation: concentration of a native or slightly modified contaminant in bacterial cells, plant tissues, or fruit bodies of fungi

As we can see, these are three possible outcomes almost completely repeating the waste-to-waste concept set out above herein, with the only difference that, in conditions of a real technical solution, these outcomes are not divided fundamentally, but they occur simultaneously virtually in any solution in different percentage shares.

Turning to the issue of oxidative intensification of biological remediation of POPs, we obviously allege that such intensification leads to a shift in the resulting remediation balance towards degradation and mineralization from simple accumulation of contaminant in live cells.

Among other things, as mentioned before, oxidative intensification consists in a slight oxidation that does not require infrastructure solutions on the site, is quick and cheap, but makes the combined process much more powerful, thus making it cheaper

as well (Seryy et al. 2020). It is especially relevant for microbiota and plays a less considerable role for phytoremediation in particular.

One more important aspect of oxidative acceleration of bioremediation should also be noted: the efficiency of biological processes is often very strongly dependent on its seasonal climatic changes. In a desert, continental or other harsh climate, 90–180 days in a year can be effective, and in the rest of the time, contaminated soil just occupies the remediation site with negligible efficiency of treatment processes due to unsuitable temperature conditions and improper humidity. It means that if the required LOC is not reached within the favorable season, the waste ground rent may rise significantly, which will naturally affect the total price for the process. In such case, if oxidative intensification makes it possible to reduce the process duration and fit into the favorable season, it will obviously become the most sustainable solution.

2.6 Managing the Bioremediation Pattern

As mentioned before, bioremediation in substrate can flow in various patterns. With good natural aeration or with intensive cultivation or forced aeration, aerobic flora will prevail for natural reasons, and, at the same time, biological processes will take course in the soil depth with no access of sufficient oxygen. Apart from apparent narrowing of the range of potential destructor organisms to the level of unicellular microbiota, the metabolism intensity obviously decreases in the microbiota. To understand the degree of decrease in the intensity of metabolic processes, we can compare the amount of ATP (adenosine triphosphate) obtained upon oxidation of one glucose molecule in both cases: the anaerobic process produces two molecules, whereas 38 or 39 molecules are produced by the aerobic process.

However dramatic decrease in the speed of processes is not the only adverse effect of exclusively anaerobic bioremediation. Thus, for instance, a part of anaerobic bacteria are capable to produce methane. It could pose a serious problem for underground ISCO methods, the drilling-wells system starts producing large volumes of gas. Gas is very intensively produced if such additives as natural gums or polysaccharides serving as excellent substrate nutrients for bacteria which are so widespread in drilling are used in pumping reagents into the layer. Instead of decomposition of the target contaminant, a part of microbiota will inevitably proceed to the consumption of a more bioavailable and “healthy” substrate. On the one hand, such fertilization is good because it finally increases the total amount of potential destructors, which should additionally accelerate remediation in the outcome. On the other hand, disadvantages of side effects are apparent.

To surmount such problems in industry, oxidants intended for pumping into layers have become widespread, and, what is noteworthy, they are targeted at partial reorientation of decomposition processes towards the aerobic path rather than at contaminant oxidation (e.g. the hydrogen peroxide aqueous solution).

Therefore, biocenosis is created in the layer, thus creating a highly productive microbiological consortium which not only accelerates contaminant degradation processes, but is also free of adverse side effects. For the ISCO processes usually

lasting for several months to a year of active operation of costly infrastructure, such acceleration is very substantial, as well as reduced risks of gas generation.

2.7 Bioremediation Approaches

There are a lot of bioremediation methods, and they are obviously much more long-standing than their mindful utilization. In part, any soil cultivation, moreover the use of such techniques as green manure, is already bioremediation.

However, current understanding of the process in industry is based upon the sustainability principles and, in part, upon the use of the newest biotechnologies. Here it is relevant to classify the approaches to the bioremediation of the POPs which have become widespread in industry, namely (Kantachote 2001):

In situ approach which is confined to:

- manipulations with the adding liquid trophic factors with concurrent humidity control on the site (bioaugmentation and biostimulation)
- bioventing

Ex situ approach including the following:

- reactor technologies
- partially landfarming and biopiling
- biologically enhanced soil washing
- composting

However, this division is conditional, and for instance, landfarming technologies can be applied in situ, whereas bioventing is used in infrastructure solutions for biopiling.

In this work, we also want to express our opinion about the role the "high" biotechnologies play in the field of remediation of POP-contaminated soils. To achieve high performance of the process in biotechnology, it is specific nature of the action that is essential. Thus, many contemporary achievements, e.g. in medicine, are built upon the possibility of specific interaction between the drug molecule with the definite pathogen.

Precise and specific interactions lead to reaching high efficiency of treatment with a small amount of side effects.

But what should be done if it is difficult to determine the particular target for treatment or remediation in our case? Relatively rarely are soils contaminated with one particular high purity pollutant. Pollution, especially long-standing, typically involves different molecular types of the contaminant at different decomposition stages. When it comes to soils contaminated with prohibited POPs from the list specified in the Stockholm Convention, more often such contaminations are long-standing and already partially transformed as a result of biological activity, under the influence of ultraviolet radiation, etc. It follows that when dealing with a mixture of

various forms of the contaminant associated with soil organics and partially assimilated microbiota, very rarely we can use quite specific methods, such as the GMO-enzymatic methods described above (Wang and Chen 2007), therefore, we should be guided by the conventional approaches

Such approaches are more confined to monitoring the ecosystem developing on a particular contaminated site of such type, and to its enrichment with new components, enhancement through adding trophic factors or chemicals boosting its effectiveness. Methods based on breeding followed by inoculation of native destructive microbiota in reactors (where it proliferates in the presence of low concentration of the target contaminant in favorable conditions) are also widely used. After a sufficient mass of destructors is accumulated, they are reinoculated back to the site, thus increasing the productivity of bioremediation, as described above (Kantachote 2001). It is essential to note that such approach does not imply specific discharge of any single strain: a holistic microbiological consortium is selected from the soil, and then it is cultivated and/or selected depending on the best ability to destroy the target contaminant. It is also important that empirically such approach often demonstrates a greater effectiveness than introducing destructors from another region or climatic zone (even proven to be efficient). It is quite logical: native or autochthonous destructors that are already adapted to the conditions of a particular site are able to show greater tolerance to POPs than introduced organisms (Russo et al. 2019) which have to adapt to such conditions under the influence of stress caused by an increased content of the contaminant in the substrate.

At the same time, numerous works are currently underway to determine the diversity, to classify, and to transcript the genomes of destructive microbiota, which are of great academic interest and are gradually being implemented in industry with proven effectiveness.

For example, in the research work of Pan et al. (2016), the strain of *Stenotrophomonas* sp. extracted from the soil is selected as a monoculture in the presence of DDT, and at the same time, it is characterized both in terms of detailed genome study and by means of chromatography and mass spectrometry, with a view to determine the destructive capabilities of this strain and to potentially distribute DDT metabolites in the soil after its inoculation.

Increasingly numerous works convincingly prove the necessity for complex bioremediation involving microbiological cenosis or even for more complex systems: for example, it was shown (Tarla et al. 2020) that the diversified microbiota most actively degrades DDT and other persistent pesticides exactly in the rhizosphere of plant roots due to the interaction between bacterial and plant enzymes.

Therefore, we face the necessity to evaluate the ecosystem on the remediation site quite traditionally, based on the very basic features which we regard through their practical meaning: aerobic/anaerobic, resistant to a wide range of pH and salinity/unstable, etc.

Thus, we believe that creating a harmonious and stable multilevel ecosystem which would be ultimately close to the native one for this site, i.e. most adapted to the environmental conditions, is an important fundamental for arranging bioremediation processes.

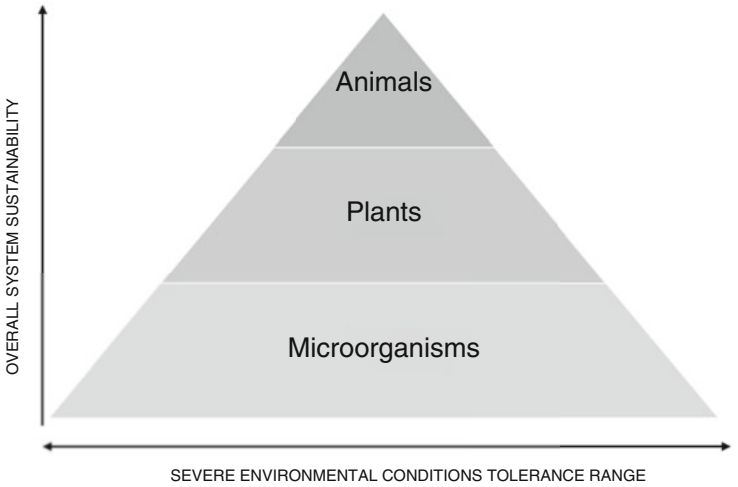


Fig. 2.3 The diagram shows that the ecosystem made from different species demonstrates high resulting sustainability, even if the species applied by themselves are sensitive to the severe environment. The microorganisms that possess the biggest tolerance range for bearing severe conditions make the basis for more sensitive plants (or sometimes fungi) and animals, thus restoring or creating ad hoc the healthy ecosystem. For a good reason they create the most sustainable form—pyramid

At the same time, if we deal with a remediation site, for instance, in a desert with meagre soils and climatic conditions disabling any development of complex highly productive ecosystems while we need an intensive process, we can be guided by one most crucial factor of the environment. For instance, if the substrate's nature is a critical factor for the system which we intend to create, we may try to construct an ecosystem based on the example of other sites with sandy soils, but more humid ones, since we are going to carry out intensive artificial moisturizing. Thus, for instance, the study conducted by (Benyahia and Embaby 2016) displays a classical approach to bioremediation of meagre desert substrate by adding necessary biomass (bioaugmentation) and trophic factors (biostimulation) to create suitable conditions for the life of a prepared microbiological consortium which the authors found the most appropriate one for solving their problem, given that it was suitable for the site's critical conditions.

Each new level of the ecosystem itself is less stable and more fastidious than the previous one, but being correctly realized, it significantly increases the stability of the system as a whole (Fig. 2.3). Thus, it follows that each element introduced into the ecosystem should improve the conditions for the subsequent ones, by narrowing the possible variety of conditions to the optimal pattern in which the most highly organized life forms can potentially exist.

Let us examine the following example: various types of higher plants are used for phytoremediation of contaminated soils. Most commonly, unfastidious species which should accumulate contaminants in their tissues for subsequent disposal are

selected as technical site purification cultures. And still, higher plants rather badly tolerate high soil salinity, being vulnerable to toxic effects, such as from heavy metals. At the same time, less organized life forms, such as microscopic fungi are more tolerant to high levels of salinity and contamination with metal ions, but they are much less effective in remediation of such contaminants.

Li et al. (2019) took advantage of such specific features in their work, by utilizing the aboriginal fungus *Trichoderma asperellum* for bioaugmentation of the phytoremediation in the saline substrate contaminated with lead ions. The fungus prepared the soil and considerably improved the growth conditions for *Suaeda salsa* badly affected simultaneously by salinity stress and by lead phytotoxicity in the absence of suitable microflora. Influenced by the mycelium of the fungus that formed mycorrhiza with plant roots, the latter began to grow better, experienced less toxic stress, their green mass grew faster, and most importantly, they started a better accumulation of the target lead contaminant.

Our next example is more complex, with combined soil contamination with cadmium and DDT, studied by (Zhu et al. 2012). In this research the authors opted for the original strategy of simultaneous cadmium phytoaccumulation by the *Sedum alfredii* plant and DDT destruction by the bacterial strain *Pseudomonas* sp., where the latter was specially extracted from a DDT-contaminated site in the same region where the experiment was conducted. Such combination had a cumulative effect: cadmium was accumulated faster, since the use of the inoculated strain beneficially influenced the development of plants by increasing their biomass, whereas DDT destruction was accelerated, since the destructor bacteria found a favorable medium for the growth on plant roots, which was separately denominated by the authors as "DDT rhizodegradation" in their work.

Thus, the bioremediation system which is more complicated to create finally manifests much higher efficiency and self-recovery resource, which means a higher sustainability, provided that the process is adequately cost-effective. At the same time, the logic of the process apparently implies using a less effective biological form with low remediation rates in the base for the activity of a more organized and more effective form.

Among other things, the aforementioned complex approach obviously enables increasing the amount of the organic component in soil, which is very important for subsequent return of purified soil into soil turnover—and we believe that it is the very ultimate objective of remediation. It is currently evident that the organic content in soil is a significant evaluation criterion largely predetermining the success of remediation procedures (Haller 2017).

Figure 2.3 also shows which destructors can be used for remediation: unicellular aerobes and anaerobes, multicellular plants and fungi, as well as some animals, where the most common example is earthworms which are equally used for remediation and for testing of its results (Fründ et al. 2011). The fact of using earthworms as a biological indicator does confirm the statement on correlation between narrowing of the range of acceptable site conditions, the growth of the organization degree of biodestructor organisms, and an increase in system sustainability. Therefore, the purest soil will be suitable for the growth of earthworms, whereas they accomplish

the destruction of the contaminant's metabolites with high efficiency after fungal and bacterial/plant flora.

This approach is excellently demonstrated in the study conducted by Cheng-Kim et al. (2016) who succeeded in using bioaugmentation, fungal mycelium, and the *Lumbricus rubellus* earthworm to remediate a site contaminated with heavy metals: this complex system made it possible to enhance the bioavailability of heavy metal compounds for worms which, while building up the biomass, were bounding the heavy metals in their tissues, thus removing them from the substrate, and, in parallel, reducing the bioavailability of the heavy metal residues in the soil for the ecosystem as a whole. Our specific experience in DDT disposal (Fig. 2.2) evidently included only one organization level of bioremediation, which is developing a stable cenosis of aerobic and anaerobic microorganisms, still remaining quite difficult to implement. And such microbiological consortium, if used properly, enables achieving sufficiently high process efficiency.

Nevertheless, the above examples make us confident that it is construction of multilevel systems that is the most promising way.

2.8 Analytics

It should be noted in conclusion that whatever remediation strategy is chosen, it is analytics that finally evaluates its success, whether it be intermediate analytics performed by a contractor as part of internal project audit or a final assessment carried out by a regulator. Based on the industry's experience, we can assert that, irrespective of the degree of excellence of site remediation, improper selection of an analytical methodology can lead to dramatic underestimation of project success both by the contractor and by the regulator.

This seemingly evident statement encounters a lot of obstacles in practice for coordination of analytics between process stakeholders both at the level of methodology selection and within one technique. We explain it through the example of DDT: to analyze the DDT content in soil and water medium, the techniques based upon EPA recommendations are commonly applied. At the same time, there are currently several such methods: US EPA 8081 (GC ECD), US EPA 1699 (HRGC/HRMS), US EPA 525.3 (GC MS), etc. (Method 1699: pesticides in water, soil, sediment, biosolids, and tissue by HRGC/HRMS n.d.; Munch et al. 2012). Apart from the EPA technologies which are considered to be the "golden standard" in industry, there are also the ISO methods and local interpretations of EPA and ISO, which are arbitrarily applied by laboratories of customers and regulators. And such variety of methods is used to determine only one type of POPs!

We must not forget that the most accurate and up-to-date analytical techniques capable of detecting very low contaminant amounts with a high accuracy in a homogeneous carrier (matrix), for example, in pure water or in sand, appear not to be adapted for analyzing "dirt" in which several contaminants are mixed, their metabolites and decomposition products in a matrix rich in organic matter (almost any fertile soil or silt). In such case, the method requires rather a complex adaptation,

and, having achieved accuracy in realizing one method, an analytical laboratory will specialize exactly in such method. Apparently, to attain convergence in findings, all process stakeholders should agree upon using only one analytical method in a project, otherwise, as it often happens, the contractor, customer, and regulator will obtain contradictory and incomparable results, which will immediately case a doubt on the quality of works performed. It particularly concerns express evaluation of findings on a site, which is sometimes carried out by means of IR detectors, for instance. Being accurate and sensitive to one type of molecules (pure target contaminant), such devices turn out to be blind to the target contaminant once it is oxidized or otherwise changed. Thus, an insufficiently intensive procedure can show enormous effectiveness on an express test, which will not be confirmed by a laboratory afterwards.

At the same time, there is one unobvious and purely empirical consequence: subcontractors may question third-party analytics, even though it is provided at a very high technical level, but by an "unverified" laboratory. But, what is strange, findings obtained through bioindication have a large, purely emotional weight, and for several reasons:

1. A green lawn with animal species (e.g. earthworms and insects) on the site of a former "lunar landscape" always looks convincing.
2. By and large, any remediation is intended to critically decrease the threat of a contaminated site for the ecosystem in which it is contained, and for the human as for a part of such ecosystem. Therefore, it is the well-being and health of the inhabitants of such ecosystem that is the final criterion for the success of the whole process.

This is the very reason why bioindication is universally recognized as the "final" test for almost any soil and water system purification project. Bioindication methods are typically simple and do not require any complex equipment, but their effectiveness and convincing nature have been attracting both private contractors and global regulators to them for many years.

2.9 Conclusion

The application of the combined chemical-biological methodologies in soil remediation described above becoming more and more widespread all over the world and out of doubts has big future in the industry. Especially this is relevant to POPs contamination that offers big difficulties and strong challenges to the world. Today it becomes obvious that scales of POPs emergencies in the world are so high, that it is no chance to turn a blind eye to the problem: it directly refers to the UN SDGs troubling, such as "zero hunger" or "no poverty" by undermining agriculture and overall life safety. This means that the industry has a lot of work ahead, and this work would not always be provided on well-equipped small sites with modern infrastructure and advanced technologies. We rather will deal with big and unfitted spaces,

where the only weapon against the POPs would be well planned combined application of the basic and approachable technologies. The art of such combination and balance between the conventional chemical and biological technologies to gain the truly sustainable results is what we consider the very demanded skill in upcoming period.

Acknowledgements The authors want to express their grateful acknowledgements to Dr. Elbay Babayev from Institute of Chemistry of Additives, Azerbaijan National Academy of Sciences. Of particular note we want to acknowledge input from Ph.D. Maryna Kit, who bravely assisted us in revision of the text.

References

Arnold SM, Hickey WJ, Harris RF, Talaat RE (1996) Integrating chemical and biological remediation of atrazine and S-triazine-containing pesticide wastes. Environ Toxicol Chem 15 (8):1255–1262. https://doi.org/10.1002/etc.5620150802

Babayev R, Ali-zade AM, Babayev VA, Harkavenko VV, Seryy SS (2019) The new combined chemical-biological remediation method for oil-polluted soils: oxidative disposal and establishing sustainable soil cenosis. J Bioremed Biodegr 10:464–470

Baldissarelli DP, Vargas GDLP, Korf EP, Galon L, Kaufmann C, Santos JB (2019) Remediation of soils contaminated by pesticides using physicochemical processes: a brief review. Planta Daninha 37:54. https://doi.org/10.1590/s0100-83582019370100054

Bardos P, Bone B, Elliott DW, Hartog N, Henstock J, Nathanail P (2011) Risk/benefit approach to the application of iron nanoparticles for the remediation of contaminated sites in the environment. Technical report, contaminated land: Application in real environment. CB0440, p 110

Bartakova I, Kummerova M, Mandl M, Pospisil M (2001) Phytotoxicity of iron in relation to its solubility conditions and the effect of ionic strength. Plant Soil 235:45–51

Benyahia F, Embaby AS (2016) Bioremediation of crude oil contaminated desert soil: effect of biostimulation, bioaugmentation and bioavailability in biopile treatment systems. Int J Environ Res Public Health 13(2):219–225

Cao M, Wang L, Wang L, Chen J, Lu X (2013) Remediation of DDTs contaminated soil in a novel fenton-like system with zero-valent iron. Chemosphere 90(8):2303–2308

Chang YC, Kikuchi S (2012) How can we overcome limitations of bioremediation? J Bioremed Biodegr 3:e106. https://doi.org/10.4172/2155-6199.1000e106

Cheng-Kim S, Azizi AB, Mahmood NZ, Abdullah N (2016) Heavy metal contaminated soil bioremediation via vermicomposting with spent mushroom compost. Sci Asia 42(6):367–375

Collins D (2009) The full cost of landfill disposal in Australia. National Waste Policy - Less Waste, More Resources BDA Group p 78

De la Calle RG, Gimeno O, Rivas J (2012) Percarbonate as a hydrogen peroxide carrier in soil remediation processes. Environ Eng Sci 29(10):951–956

De Waele R (2017) European perspective in situ and on site soil remediation. Green soil: Sustainable soil remediation https://asiakas.kotisivukone.com/files/mutku.kotisivukone.com/3_Rogier_De_Waele.pdf

Dessie Y, Tadesse S, Eswaramoorthy R (2020) Review on manganese oxide based biocatalyst in microbial fuel cell: nanocomposite approach. Mater Sci Energy Technol 3:136–149

Efroymson RA, Nicolette JP, Suter GW (2004) A framework for net environmental benefit analysis for remediation or restoration of contaminated sites. Environ Manag 34(3):315–331

Environmental Management Act Pub. L. No. B.C. Reg. 375/96 (2019) Contaminated sites regulation. http://www.bclaws.ca/EPLibraries/bclaws_new/document/ID/freeside/375_96_00

European Environment Agency (2014) Waste: a problem or a resource? Signals 2014 - Well-being and the environment. https://www.eea.europa.eu/signals/signals-2014/articles/waste-a-problem-or-a-resource

Fenton HJH (1894) LXXIII - oxidation of tartaric acid in presence of iron. J Chem Soc Trans 65:899–910. https://doi.org/10.1039/CT8946500899

Foght J, April T, Biggar K, Aislabie J (2010) Bioremediation of DDT-contaminated soils: a review. Biorem J 5(3):225–246. https://doi.org/10.1080/20018891079302

Fründ HC, Graefe U, Tischer S (2011) Earthworms as bioindicators of soil quality. Biol Earthworms 24:261–278. https://doi.org/10.1007/978-3-642-14636-7_16

Galdames A, Mendoza A, Orueta M, de Soto García IS, Sánchez M, Virto I, Vilas JL (2017) Development of new remediation technologies for contaminated soils based on the application of zero-valent iron nanoparticles and bioremediation with compost. Resour Efficient Technol 3 (2):166–176. Doi: https://doi.org/10.1016/j.reffit.2017.03.008

Gupta R, Xie H (2018) Nanoparticles in daily life: applications, toxicity and regulations. J Environ Pathol Toxicol Oncol 37(3):209–230. https://doi.org/10.1615/JEnvironPatholToxicolOncol.2018026009

Haller H (2017) Soil remediation and sustainable development-creating appropriate solutions for marginalized regions [Doctoral dissertation, Mid Sweden University]. https://www.diva-portal.org/smash/get/diva2:1094867/FULLTEXT02.pdf

Hatzikioseyian A (2010) Principles of bioremediation processes. In: Trends in bioremediation and phytoremediation. Research Singpost, pp 23-54.

Hooda V, Chauhan N, Pundir CS (2013) Effect of metal oxide nanoparticles on barley oxalate oxidase. J Biosens Bioelectron 3(4):21. https://doi.org/10.4172/2155-6210.S1.021

HRGC/HRMS (n.d.) Method 1699: pesticides in water, soil, sediment, biosolids, and tissue by HRGC/HRMS, EPA-821-R-08-001, p 96

Huang Y, Wang J (2013) Degradation and mineralization of DDT by the ectomycorrhizal fungi, *Xerocomus chrysenteron*. Chemosphere 92(7):760–764. https://doi.org/10.1016/j.chemosphere.2013.04.002

Huling SG, Pivetz BE (2006) In-situ chemical oxidation- engineering issue. US Environmental Protection Agency (USPEA). https://archive.epa.gov/ada/web/pdf/insituchemicaloxidation_engineering_issue.pdf

Ifon BE, Togbé ACF, Tometin LAS, Suanon F, Yessoufou A (2019) Metal contaminated soil remediation: phytoremediation, chemical leaching and electrochemical remediation. Metals Soil. https://doi.org/10.5772/intechopen.81223

Листов Е, Пыстина Н, Балакирев И, Никишова А, Липник С (n.d.) Способ очистки почвы от углеводородных загрязнений (Patent No. RU 2502569). Retrieved March 29, 2020, from https://findpatent.ru/patent/250/2502569.html

Kantachote, D. (2001). The use of microbial inoculants to enhance DDT degradation in contaminated soil. Ph.D. Thesis, Department of Soil and Water, University of Adelaide p 191

Кузнецов АЕ, Колотилин ДВ, Хохлачев НС, Калёнов СВ, Занина ОС (2013) Аэробная биологическая очистка сточных вод в условиях гранулообразования активного ила. I. Гранулообразование активного ила при очистке модельных стоков. Вода: химия и экология 7:35–44

Li XN, Jiao WT, Xiao RB, Chen WP, Chang AC (2015) Soil pollution and site remediation policies in China: a review. Environ Rev 23(3):263–274. https://doi.org/10.1139/er-2014-0073

Li X, Zhang X, Wang X, Yang X, Cui Z (2019) Bioaugmentation-assisted phytoremediation of lead and salinity co-contaminated soil by *Suaeda salsa* and *Trichoderma asperellum*. Chemosphere 224:716–725. https://doi.org/10.1016/j.chemosphere.2019.02.184

Liao X, Wu Z, Li Y, Cao H, Su C (2019) Effect of various chemical oxidation reagents on soil indigenous microbial diversity in remediation of soil contaminated by PAHs. Chemosphere 226:483–491. https://doi.org/10.1016/j.chemosphere.2019.03.126

Mansouri A, Cregut M, Abbes C, Durand M-J, Landoulsi A, Thouand G (2017) The environmental issues of ddt pollution and bioremediation: a multidisciplinary review. Appl Biochem Biotechnol 181(1):309–339. https://doi.org/10.1007/s12010-016-2214-5

Mora VC, Morelli IS, Rosso JA (2020) Co-treatment of an oily sludge and aged contaminated soil: permanganate oxidation followed by bioremediation. J Environ Manag 261:110169. https://doi.org/10.1016/j.jenvman.2020.110169

Morrison DE, Robertson BK, Alexander M (2000) Bioavailability to earthworms of aged DDT, DDE, DDD, and dieldrin in soil. Environ Sci Technol 34(4):709–713. https://doi.org/10.1021/es9909879

Morsi R, Bilal M, Iqbal HMN, Ashraf SS (2020) Laccases and peroxidases: the smart, greener and futuristic biocatalytic tools to mitigate recalcitrant emerging pollutants. Sci Total Environ 714:136572. https://doi.org/10.1016/j.scitotenv.2020.136572

Mosa KA, Saadoun I, Kumar K, Helmy M, Dhankher OP (2016) Potential biotechnological strategies for the cleanup of heavy metals and metalloids. Front Plant Sci 7:303. https://doi.org/10.3389/fpls.2016.00303

Mu Y, Jia F, Ai Z, Zhang L (2017) Iron oxide shell mediated environmental remediation properties of nano zero-valent iron. Environ Sci Nano 4(1):27–45. https://doi.org/10.1039/C6EN00398B

Mudhoo A, Mohee R (2012) Elements of sustainability and bioremediation. Bioremediation and sustainability: research and applications pp 1–41. https://doi.org/10.1002/9781118371220.ch1

Munch J, Grimmett P, Munch D, Wendelken S, Domino M, Zaffiro A, Zimmerman M (2012) EPA method 525.3—determination of semivolatile organic chemicals in drinking water by solid phase extraction and capillary column gas chromatography/mass spectrometry (GC/MS). Environmental Protection Agency, Washington, DC

Pan X, Lin D, Zheng Y, Zhang Q, Yin Y, Cai L, Fang H, Yu Y (2016) Biodegradation of DDT by *Stenotrophomonas* sp. DDT-1: characterization and genome functional analysis. Sci Rep 6 (1):21332. https://doi.org/10.1038/srep21332

Purnomo AS, Mori T, Kamei I, Kondo R (2011) Basic studies and applications on bioremediation of DDT: a review. Int Biodeterior Biodegrad 65(7):921–930. https://doi.org/10.1016/j.ibiod.2011.07.011

Russo F, Ceci A, Pinzari F, Siciliano A, Guida M, Malusà E, Tartanus M, Miszczak A, Maggi O, Persiani AM (2019) Bioremediation of dichlorodiphenyltrichloroethane (DDT) contaminated agricultural soils: potential of two autochthonous saprotrophic fungal strains. Appl Environ Microbiol 85:e01720–e01719. https://doi.org/10.1128/AEM.01720-19

Saier MH, Trevors JT (2010) Phytoremediation. Water Air Soil Pollut 205(1):61–63. https://doi.org/10.1007/s11270-008-9673-4

Santos A, Firak DS, Emmel A, Siedlecki K, Lopes A, Peralta-Zamora P (2018) Evaluation of the Fenton process effectiveness in the remediation of soils contaminated by gasoline: effect of soil physicochemical properties. Chemosphere 207:154–161. https://doi.org/10.1016/j.chemosphere.2018.05.087

Sarkar A, Sengupta S, Sen S (2019) Nanoparticles for soil remediation. In: Gothandam KM, Ranjan S, Dasgupta N, Lichtfouse E (eds) Nanosci biotechnol environ applications, vol 22. Springer, New York, pp 249–262. https://doi.org/10.1007/978-3-319-97922-9_9

Seryy S, Harkavenko VV, Babayev ER, Ali-zade AM (2020) Combined oxidative and bio method for removal, degradation or disposal of chlorinated persistent organic pollutants. J Bioremed Biodegr 11(1):466

Stage 8 Amendments to the Contaminated Sites Regulation Environmental Management Act (2013) Ministry of environment British Columbia. https://www2.gov.bc.ca/assets/gov/environment/air-land-water/site-remediation/docs/updates/stage-8-csr-amendments.pdf

Stockholm Convention on Persistent Organic Pollutants (POPs) Texts and Annexes (2017) Pops. Int. http://www.pops.int/TheConvention/Overview/TextoftheConvention/tabid/2232/Default.aspx

Stylianou MA, Kollia D, Haralambous KJ, Inglezakis VJ, Moustakas KG, Loizidou MD (2007) Effect of acid treatment on the removal of heavy metals from sewage sludge. Desalination 215 (1):73–81. https://doi.org/10.1016/j.desal.2006.11.015

Surriya O, Saleem S, Waqar K, Kazi AG (2015) Chapter 1 - phytoremediation of soils: prospects and challenges. In: Soil remed plants. Academic, New York, pp 1–36. https://doi.org/10.1016/B978-0-12-799937-1.00001-2

Sutton NB, Grotenhuis JTC, Langenhoff AAM, Rijnaarts HHM (2011) Efforts to improve coupled in situ chemical oxidation with bioremediation: a review of optimization strategies. J Soils Sediments 11(1):129–140. https://doi.org/10.1007/s11368-010-0272-9

Tarla DN, Erickson LE, Hettiarachchi GM, Amadi SI, Galkaduwa M, Davis LC, Nurzhanova A, Pidlisnyuk V (2020) Phytoremediation and bioremediation of pesticide-contaminated soil. Appl Sci 10(4):1217. https://doi.org/10.3390/app10041217

Wang GD, Chen XY (2007) Detoxification of soil phenolic pollutants by plant secretory enzyme. Methods Biotechnol 23:49–57. https://doi.org/10.1007/978-1-59745-098-0_4

Wang JY, Stabnikova O, Lee SS, Tay JH (2004) Integrated chemical-biological remediation for polycyclic aromatic hydrocarbons contaminated soil. Pract Period Hazard Toxic Radioact Waste Manage 8(2):79–83. https://doi.org/10.1061/(asce)1090-025x(2004)8:2(79)

Warner SD, Hadley PW (2012) Sustainable remediation: integrating risk, science, and sustainability principles. In: Meyers RA (ed) Encyclopedia of sustainability science and technology. Springer, New York, pp 10435–10448. https://doi.org/10.1007/978-1-4419-0851-3_55

Yu Y, Zhou D, Li Z, Zhu C (2018) Advancement and challenges of microplastic pollution in the aquatic environment: a review. Water Air Soil Pollut 229(5):140. https://doi.org/10.1007/s11270-018-3788-z

Zhu ZQ, Yang XE, Wang K, Huang HG, Zhang X, Fang H, Li TQ, Alva AK, He ZL (2012) Bioremediation of Cd-DDT co-contaminated soil using the Cd-hyperaccumulator Sedum alfredii and DDT-degrading microbes. J Hazard Mater 235–236:144–151. https://doi.org/10.1016/j.jhazmat.2012.07.033

Zhilin M, Shuchu B, Bing X (2014) Environmental Legislation in China: Achievements, Challenges and Trends. Sustainability 6(12): 8967–8979. https://doi.org/10.3390/su6128967

Biosurfactants: A Green and Sustainable Remediation Alternative

3

Grazielly Maria Didier de Vasconcelos, Jéssica Mulinari, Talita Corrêa Nazareth, Éllen Francine Rodrigues, Bianca Chieregato Maniglia, and Cristiano José de Andrade

Abstract

The wide range of human interventions on the environment has made easier the lifestyle of people worldwide; on the other hand, these interventions have serious environmental drawbacks, since petroleum derivatives, solvents, heavy metals, among others, that are potentially toxic, are used. Thus, there is an increasing concern for the development of green and sustainable alternatives to reduce the contaminant effects, including soil contamination which is well-known as bioremediation. Biosurfactants are amphipathic molecules that are synthesized by living cells, in particular microorganisms. Also, biosurfactants can be organized into five clusters, in which lipopeptides and glycolipids are the most well-known groups of biosurfactants. In this sense, biosurfactants can be applied as a bioremediation agent. Therefore, this chapter aims to put light on the chemical structures of biosurfactants and also some biological properties. Then, it focuses mainly on the application of biosurfactants for soil remediation, that is, bioremediation, which is one of the most promising alternatives for environmental safety and green technology. In conclusion, the group and also the subgroups of biosurfactants should be related to their applications (bioremediation), in which the current literature is scarce, however, some trends can already be spotted, such as iturin shows great potential as a remediation agent for both soil and water remediation (oil); lichenysin can be used for chelating divalent cations; rhamnolipid can be used to Cu and Ni remediation and also drill cuttings and oil-contaminated soil; There are few studies on MELs for remediation, and the

G. M. D. de Vasconcelos · J. Mulinari · T. C. Nazareth · É. F. Rodrigues · C. J. de Andrade (✉)
Department of Chemical Engineering and Food Engineering, Technological Center, Federal University of Santa Catarina, Florianópolis, SC, Brazil

B. C. Maniglia
Ecole Nationale Vétérinaire, Agroalimentaire et de l'Alimentation, Nantes, France

© The Author(s), under exclusive licence to Springer Nature Singapore Pte Ltd. 2021

V. Kumar et al. (eds.), *Rhizobiont in Bioremediation of Hazardous Waste*,
https://doi.org/10.1007/978-981-16-0602-1_3

majority of them is for oil contamination or contaminants derived from the oil industry, such as aromatic hydrocarbons, alkanes, and kerosene.

Keywords

Biosurfactants · Bioremediation · Organic contaminants heavy metals

3.1 Introduction

Technological advances have assisted mankind in the life quality, laboratory research, exploration of natural resources, among others. Thus, activities such as the arrival of pharmaceutical products, agricultural chemicals, crude oil exploration, excavation of fossil fuels, and related product usage have eased the lifestyle of people worldwide (Jimoh and Lin 2019). However, these interventions have some drawbacks, since chemicals, solvents, heavy metals, etc., that are used are potentially toxic to the environment, including human health. In this sense, there is an increasing concern for the development of green and sustainable alternatives to reduce the contaminant effects, including soil contamination which is known as bioremediation.

Ideally, the technology used for the recovery of soil properties should be produced at an industrial scale and also be environmentally friendly. A green and sustainable remediation alternative is related to surface-active molecules that are synthesized by living cells, well-known as biosurfactant since biosurfactant are compounds produced by particular microorganisms with amphiphilic behavior (Parthipan et al. 2017), good ecological compatibility, low toxicity, and biodegradability (Singh et al. 2019). Biosurfactants can complex heavy metals, lower the surface tension of hydrophobic compounds (higher surface area; higher microbial degradation rate), among others.

This chapter aims to put a light on the chemical structures of biosurfactants and also some biological properties. Then, it focuses mainly on the application of biosurfactants for soil remediation, that is, bioremediation, which is one of the most promising alternatives for environmental safety and green technology.

3.2 Biosurfactants; Chemical Structure and Properties

Amphipathic molecules that are synthesized by living cells are known as biosurfactants. Biosurfactants are biosynthesized fundamentally by microorganisms, in which they are mainly separated into five groups, according to their chemical structure: (1) fatty acids, neutral lipids, and phospholipids, (2) glycolipids, (3) lipopeptides and lipoproteins, (4) particulate, and (5) polymeric surfactant. Lipopeptides and glycolipids are the most important (industrially) biosurfactants—briefly described below. In addition, there is a variety of applications of

biosurfactants such as bioremediation, skincare products, and substitutes to pesticides, biostimulants, microbial enhanced oil recovery, among others.

3.2.1 Lipopeptides

The chemical structure of lipopeptides consists of fatty acid(s) that are chemically bonded to peptide moiety. The main subgroups are surfactin, iturin, bacillomycin, and mycosubtilin. It is worth noting that the peptide moiety contains (often) $_{D}$-amino acids, which are the most unusual amino acid form in nature—and thus probably related to their biological properties.

3.2.1.1 Surfactin

Surfactin is composed of seven amino acids—lactone ring connected to one β-OH fatty acid chain. The amino acid sequence changes according to the surfactin producer, culture medium, bioprocess conditions, etc. However, the most usual amino acid sequence is Glu (1st); Leu (2nd); Leu (3rd); Val (4th); Asp (5th); Leu (6th), Val or Leu (7th—mostly) (Fig. 3.1).

3.2.2 Glycolipids

Similar to lipopeptides, glycolipids also have fatty acid(s) in their chemical structure (hydrophobic moiety) but fatty acid(s) is bounded to one or more monosaccharide moieties instead of peptide moiety. It is noteworthy that, when compared to the

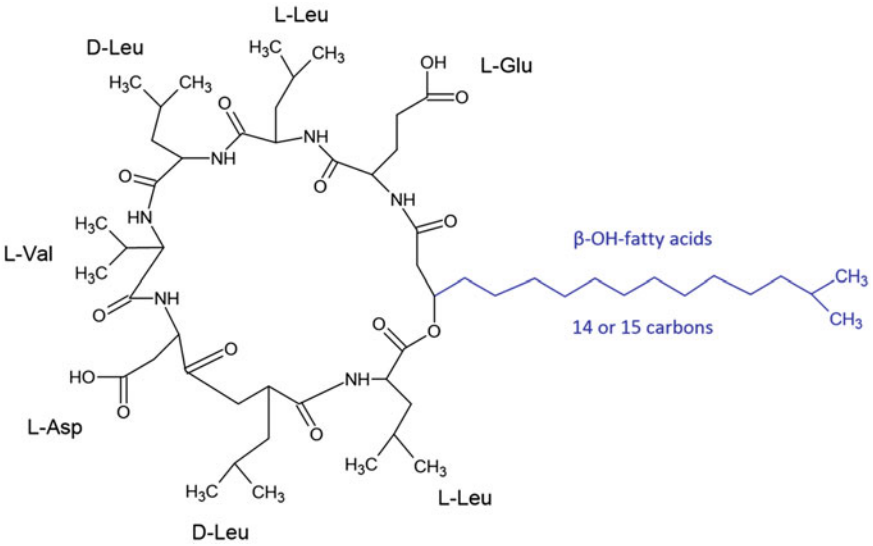


Fig. 3.1 The structural formula of surfactin

yields of lipopeptide production (≈mg/L), glycolipids show much higher yields of production (g/L). This difference occurs, very likely, due to their simpler chemical structure, a smaller number of metabolic pathways involved, among others. The most well-known subgroups of glycolipids are rhamnolipids, sophorolipids, and recently mannosylerythritol lipids (MEL)—briefly described below:

3.2.2.1 Rhamnolipids

Rhamnolipids (Fig. 3.2) are glycolipids obtained from reactions performed using bacterial species, in particular *Pseudomonas aeruginosa*. The chemical structure of rhamnolipids includes 4 congeners (Radzuan et al. 2018):

- *α-L*-rhamnopyranosyl-*α-L*-rhamnopyranosyl-*β*-hydroxydecanoyl-*β*-hydroxydecanoate (Rha-Rha-C_{10}-C_{10}),
- *α-L*-rhamnopyranosyl-*α-L*-rhamnopyranosyl-*β*-hydroxydecanoate (Rha-Rha-C_{10}), and
- mono-rhamnolipid congeners Rha-C_{10}-$C_{10}$and Rha-C_{10}.

3.2.2.2 Sophorolipids

Sophorolipids are composed of disaccharide sophorose—as hydrophilic moiety—bonded to long-chain hydroxylated fatty acid—as hydrophobic moiety (Fig. 3.3).

3.2.3 Mannosylerythritol Lipids

Mannosylerythritol lipids (MEL) are amphiphilic glycolipids that present high surface activity and low toxicity, functional properties, and production yields (Fukuoka et al. 2012; Fai et al. 2015; Simiqueli et al. 2017; Beck et al. 2019). MEL consists of a mix of a partially acylated derivative of 4-*O*-*β*-$_D$-mannopyranosyl-$_D$-erythritol as shown in Fig. 3.4. In general, MEL can be classified as MEL-A, -B, -C, and -D depending on the mannose acetylation in the positions

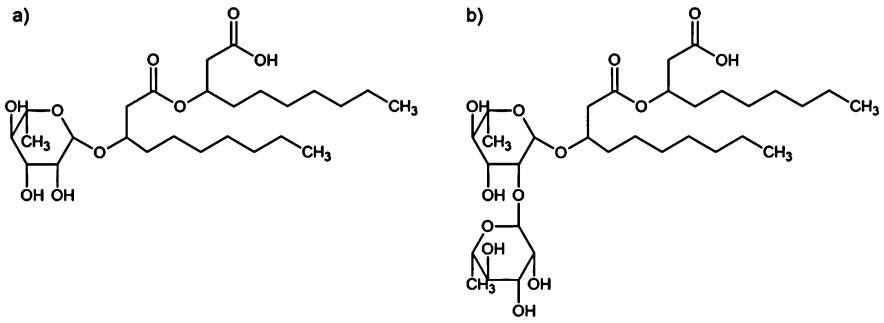


Fig. 3.2 Chemical structure of rhamnolipid: (**a**) mono-rhamnolipid and (**b**) di-rhamnolipid

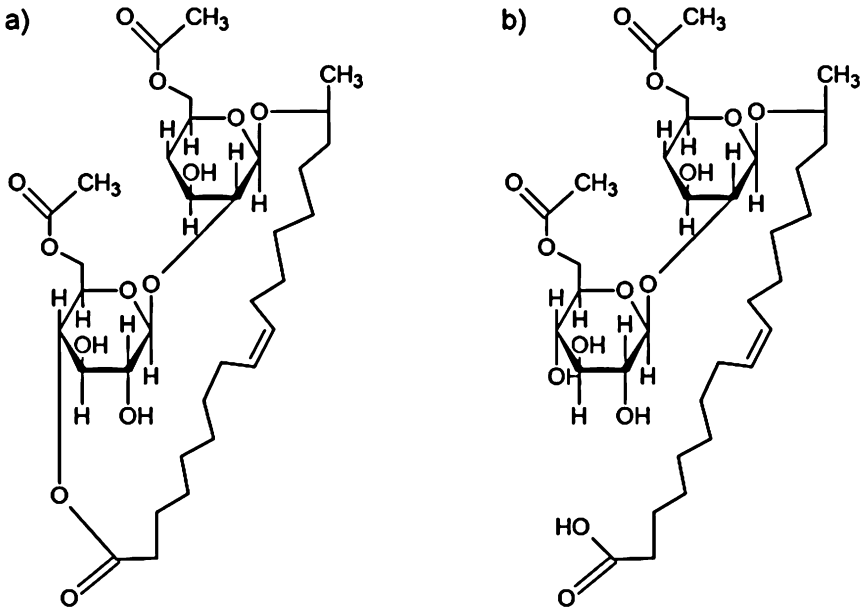


Fig. 3.3 Chemical structure of (**a**) lactonic sophorolipid and (**b**) acidic sophorolipid

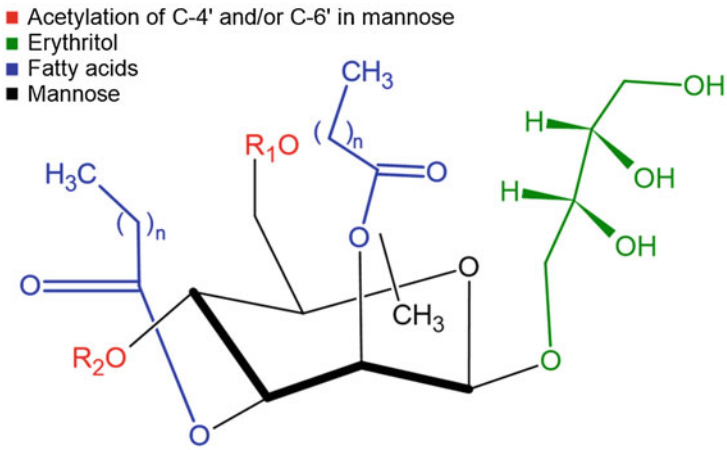


Fig. 3.4 Chemical structure of MEL, with n ranges from 8 to 14 carbons

C-4′ and C-6′. MEL-A has acetyl groups in both R_1 and R_2 (see Fig. 3.4), MEL-B presents an acetyl group at R_1 and hydrogen at R_2, MEL-C has hydrogen at R_1 and an acetyl group at R_2, and MEL-D has hydrogen at both R_1 and R_2 (Simiqueli et al. 2017).

Microorganisms have the ability to produce MELs, such as some of *Ustilago* genus (Boothroyd et al. 1956; Spoeckner et al. 1999; Morita et al. 2008; Morita et al.

2009), *Kurtzmanomyces* sp. (Kakugawa et al. 2002), and yeast strains belonging to the genus *Pseudozyma* (Fukuoka et al. 2012; Yu et al. 2015; Simiqueli et al. 2017; Konishi et al. 2008). *Pseudozyma tsukubaensis* has been outstanding due to its ability to exclusively produce MEL-B, while other species generally produce a concoction of distinct MEL homologs (Arutchelvi et al. 2008; Fukuoka et al. 2008; Simiqueli et al. 2017).

3.3 Biosurfactants for Remediation

Currently and near-future the energy resources are, heavily, related to fossil fuels. In this sense, petroleum hydrocarbons and their derivatives can harm the environment, since they have low water solubility and high interfacial tension, thus petroleum hydrocarbons and their derivatives are not easily removed from the environment. Therefore, sustainable alternatives for remediation of these contaminants have been developed, in which biosurfactant is one of the most promising technologies, mainly due to low toxicity and high biodegradability. However, biosurfactants are not commercially competitive to synthetic surfactants, yet. The two main groups of biosurfactants (lipopeptides and glycolipids) that have been applied for bioremediation are described below.

3.3.1 Lipopeptides

Lipopeptides are the greatest preferred and efficient biosurfactants. Synthesized by the strain belonging to the *Bacillus* genera, especially by *B. subtilis* that is normally found in the soil, these surfactants facilitate the emulsification process of hydrophobic molecules in water-based solutions by micelles formation, which can favor the access of microorganisms to these molecules, increasing biodegradation (Mnif et al. 2012; Rufino et al. 2013).

Surfactin is a lipopeptide with potent interfacial and self-assembly characteristics. The peptide portion of surfactin assumes a "horse saddle" configuration which affords stability to the molecule and provides its application as antiviral, antimicrobial, hemolytic being the widest surfactant used in therapeutic purposes (Peypoux et al. 1999; Hoefler et al. 2012; Liu et al. 2015).

Surfactin has been evaluated for bioremediation because of its exceptional surface activity, by the reduction of surface tension of water (20 °C) from 72 to 27 mN/m, considering concentrations below 20 μM, (Walia and Cameotra 2015). In a tertiary oil recovery process, known as microbial enhanced oil recovery (MEOR), the induced production of this lipopeptide can diminish the interfacial tension and promote the required pressure to liberate the oil that is contained in the pores of the rocks (Banat 1995; Sen 2008). This technique can be useful by in situ or ex situ conditions. The in situ process is grounded on the use of isolated microorganisms capable to grow under critical conditions (extreme salinity, oxygen, pH, and temperature), but do not make possible complete control of bioproducts production and cell

growth. The opposite is observed by the ex-situ condition process, where the peptide can be directly applied for oil recovery enhancement besides providing a feasible production of biosurfactants in the external area of an oil well (Al-Wahabi et al. 2014; Lazar et al. 2007).

Kotoky and Pandey (2019), applied surfactin for the bioremediation of benzo (a)pyrene (BaP), a polycyclic aromatic hydrocarbon with high-molecular-weight and high persistence in the environment, that representing a biohazard. *Paenibacillus* sp. S1I8 (KX602663) and *Bacillus flexus* S1I26 (NCBI accession n^{o} KX692271) were used isolate to produce surfactin which presented an excellent emulsification index that solubilized BaP efficiently. Solubilization levels of BaP were found up to 24.41 and 23.25% from *B. flexus* and *Paenibacillus* sp. S1I8, respectively. The potential to solubilize BaP of the extracted produced surfactin showed great performance and possibly could be used in the recovery of oil, also as an important object in the bioavailability of hydrocarbon.

Surfactin obtained from *Bacillus subtilis* was also practically applied for the remediation of heavy metals contaminated soil and also sediments. After 1st and 15th washings of soil samples with 0.1% surfactin along with 1% NaOH, the results were 6% and 25% of the Zn; 25% and 70% of the Cu; and 5% and 15% of the Cd; respectively (Mulligan et al. 1999). Another applicability of this lipopeptide was investigated by Maity et al. (2018), with an association to hydroxyapatite nanoparticle adsorption aiming the withdrawal of fluoride from water. Uniform particles of bacterial-surfactin mediated nano-hydroxyapatite (HAp) were synthesized by the hydrothermal method without any impurities and uniform morphology. The adsorption process is processed in two-steps, which first occurs as fast adsorption during the first 1.5 h and after that, the equilibrium was slowly reached. The higher adsorption level of 7.004 mg/g was achieved at pH 3, which affirms HAp nanoparticle mediated by bacterial-surfactin as a remarkable option for environmental pollution control by removing fluoride from water.

Nevertheless, the high production and purification costs of surfactin restrict the wide range of utilizations. In this sense, fermentation modes have been extensively studied (Chen et al. 2015). Genetic modification to obtain recombinant and indigenous strains is an alternative to produce large amounts of surfactin through various cheap nutrients (Mulligan et al. 1989; Carrera et al. 1992; Ohno et al. 1995; Qingmei et al. 2006; Gong et al. 2017). Other approaches include the substitution of regular culture medium by agro-industrial residues, which contain a high content of fermentable sugar with important macro and micronutrients essentials to microorganism growth and bioproducts production (Andrade et al. 2016). Nitschke and Pastore (2004), reported the surfactin production using a residue from cassava flour as an alternative culture medium at 150 mL working volume by *B. subtilis* LB5a. Gudiña et al. (2015) evaluated the corn liquor as a culture medium for *Bacillus subtilis* #573 achieving approximately 1.3 g/L of surfactin production. Zhu et al. (2013) have obtained values above than 1.56 g of surfactin in which gram of dry substrate of bean cake, cornmeal, rapeseed meal, rice straw, soybean flour, and wheat bran through *B. amyloliquefaciens* XZ-173 culture.

Optimized conditions of bioremediation using biosurfactants are also a usual subject, for instance, Liu et al. (2014) studied the influence of distinct medium for the fermentation by *Bacillus subtilis* BS-37 in the oil recovery and its removal from oil sand. At 0.3 g/L, both, glucose medium and Luria–Bertani (LB) medium obtained surfactin provided 96% removal rate of crude oil from oil sand. Considering 0.03 g/L surfactin obtained from LB medium presented a better efficiency at oil washing and displacement at a low concentration which combined with its lower surface tension indicates its possible utilization at enhanced oil recovery, and could enhance the oil recovery (MEOR).

A first evaluation of the pH impact in surfactin emulsification or surface activities was analyzed by Long et al. (2017) focusing on its application in MEOR, and the demulsification of previous stabilized surfactin through down-regulation of pH and its reuse for enhanced oil recovery. The emulsifying activity was better performed by pH beyond 7.4 presenting a rapid decrease at levels below 3.0 which have a direct influence on the dissolution–precipitation of surfactin promoting easily control by pH adjustments of oil emulsification and separation.

Andrade et al. (2016) studied the mannosylerithritol lipids-B (MEL-B) surface activity and surfactin at critical conditions to be applied in MEOR. The main parameter on the surface activity of surfactin was the ionic strength, besides that, it was also found a significant influence of pH.

Bayoumi et al. (2011) isolated 25 bacterial cultures from 20 samples of contaminated soil with crude oil. The 10 bacterial isolates were analyzed in concern of capability to surface-active compounds (SACs) biosynthesis by oil spread and blood agar lysis techniques in a liquid culture media which carbon and energy source was crude oil. Through the measure of surface tension, the most potent bacterial isolate (*Bacillus subtilis-KG82-KSA*) was chosen and showed the highest reduction of surface tension. The SAC was identified based on ultraviolet, infrared, and high-performance liquid chromatography (HPLC) analysis techniques as iturin, which has a great capability to be utilized as an agent for the remediation of soil and water that were contaminated with oil. Its optimized synthesis process conditions were also determined.

Statistical optimization of iturin A production was proposed by Kumar et al. (2017) by analyzing 100 bacterial isolates from the soil. The *Bacillus amyloliquefaciens* RHNK22 strain owns the best emulsification index and assay. The biosurfactant produced was identified by HPLC and FTIR. Then, alternative culture media were tested as medium culture using response surface methodology, which results highlighted that sunflower oil cake presented threefold higher production of biosurfactant.

Bezza and Chirwa (2017) studied the polycyclic aromatic hydrocarbons (PAHs) bioremediation on a heavily contaminated soil sample from an aged wood treatment plant by biosurfactant produced by *Bacillus cereus* SPL-4. The main concerns about PAHs are related to their teratogenic, mutagenic, and carcinogenic properties, high hydrophobicity, low water solubility, and hard sorption to the soil. At laboratory scale, Bezza and Chirwa (2017) performed a batch with 6.7455 g/kg—a total of 13 PAHs, in which 55% and 79% of 5- and 6-ring PAHs were eliminated, using

microorganisms supplement with 0.2 and 0.6% (w/w) of lipopeptide, respectively. The analysis of mass spectrometry indicated that the biosurfactant studied was a mixture of surfactin and iturin.

Liu et al. (2012) isolated over a hundred microorganisms capable of biosurfactant production from petroleum-contaminated soil and oily sludge. In the investigation, 16 of out all bacterial isolates reduced the surface tension of the growth medium from 71 to 30 mN/m with more than 72 h (fermentation). Nevertheless, the *Bacillus amyloliquefaciens* strain produced biosurfactant resulted from four different homologs of fengycin A that shown the best efficiency to separate the three phases of oily sludge (oil, sediment, and water), achieving 88% separate level after 24 h.

Etchegaray et al. (2017) developed a first biorefinery concept study on the production of biosurfactants. The inoculation in modified Landy's medium formed three principal metabolites: acetoin (which enhances plant growth), fengycin, and surfactin. Glycerol was used to increase surfactin-specific origination; arginine improved, significantly, the yields of biomass, fengycin, and surfactin. It was observed an increase of fengycin specific production at approximately ten times, which can be associated with a connecting pathway involving ornithine and arginine. The process of adding value to biomass and crude extracts shown to be useful for biodiesel production and the *p*-xylene elimination from contaminated water, respectively.

According to Farias et al. (2018) the NaCl concentration (2.7, 66, and 100 g/L) interferes with the surface activity and composition of cyclic lipopeptides (CLPs) from *Bacillus* strains regarding MEOR. Through 16S rDNA, rpoB, and gyrB sequences analysis, the strains were identified as *Bacillus amyloliquefaciens*, *Bacillus subtilis*, and *Bacillus vallismortis*. Concentrations higher than 100 g/L NaCl were tolerated by all strains, nevertheless, *B. amyloliquefaciens* was not able to decrease surface tension. *Bacillus subtilis* exhibited emulsification activity at 66 g/L NaCl concentrations. High NaCl concentrations assisted the synthesis of fengycins and/or surfactins that is compatible with the surface activities of *B. vallismortis* and *B. subtilis*, while low concentration assisted the iturins production. These results, when analyzed together, propose that the definition of CLP under a known and expected oil reservoir condition could guide the definition of the strain to MEOR.

Lichenysin is a monoanionic lipopeptide with the same properties as surfactin but presents better effectiveness in chelating properties and surface activity. It can complex divalent cations in a relation of 2:1 and, associated with Ca^{+2} and Mg^{+2} (Grangemard et al. 2001).

Amodu et al. (2014) isolated a new strain from rotting wood for biosurfactant production, which posteriorly was identified as *Bacillus vulgaris*, being the first report of this strain in surfactant production. The synthesized biosurfactant presented a high propensity for hydrocarbon emulsification and surface tension reduction of water to lower than 30 mN/m. Based on the FTIR analysis report, the biosurfactant was associated with lichenysin cyclic LMW lipopeptide.

Ngwenya (2016) developed a study to upgrade the yield of biosurfactant from this *Bacillus* sp., by optimizing bioprocess conditions with supplementation of a broth of biocompatible nanoparticles synthesized from *B. vulgaris* agro-waste extracts,

which was used as a culture medium for biosurfactant production, to reducing production costs. The supplementing of the biocompatible Ca-based nanoparticles in the reaction media by *Bacillus licheniformis* STK 01 promoted an improvement in the emulsification index of the biosurfactants to 50% using kerosene. Biochemical tests confirmed the ability of strain STK 01 to generate lichenysin biosurfactant. This research indicated the high production yield, the emulsification activity of the lichenysin biosurfactant produced, and the influence of the biocompatible Ca-based nanoparticles.

The evaluation of n-alkanes and polycyclic aromatic carbons biodegradation was taken by Xia et al. (2014) that isolated *Pseudomonas* sp. WJ6 from soil contaminated by oil and tested its performance on long-chain alkanes and PAHs degradation. The crude biosurfactant was analyzed through HPLC that proposed a mix of surfactin, fengycin, and lichenysin which efficiency to remove heavy oil from quartz sand reached 92.46% of heavy oil washing.

Therefore, lipopeptides are biodegradable, eco-friendly, more biocompatible, and less toxic than chemical surfactants. Due to their extensive variety and interesting functional properties, lipopeptide biosurfactants can be applied for many purposes. They can decrease the interfacial and surface tension which promotes their application to hydrocarbon mobilization and solubilization—enhanced biodegradation and enhanced oil recovery from petroleum well. It is observed their participation in the heavy metal remediation is due to their sequestering characteristic, biodegradability, and low toxicity. Furthermore, biosurfactant production using agro-industrial wastes as alternative culture media which makes their production economically competitive.

3.3.2 Rhamnolipids

3.3.2.1 Remediation of Metal Contamination

Over the years, industrial activities have led to heavy metal contamination of the environment (aquatic and terrestrial) (Yang et al. 2018). According to Sarubbo et al. (2015), activities such as incineration, mining, galvanization, and production of vehicle batteries are some examples of processes responsible for the contamination of the environment by heavy metals, since these are not biodegradable, leading to the destruction of biological systems, soil, and underground due to leaching.

These pollutants, especially Pb^{2+}, Zn^{2+}, Cr^{3+}, Cd^{2+}, and Hg^{2+}, are potentially reactive, toxic, and motile in the soil, being easily disseminated into the environment (Aşçi et al. 2008). Furthermore, heavy metals have recalcitrant behavior more accentuated compared to oil derivatives and other organic pollutants (Sarubbo et al. 2015). Classical remediation techniques for these compounds include chemical oxidation, electrokinetics, excavation, thermal extraction of volatile metals, solidification/stabilization, and soil washing (Aşçi et al. 2008). For these pollutants to be removed, physical removal or modification of their redox state to a less toxic form is required (Franzetti et al. 2014).

Bioremediation involves biological processes in the elimination of pollutants through solubilization or chemical mineralization, being a promising method for the recovery of contaminated environments (Jimoh and Lin 2019). In this sense, biosurfactants stand out due to the ability of metals removing from the soil by bio-extraction or biosurfactant washing, in which the mechanisms involved are counter ion binding, electrostatic interactions, and ion exchange (Liu et al. 2018). In addition, biosurfactants show higher selectivity by metallic compounds when compared to synthetic surfactants (Aşçi et al. 2008).

For removal of metals from water bodies, biosurfactants act as ion collectors through the foam flotation process, in which the biosurfactant adsorbs the metals from the liquid medium, followed by separation by foam flotation, allowing the contaminant material to be separated (Franzetti et al. 2014).

Rhamnolipids are biosurfactants from the glycolipid class with a negative charge, being able to form stronger stabilizing bonds between the cationic metal and the biosurfactant than between the metal and the soil. According to Singh and Cameotra (2004), biosurfactant soil bioremediation efficiency is influenced by soil composition, particle size, ion exchange capacity, and contamination time.

The mechanisms of metals removal from soil by rhamnolipids consist of three stages, whereas the first one is the formation of the rhamnolipid–metal complex. On the surface, which represents the interface between the matrix and the soil solution, there is the accumulation of rhamnolipid molecules due to their amphoteric characteristics, favoring the formation of the complex (Liu et al. 2018). In the second stage, the complex dissolves, allowing the metal to be released into the solution. Finally, in the third stage, the metal is bonded to the polar group of rhamnolipid micelles through electrostatic interactions (Sarubbo et al. 2015; Liu et al. 2018). This process of removing metals allows recycling and reuse of the soil (Rocha Junior et al. 2018).

The technologies involved in heavy metal soil remediation can be divided into two categories. The first one consists of ex situ washing of the soil with a biosurfactant solution on a glass column. Contaminants are removed due to interfacial tension reduction, allowing the pollutant mobilization along the column. Then, the contaminant is recovered at the bottom of the column (Kumar et al. 2017). The second is the installation of a pipe and drainage system used to introduce and collect biosurfactant during the process. Initially, injection wells are drilled into contaminated soil where solutions containing biosurfactants will be injected. After the solution is injected into the wells, the metal–biosurfactant complex is formed and directed to the extraction wells. Pollutants are collected from extraction wells and treated. Subsequently, the biosurfactant is recovered by precipitation (Sarubbo et al. 2015; Das et al. 2017; Kumar et al. 2017).

The removal of metals from aquatic environments by biosurfactants is possible with the addition of oppositely charged biosurfactant considering the metal contaminant, causing the synthesis of the biosurfactant–metal complex. After the complex formation, air bubbles are introduced into the system, causing foaming. Due to the presence of the hydrophobic and hydrophilic portion in the biosurfactant molecule, the complexes are collected by the bubbles due to the interaction between the

hydrocarbon chains and the air bubbles. As a result, the contaminant is separated by foam flotation at the solution interface, which is removed at the process termination (Franzetti et al. 2014; Peng et al. 2019).

Many studies of remediation by rhamnolipid of soil and water contaminated by metals have been reported in the literature, in which the technologies involved are mostly soil washing and flotation (Slizovskiy et al. 2011; Venkatesh and Vedaraman 2012; Wan et al. 2015; Lee and Kim 2019).

Salmani Abyaneh and Fazaelipoor (2016) investigated the rhamnolipid (RL) property to eliminate Cr (III) from aqueous solutions. The authors verified through a Full Factorial Design (24), the effect of airflow rate, pH, molar ratios Fe/Cr and RL/Cr on the percentage of chromium removal, concluding that all factors had a significant effect for the response variable, with the highest removal of 96.1%, and around 90% removal for the central point assays. In the study of interfering ions in removal, the authors found that NaCl had little effect on Cr removal, and the presence of $CaCl_2$ negatively impacted removal, reducing it by 36%. According to the authors, Ca ions interact with the biosurfactant carboxyl group, decreasing removal efficiency. Furthermore, the authors concluded that the biosurfactant significantly remediated Cr.

Chen et al. (2017) investigated bioremediation of sediments containing high amounts of Cu, Cd, Pb, and Cr by using rhamnolipids. Seven concentrations of rhamnolipid were evaluated, ranging from 0.2 to 3% (w/v). Cd presented the highest percentage of washing efficiency, between 75 and 86.87% for concentrations between 0.8 and 3.0%. Lower efficiency was observed in chromium removal, reaching the highest percentage of 47.85% for the 3.0% rhamnolipid treatment. Pb and Cu had the maximum removal of 80.21 and 63.54% for a 3.0% rhamnolipid treatment. The washing time was also an important factor in the washing efficiency for all studied metals. There was a rapid increase in efficiency in the first 12 h and higher efficiencies were obtained after 24 h of batching, remaining constant up to 40 h for all metals studied. When investigating the effect of pH, the authors verified that basic medium favored the washing efficiency for all metals evaluated. The higher impact was observed in the removal of Pb and Cu, reaching efficiencies between 70 and 90% approximately, for pH values between 7.0 and 11.0. In an acid medium, for the same metals, the removal efficiency was below 50%. The authors report that the different efficiency values are due to biosurfactant structure modification. The structural differences of rhamnolipid as a function of the pH medium is associated to the rise in the carboxyl group charge density, conducting to the formation of a hydrophilic head group with more repulsive characteristic, and an increase in the dimensions of the head group, culminating in micelles with high curvature.

Mn nodules are widely distributed on the deep-sea and have valuable metals such as Cu, Ni, and Co, which are used in many industrial segments. Thus, ocean mining has become increasingly attractive due to the gradual depletion of land resources (Lee and Kim 2019).

Lee and Kim (2019) reported an unprecedented study on heavy metals removal from Mn nodules by rhamnolipids. The nodules were taken from Clarion-Clipperton

Fracture Zone, presenting high concentrations of Ni and Cu, and also composed of Al, Fe, Cr, Zn, As Cd, and Pb. The authors concluded that Cu removal is affected by rhamnolipid concentration, and by the reaction time of the treatment. In Ni removal, the reaction time had a greater effect on removal compared to biosurfactant concentration. After 7 days of reaction time, Cd removal was the most efficient (approximately 100%) using 0.3% rhamnolipid, also being mainly influenced by the biosurfactant concentration used.

Tang et al. (2017) studied the elimination of heavy metals from sewage sludge from a wastewater treatment plant in Qun Li (China). For this, an improved electrokinetic decontamination treatment combined with rhamnolipid and Tetrasodium of N, N-bis (carboxymethyl) glutamic acid (GLDA) was performed. Higher removal was observed by replacing rhamnolipid as an electrolyte when compared to the use of GLDA. The metal with the highest removal efficiency was Mn (69.9%), followed by Cu (64.8%) and Ni (60.4%). For Zn, Cr, and Pb, the removal efficiencies were 56.8, 49.4, and 46.6%, respectively. The authors also report a synergistic effect between GLDA and rhamnolipid, since higher removals were obtained in the electrokinetic process, with the highest removal percentage for Cr (89.0%) and the lowest for Pb (60.0%). The chelating action of GLDA was favored by the simultaneous addition of rhamnolipid and chelating agent, allowing greater removal efficiency of heavy metals.

3.3.2.2 Remediation of Organic Contamination

Industrial and technological developments have been increasing energy demand, intensifying oil exploration, and processing. These compounds are toxic to the environment, requiring efficient remediation actions due to the low recovery through physicochemical and oxidative treatments, and also limited bioavailability to hydrocarbon degradation bacteria (Liu et al. 2018). Spills and leaks from refineries, factories, and oil product distribution depots are examples of potential sources of environmental contamination (Befkadu and Chen 2018). In this sense, biosurfactants may be remedial agents due to their ability to solubilize hydrocarbons and toxic polyaromatic compounds from contaminated soil and aquifers (Joy et al. 2017).

According to Liu et al. (2018), rhamnolipids increase the uptake of organic compounds by degrading bacteria, due to the variation of cell surface hydrophobicity by the surfactant, however, the concrete mechanisms for these types of effects are still not elucidated (Zhong et al. 2017). Rhamnolipids also present a strong potential to modify the properties of porous media, being capable to enhance bacterial transport efficiently. This can be useful for bioaugmentation, which is a remediation technique responsible for the improvement of the degradative capacity of contaminated soil, through the introduction of specific microorganisms (Mrozik and Piotrowska-Seget 2010; Tahseen et al. 2016). Instead, higher permeabilization of the plasma membrane can be promoted by rhamnolipids, allowing the passage of hydrocarbons into bacterial cells (Zeng et al. 2018).

At low concentrations, rhamnolipid monomers stand themselves at the interface between the organic contaminant and the liquid phase, allowing the formation of microdroplets due to interfacial tension reduction, decreasing the repulsive forces

between the two phases. Values above the critical micellar concentration, organic pollutants are captured in the hydrophobic nucleus of the micelles, facilitating the mobilization and availability of organic contaminants, and the next steps of pollutant remediation (Zeng et al. 2018).

Soils contaminated by metal can also be recovered by phytoremediation, encouraging researchers to explore metal resistant microorganisms capable of biosurfactants production and plant-growth stimulating compounds to the efficiency intensification of metal phytoextraction (Franzetti et al. 2014). In this context, Zhen et al. (2019) reported the synergic action of biochar (BC) and rhamnolipid (RL) on phytoremediation of oil-contaminated soil using *Spartina anglica*. According to the authors, the biochar and rhamnolipid effects on phytoremediation of soil with oil contamination by *Spartina anglica* were reported for the first time. Different treatments were carried out for petroleum-contaminated soils, which are rhamnolipid modified biochar (RMB), BC, and BC + RL for the respective contaminant concentrations of 50, 10, and 30 g/kg. The maximum removal rate of total petroleum hydrocarbons (TPHs) at a concentration of 30 g/kg was 35.1% for cultivated soil with the RMB addition.

Câmara et al. (2019) investigated rhamnolipids production by *P. aeruginosa* followed by its application on MEOR, where retained oil is extracted from the pores due to the interfacial tension reduction between water and oil, caused by biosurfactant injections during treatment. Rhamnolipid was efficient in contaminated soil remediation, since the maximum recovery was 50.45%, with 11.91% resulting from MEOR. This value corresponded to the treatment of 2× critical micellar concentration (CMC) for API grade oil of 21.90 and represented almost twice the recovery factor when the biosurfactant concentration was only 30% above CMC. The authors also reported that the high biodegradability of the biosurfactant did not impair oil recovery, since remediation was possible even after 2 months of biosurfactant production, although the time may influence the surface activity of the surfactant.

Zhao et al. (2020) analyzed the *P. aeruginosa* potential of rhamnolipid production using soybean oil or glucose as a carbon source. The biosurfactant obtained from glucose presented better superficial activity, while the biosurfactant from oil presented better emulsifying activity. On the other hand, the authors investigated the removal of oil present in sludge by using rhamnolipids. Sludge containing 22.91% of the oil was treated with 200 mg/L of the rhamnolipid solutions obtained from both carbon sources, achieving total petroleum hydrocarbon (TPH) removal of 35.81% for the biosurfactant obtained from soybean oil, and 32.06% from glucose.

Petroleum exploration produces different kinds of waste, including drill cuttings, which is a major waste produced mainly due to the huge amount of volumes generated. In addition, the mixture of oil-based drilling fluids and excavated materials may become a potential long-term pollutant (Olasanmi and Thring 2019). In this scenario, Olasanmi and Thring (2019) investigated the use of rhamnolipids in the improved rinsing of drill cuttings and oil-contaminated soil samples from British Columbia (Canada). The authors used the Taguchi method to optimize the process parameters in petroleum hydrocarbon remediation, such as

temperature, rhamnolipid concentration, time of washing, and agitation, in order to evaluate its effect on the independent variable (Petroleum Hydrocarbon Reduction, %). The authors concluded that the ideal process parameters, which led to the best reduction of pollutants for both soil and drill cuttings, corresponded to a concentration of rhamnolipid of 500 mg/L at 23.5 °C during 30 min of washing. Regarding agitation and solution-to-sample ratio, a higher agitation (200 rpm) and ratio (4:1) were required for a higher drill cutting washing efficiency. The agitation and solution-to-sample ratio to contaminated soil were 100 and 1:1, respectively. The higher value of petroleum hydrocarbon fractions reduction was 85.4% for drill cuttings and 63.5% for soil with petroleum contamination. The authors suggest that the optimized technique is an efficient primary step in the bioremediation of drill cuttings and oil-contaminated soils.

Pi et al. (2017) studied the remediation of crude oil (Haierzhan) through a simulated spill. Dispersants and biosurfactants have been evaluated by the Box–Behnken design of RSM, in order to analyze their ability to decrease the total petroleum hydrocarbons percentage in water. The authors report that rhamnolipid effectively improved pollutant removal and that biosurfactant concentration has a significant impact on the removal rate. The maximum petroleum hydrocarbon removal achieved was 39% for rhamnolipid (B). For rhamnolipid (L), the removal percentage achieved was 31%, probably due to the lower biosurfactant concentration, which was 10 times lower than rhamnolipid (B).

3.3.3 Mannosylerythritol Lipids

The most studied applications of MELs are in food, cosmetic and pharmaceutical industries, medical uses, and antimicrobial agents. However, they can also be used for environmental applications due to their low toxicity, biodegradability, and ability to solubilize low solubility contaminants, enhancing their biodegradation (Yu et al. 2015). Few studies have explored MELs for remediation, and the most is for oil contamination or contaminants derived from the oil industry, such as aromatic hydrocarbons (Souza et al. 2014), alkanes, and kerosene (Hua et al. 2004). Some studies also show that MELs can be utilized for heavy metals remediation in contaminated soil and wastewater (Arutchelvi et al. 2008) and pesticide residues, such as lindane (Salam and Das 2013).

Some studies have shown that MELs can be great alternatives to chemical surfactants since they are able to emulsify solutions with equal or better performance than some chemical surfactants commercially available, besides presenting lower toxicity. According to Kitamoto et al. (2001), MEL-A showed much higher emulsifying activity to n-tetradecane and soybean oil when compared to Tween 80 (polyoxyethylene sorbitan monooleate), and both MEL-A and MEL-B showed similar activity to that of Tween 80 towards a hydrophobic phase containing the polycyclic aromatic hydrocarbon 2-methylnaphthalene. This occurred because the MELs obtained by Kitamoto et al. (2001) had much lower CMC (below 3 μg/mL) than Tween 80 (13 μg/mL). Kim et al. (2002) compared the toxicity of MEL and two

commercial surfactants (dodecylbenzene sulfonate—LAS and sodium lauryl sulfate—SDS) through a Neutral Red (NR) test to transformed mouse fibroblast L929 cells post 48h of contact. The results were expressed in terms of surfactant concentration that diminished the NR uptake by 50% when compared to control (untreated cells). The authors observed that the NR_{50} was 5 g/L for MEL, while LAS and SDS showed NR_{50} of 0.01 and 0.05 g/L, respectively. With this, the authors showed that the tested MEL presented much lower cytotoxicity than the chemical surfactants.

MELs can be produced in situ by microorganisms that use the contaminants as substrate, or by biological routes and then be used for remediation. The action of MELs, as well as other biosurfactants, is associated with the metabolism of the microorganism used for the remediation. Based on this, MELs can act through two possible metabolic vias in order to improve biodegradation: increasing the solubility of the substrates for the microbial cells, and/or promoting a better interaction between the substrate and the cell surface by increasing the hydrophobicity of the surface (Zhang and Miller 1992).

3.3.3.1 Microbial Conversion of Contaminants/Wastes to MELs

The carbon source generally used for the production of MELs is an oil, mainly soybean oil since it provides higher yields (Yu et al. 2015). However, one of the main drawbacks of using biosurfactants, including MELs, is the higher cost of production and purification. The culture medium can represent around 30% of total costs (Andrade et al. 2016). Based on this, some researches started to study the use of waste materials as the substrate, such as cassava wastewater (Fai et al. 2015; Andrade et al. 2017), waste cooking oil (Niu et al. 2019), wheat straw (Faria et al. 2014a), glycerol (Morita et al. 2007), and *n*-alkanes (Kitamoto et al. 2001). The use of waste substrates favors the reduction of production costs, and also adds value to a material that would have to be treated or properly discarded. Thus, this economic technology can decrease the costs of industrial/municipal waste management and ease the pressure on the environment.

Fai et al. (2015) and Andrade et al. (2017) investigated the generation of MEL by *Pseudozyma tsukubaensis* and using cassava wastewater as a culture medium. Fai et al. (2015) reached a surface tension of 26.87 mN/m using 80% (v/v) of cassava wastewater at 200 rpm and 30 °C for 48 h. The MELs showed good thermal, pH, and ionic strength stability, and excellent emulsifier activity. Andrade et al. (2017) obtained a MEL-B production yield of 1.26 g/L using 100% cassava wastewater in a bioreactor (100 rpm, 3.0 L of working volume, 0.4 vvm of aeration rate in the first 24 h, and then 150 rpm and 0.8 vvm for more 60 h). According to the authors, the cassava wastewater is a promising alternative to conventional synthetic culture mediums.

Niu et al. (2019) studied the use of waste cooking oil as carbon source for the synthesis of MELs by *Pseudozyma aphidis*. By using a culture medium composed of 95 mL/L of waste cooking oil, 29.95 mL/L of inoculum size, 48.65 mL of medium per 250 mL, at 5.76 of initial pH, the MEL production reached 61.50 g/L. The authors also compared the use of waste cooking oil with conventionally used

soybean oil and concluded that MELs produced in the medium containing waste cooking oil had better surface activity, performance, and application stability.

Faria et al. (2014b) evaluated the growth and MEL production ability of three yeasts from the genus *Pseudozima* (*P. antarctica*, *P. aphidis*, and *P. rugulosa*) using pure lignocellulosic sugars (arabinose, glucose, and xylose) as carbon source. All the strains were able to grow in mediums containing the three sugars, although the one with glucose provided a higher growth rate. MEL was produced from both glucose and xylose, but no production was detected from arabinose. The authors observed that between the microorganisms tested, *P. antarctica* was the most promising strain for MEL production from lignocellulosic sugars with a yield of 5 g/L. The same research group investigated the conversion of hydrothermally pretreated wheat straw into MEL (Faria et al. 2014a). The production yield reached 2.5 g/L of MEL using cellulolytic enzymes (Celluclast 1.5L® and Novozyme 188®) and *P. antarctica* in the fed-batch saccharification and fermentation process. Thus, the authors suggested that the yeasts have the potential for valuable biosurfactant production from lignocellulosic biomasses. The use of lignocellulosic material for MEL production decreases the spending of the substrate but requires the adding of hydrolytic enzymes, which may not yet be cost-effective, besides increasing the process complexity (Beck et al. 2019).

Morita et al. (2007) studied the microbial conversion of waste glycerol into MELs by *Pseudozyma antarctica*. The MEL yield reached 16.3 g/L after 21 days at 30 °C. The authors used a fed-batch reactor with a working volume of 1 L, to which, every seven days, 100 g/L of glycerol and 20 mg/L of mannose were added. The same research group also investigated the production of MELs by *Pseudozyma churashimaensis* from cuttlefish oil (Morita et al. 2013). This oil contains high amounts of polyunsaturated fatty acids and, because of this, can permit the synthesis of MELs containing unsaturated fatty acids such as MEL-A. The MEL-A from cuttlefish oil showed a CMC and surface tension at CMC of, respectively, 5.7×10^{-6}M and 29.5 mN/m, while MEL-A from soybean oil presented a CMC of 2.7×10^{-6}M sand surface tension of 27.7 mN/m. Thus, according to the authors, the produced MEL-A could be an attractive new functional surfactant with excellent surface-active properties.

Kitamoto et al. (2001) investigated the use of *n*-alkanes as an alternative for vegetable oils in the production of MEL by *Pseudozyma antarctica* resting cells. The authors used *n*-alkanes fluctuating from C_{12} to C_{18} and the maximum yield of 0.87 g/g of the substrate was found using an initial pH of 5.7 and 6% (v/v) of *n*-octadecane after 7 days. The production of MEL using 16.1 g/L of resting cells reached 140 g/L after 4 weeks using a fed-batch system, to which, every 7 days, 1.8 mL of *n*-octadecane was added. Thus, MELs show a great potential to be applied in bioremediation of long-chain alkanes since they are less volatile and generally remain as main contaminants in environments contaminated by oil.

Dziegielewska and Adamczak (2013) evaluated the use of several wastes (glycerol, free fatty acids, post-refining waste, post-refining fatty acids, soapstock, and waste cooking oil) in the synthesis of MELs by *Pseudozyma antarctica*, *Pseudozyma aphidis*, *Starmerella bombicola*, and *Pichia jadinii*. The highest yield (107.2 g/L)

was obtained by *P. antarctica* grown in a medium with post-refining waste, followed by *S. bombicola* (93.8 g/L) and *P. aphidis* (77.7 g/L) cultivated in a medium containing soapstock, and *P. jadinii* (67.3 g/L) grown in a medium with waste cooking oil.

As can be noticed, there are several processes reported in the literature on the production of MELs using agro-industrial wastes that are very promising to be applied on a large scale once optimized. The use of inexpensive fermentation substrates is expected to have an important influence on the production costs of MEL, turning its commercialization economically feasible.

3.3.3.2 Direct Use of MELs for Remediation

After production, MELs can be directly applied to enhance the degradation of contaminants present in water or soil. They can be used to increase the contaminant solubility, that is, they assist the assimilation of contaminants by the microorganisms. Biosurfactants, such as MEL, can be used as energy and carbon backup molecules remaining as a defensive deposit for the microorganisms at harsh environmental conditions and can act as a sequestrant, forming complexes with the contaminant and reducing its toxicity, as in the case of heavy metals (Arutchelvi et al. 2008).

For remediation purposes, MELs can be purified before their application or can be used mixed with the culture broth. Sajna et al. (2015), for example, compared the use of MELs purified by chromatography with the use of culture broth containing MELs produced by *Pseudozyma* sp. in the crude oil biodegradation. According to the authors, the culture broth enhanced crude oil degradation by approximately 46%, which was a higher increase than that obtained when using purer biosurfactants. Therefore, as the extraction and purification steps represent 60% of the total production costs (Desai and Banat 1997), the utilization of MELs with no purification can considerably increase the interest in their uses for bioremediation processes.

Hua et al. (2004) studied the effects of MEL produced by *Candida antarctica* on some petroleum compounds' biodegradation in an aqueous medium. They found out that the insert of 1% of MEL to the culture medium increased the degradation of crude oil from 53.0% to 74.1%. It also increased the degradation of kerosene from 80% (800 mg/L initial concentration) to 87% (4785 mg/L initial concentration) in 15 h. The addition of MEL to the culture medium enhanced the emulsification of the kerosene, enabling the use of a higher initial concentration, besides increasing its biodegradation rate.

Salam and Das (2013) showed that the use of MELs for the stabilization of oil-in-water microemulsion increased the solubility and the biodegradation of lindane, an organochlorine pesticide. *Pseudozyma* sp. was used for the MELs production and lindane biodegradation assays. The produced MEL showed excellent surface-active properties, reducing water surface tension to 29 mN/m, exhibited a CMC of 25 mg/L, and was stable over a wide range of temperature, pH, and salinity. The use of MEL in the preparation of the oil-in-water microemulsion increased the lindane solubility up to 40-fold and enhanced biodegradation by 36% in two days compared to 12 days with no MEL addition. The authors also evaluated lindane biodegradation

in a soil slurry, and the assay containing MEL showed an increase of approximately 40% in the degradation.

Park et al. (2002) used MEL produced by *Candida antarctica* as an additive to enhance the efficiency of phenanthrene removal from soil using an electrokinetic method. The role of the biosurfactant, in this case, was to enhance the desorption ability and movement of the contaminant on the soil surface. The removal efficiency in two weeks increased from 4.23% to 16.2% with the use of MEL. They also compared the biosurfactant with the synthetic surfactants alkyl polyglycosides (APG), polyoxyethylene-4 lauryl ether (Brij30), and SDS that reached removals of 11.1%, 6.31%, and 9.97%, respectively. Thus, besides increasing the phenanthrene removal from contaminated soil, MEL showed to be more efficient than commercialized chemical surfactants.

3.4 Conclusion and Future Perspectives

Biosurfactants can be applied as a bioremediation agent. Nevertheless, their cost of production needs to be reduced for an economical competition with synthetic surfactants at an industrial scale. In this sense, the group and also the subgroups of biosurfactants should be related to their applications (bioremediation), in which the current literature is scarce; however, some trends can already be spotted, as below:

- When compared to other lipopeptides, iturin presented a solid potential to be utilized as an agent for remediation of oil spills in soil and sea;
- When compared to surfactin, lichenysin, a monoanionic lipopeptide, shows better effectiveness in chelating properties and surface activity, in particular with divalent cations (e.g., Ca^{+2} and Mg^{+2});
- A mixture of surfactin and iturin seems to be more effective to remediate 5- and 6-ring PAHs;
- The concentration of rhamnolipid significantly affects the Cu remediation, whereas the retention time affects Ni removal;
- Rhamnolipids can be used to bioremediate drill cuttings and oil-contaminated soil, in particular at 500 mg of rhamnolipids/L, 23.5 °C for 30 min;
- There are few studies on MELs for remediation, and the majority of them is for oil contamination or contaminants derived from the oil industry, such as aromatic hydrocarbons, alkanes, and kerosene;
- When compared to purified MEL, the culture broth containing MEL can enhance the crude oil degradation by ≈46%;
- MEL can increase the biodegradation of lindane, an organochlorine pesticide.

References

Al-Wahabi Y, Joshi S, Al-Bahry S, Elshafie A, Al-Bemani A, Shibulal B (2014) Biosurfactant production by *Bacillus subtilis* B30 and its application in enhanced oil recovery. I. Biodet Biodegrad 114:324–333

Amodu OS, Ntwampe SKO, Ojumu TV (2014) Optimization of biosurfactant production by *Bacillus licheniformis* STK 01 grown exclusively on Beta vulgaris waste using response surface methodology. Biol Res 9(3):5045–5065

Andrade CJ, Barros FFC, Andrade LM, Rocco AS, Sforça ML, Pastore GM, Jauregi P (2016) Ultrafiltration based purification strategies for surfactin produced by *Bacillus subtilis* LB5A using cassava wastewater as substrate. J Chem Technol Biotechnol 91(12):3018–3027

Andrade CJ, Andrade LM, Rocco SA, Sforça ML, Pastore GM, Jauregi P (2017) A novel approach for the production and purification of mannosylerythritol lipids (MEL) by *Pseudozyma tsukubaensis* using cassava wastewater as substrate. Sep Purif Technol 180:157–167

Arutchelvi JI, Bhaduri S, Uppara PV, Doble M (2008) Mannosylerythritol lipids: a review. J Ind Microbiol Biotechnol 35:1559–1570

Aşçi Y, Nurbaş M, Açikel YS (2008) A comparative study for the sorption of Cd(II) by soils with different clay contents and mineralogy and the recovery of Cd(II) using rhamnolipid biosurfactant. J Hazard Mater 154(1-3):663–673

Banat IM (1995) Biosurfactants production and possible uses in microbial enhanced oil recovery and oil pollution remediation: a review. Bioresour Technol 51:1–12

Bayoumi RA, Atta HA, El-Sehrawey MA, Selim SM (2011) Microbial production of biosurfactants from some El-Korma governorate microbial isolates for bioremediation of crude oil spills in the different environments. J Basic Appl Sci Res 1(10):1541–1555

Beck A, Werner N, Zibek S (2019) Mannosylerythritol lipids: biosynthesis, genetics, and production strategies. In: Hayes DG, Solaiman DKY, Ashby RD (eds) Biobased surfactants: synthesis, properties, and applications. AOCS Press and Academic Press, New York, pp 121–167

Befkadu AA, Chen Q (2018) Surfactant-enhanced soil washing for the removal of petroleum hydrocarbons from contaminated soils: a review. Pedosphere 28(3):383–410

Bezza FA, Chirwa EMN (2017) The role of lipopeptide biosurfactant on microbial remediation of aged polycyclic aromatic hydrocarbons (PAHs)–contaminated soil. Chem Eng J 309:563–576

Boothroyd B, Thorn JA, Haskins RH (1956) Biochemistry of the Ustilaginales: XII. Characterization of extracellular glycolipids produced by *Ustilago* sp. Can J Biochem Physiol 34(1):10–14

Câmara JM, Sousa MA, Barros Neto EL, Oliveira MC (2019) Application of rhamnolipid biosurfactant produced by *Pseudomonas aeruginosa* in microbial-enhanced oil recovery (MEOR). J Pet Explor Prod Technol 9(3):2333–2341

Carrera P, Cosmina P, Grandi G (1992) Mutant of *B. subtilis* and production of surfactin by use of the mutant. Patent J04299981

Chen WC, Juang R-S, Wei YH (2015) Applications of a lipopeptide biosurfactant, surfactin, produced by microorganisms. Biochem Eng J 103:158–169

Chen W, Qu Y, Xu Z, He F, Chen Z, Huang S, Li Y (2017) Heavy metal (Cu, Cd, Pb, Cr) washing from river sediment using biosurfactant rhamnolipid. Environ Sci Pollut Res 24 (19):16344–16350

Das AJ, Lal S, Kumar R, Verma C (2017) Bacterial biosurfactants can be an eco-friendly and advanced technology for remediation of heavy metals and co-contaminated soil. Int J Environ Sci Technol 14(6):1343–1354

Desai JD, Banat IM (1997) Microbial production of surfactants and their commercial potential. Microbiol Mol Biol Rev 61(1):47–64

Dziegielewska E, Adamczak M (2013) Evaluation of waste products in the synthesis of surfactants by yeasts. Chem Pap 67(9):1113–1122

Etchegaray A, Coutte F, Chataigné G, Béchet M, Santos R-H-Z, Leclère V, Jacques P (2017) Production of *Bacillus amyloliquefaciens* OG and its metabolites in renewable media: valorization for biodiesel production and *p*-xylene decontamination. Can J Microbiol 63(1):46–60

Fai AEC, Simiqueli APR, Andrade CJ, Ghiselli G, Pastore GM (2015) Optimized production of biosurfactant from *Pseudozyma tsukubaensis* using cassava wastewater and consecutive production of galactooligosaccharides: an integrated process. Biocatal Agric Biotechnol 4:535–542

Faria NT, Santos M, Ferreira C, Marques S, Ferreira FC, Fonseca C (2014a) Conversion of cellulosic materials into glycolipid biosurfactants, mannosylerythritol lipids, by *Pseudozyma* spp. under SHF and SSF processes. Microb Cell Factories 13(155):1–6

Faria NT, Santos MV, Fernandes P, Fonseca LL, Fonseca C, Ferreira FC (2014b) Production of glycolipid biosurfactants, mannosylerythritol lipids, from pentoses and D-glucose/D-xylose mixtures by *Pseudozyma* yeast strains. Process Biochem 49:1790–1799

Farias BCS, Hissa DC, Nascimento CTM, Oliveira SA, Zampieri D, Eberlin MN, Migueleti DLS, Martins LF, Sousa MP, Moyses DN, Melo VMM (2018) Cyclic lipopeptide signature as fingerprinting for the screening of halotolerant *Bacillus* strains towards microbial enhanced oil recovery. Appl Microbiol Biotechnol 102:1179–1190

Franzetti A, Gandolfi I, Fracchia L, Hamme J, Gkorezis P, Marchant R, Banat IM (2014) Biosurfactant use in heavy metal removal from industrial effluents and contaminated sites. In: Kosaric N, Sukan FV (eds) Biosurfactants: production and utilization - processes, technologies, and economics. CRC Press, Boca Raton, pp 361–370

Fukuoka T, Kawamura M, Morita T, Imura T, Sakai H, Abe M, Kitamoto D (2008) A basidiomycetous yeast, *Pseudozyma crassa*, produces novel diastereomers of conventional mannosylerythritol lipids as glycolipid biosurfactants. Carbohydr Res 343:2947–2955

Fukuoka F, Yanagihara T, Imura T, Morita T, Sakai H, Abe M, Kitamoto D (2012) The diastereomers of mannosylerythritol lipids have different interfacial properties and aqueous phase behavior, reflecting the erythritol configuration. Carbohydr Res 351:81–86

Gong G, Zheng Z, Chen H, Yuan C, Wang P, Yao L, Yu Z (2017) Enhanced production of surfactin by *Bacillus subtilis* E8 mutant obtained by ion beam implantation. Food Technol Biotechnol 47:27–31

Grangemard I, Wallach J, Maget-Dana R, Peypoux F (2001) Lichenysin: a more efficient cation chelator than surfactin. Appl Biochem Biotechnol 90(3):199–210

Gudiña EJ, Fernandes EC, Rodrigues AI, Teixeira JA, Rodrigues LR (2015) Biosurfactant production by *Bacillus subtilis* using corn steep liquor as culture medium. Front Microbiol 6:1–7. https://doi.org/10.3389/fmicb.2015.00059

Hoefler BC, Gorzelnik KV, Yang JY, Hendricks N, Dorrestein PC, Straight PD (2012) Enzymatic resistance to the lipopeptide surfactin as identified through imaging mass spectrometry of bacterial competition. Proc Natl Acad Sci U S A 109:13082–13087

Hua Z, Chen Y, Du G, Chen J (2004) Effects of biosurfactants produced by *Candida antarctica* on the biodegradation of petroleum compounds. World J Microbiol Biotechnol 20(1):25–29

Jimoh AA, Lin J (2019) Biosurfactant: a new frontier for greener technology and environmental sustainability. Ecotoxicol Environ Saf 184(June):109607

Joy S, Rahman PKSM, Sharma S (2017) Biosurfactant production and concomitant hydrocarbon degradation potentials of bacteria isolated from extreme and hydrocarbon contaminated environments. Chem Eng J 317:232–241

Kakugawa K, Tamai M, Imamura K, Miyamoto K, Miyoshi S, Morinaga Y, Suzuki O, Miyakawa T (2002) Isolation of yeast *Kurtzmanomyces* sp. I-11, novel producer of mannosylerythritol lipid. Biosci Biotechnol Biochem 66(1):188–191

Kim H, Jeon J, Kim S, Oh H, Kwon T, Yoon B (2002) Surface and physico-chemical properties of a glycolipid biosurfactant, mannosylerythritol lipid, from *Candida antarctica*. Biotechnol Lett 24:1637–1641

Kitamoto D, Ikegami T, Suzuki GT, Sasaki A, Takeyama Y, Idemoto Y, Koura N, Yanagishita H (2001) Microbial conversion of *n*-alkanes into glycolipid biosurfactants, mannosylerythritol lipids, by *Pseudozyma* (*Candida antarctica*). Biotechnol Lett 23:1709–1714

Konishi M, Morita T, Fukuoka T, Imura T, Kitamoto D (2008) Efficient production of mannosylerythritol lipids with high hydrophilicity by *Pseudozyma hubeiensis* KM-59. Appl Microbiol Biotechnol 78:37–46

Kotoky R, Pandey P (2019) Rhizosphere mediated biodegradation of benzo(A)pyrene by surfactin producing soil *Bacilli* applied through *Melia azadirachta* rhizosphere. Intern J Phytol 21:1–10

Kumar P-N, Swapna T-H, Khan M-Y, Reddy G, Hameeda B (2017) Statistical optimization of antifungal inturin A production from *Bacillus amyloliquefaciens* RHNK22 using agro-industrial wastes. Saudi J Biol Sci 24:1722–1740

Lazar I, Pertisor IG, Yen TF (2007) Microbial enhanced oil recovery (MEOR). Pet Sci Technol 25:1353–1366

Lee A, Kim K (2019) Removal of heavy metals using rhamnolipid biosurfactant on manganese nodules. Water Air Soil Pollut 230(11):1–9

Liu W, Wang X, Wu L, Chen M, Tu C, Luo Y, Christie P (2012) Isolation, identification and characterization of *Bacillus amyloliquefaciens* BZ-6, a bacterial isolate for enhanced oil recovery from oily sludge. Chem 87:1105–1110

Liu Q, Lin J, Wang W, Huang H, Li S (2014) Production of surfactin isoforms by *Bacillus subtilis* BS-37 and its applicability to enhanced oil recovery under laboratory conditions. Biochem Eng J 93:31–37. https://doi.org/10.1016/j.bej.2014.08.023

Liu JF, Mbadinga SM, Yang SZ, Gu JD, Mu BZ (2015) Chemical structure, property and potential applications of biosurfactants produced by *Bacillus subtilis* in petroleum recovery and spill mitigation. Int J Mol Sci 16:4814–4837

Liu G, Zhong H, Yang X, Liu Y, Shao B, Liu Z (2018) Advances in applications of rhamnolipids biosurfactant in environmental remediation: a review. Biotechnol Bioeng 115(4):796–814

Long X, He N, He Y, Jiang J, Wu T (2017) Biosurfactant surfactin with pH-regulated emulsification activity for efficient oil separation when used as emulsifier. Bioresour Technol 241:200–206

Maity J-P, Hsu C-M, Lin T-J, Lee W-C, Bhattacharya P, Bundschuh J, Chen C-Y (2018) Removal of fluoride from water through bacterial-surfactin mediated novel hydroxyapatite nanoparticle and its efficiency assessment: adsorption isotherm, adsorption kinetic and adsorption thermodynamics. Environ Nanotechnol Monit Manage 9:18–28

Mnif I, Besbes S, Ellouze R, Chaabouni SE, Ghribi D (2012) Improvement of bread quality and bread shelf-life by *Bacillus subtilis* biosurfactant addition. Food Sci Biotechnol 21:1105–1112

Morita T, Konishi M, Fukuoka T, Imura T, Kitamoto D (2007) Microbial conversion of glycerol into glycolipid biosurfactants, mannosylerythritol lipids, by a basidiomycete yeast, *Pseudozyma antarctica* JCM 10317. J Biosci Bioeng 104(1):78–81

Morita T, Konishi M, Fukuoka T, Imura T, Kitamoto D (2008) Identification of *Ustilago cynodontis* as a new producer of glycolipid biosurfactants, mannosylerythritol lipids, based on ribosomal DNA sequences. J Oleo Sci 57:549–556

Morita T, Ishibashi Y, Fukuoka T, Imura T, Sakai T, Abe M, Kitamoto D (2009) Production of glycolipid biosurfactants, mannosylerythritol lipids, by a smut fungus, *Ustilago scitaminea* NBRC 32730. Biosci Biotechnol Biochem 73(3):788–792

Morita T, Kawamura D, Morita N, Fukuoka T, Imura T, Sakai H, Abe M, Kitamoto D (2013) Characterization of mannosylerythritol lipids containing hexadecatetraenoic acid produced from cuttlefish oil by *Pseudozyma churashimaensis* OK96. J Oleo Sci 62(5):319–327

Mrozik A, Piotrowska-Seget Z (2010) Bioaugmentation as a strategy for cleaning up of soils contaminated with aromatic compounds. Microbiol Res 165(5):363–375

Mulligan CN, Chow TYK, Gibbs BF (1989) Enhanced biosurfactant production by a mutant *Bacillus subtilis* strain. Appl Microbiol Biotechnol 31:486–489

Mulligan C, Raymond NY, Gibbs BF (1999) Removal of heavy metals from contaminated soil and sediments using the biosurfactant surfactin. J Soil Contamin 8(2):231–254

Ngwenya CZ (2016) Enhanced biosurfactant production by *Bacillus licheniformis* STK 01 for hydrocarbons targeted for bioremediation. Cape Peninsula University of Technology, Cape Town

Nitschke M, Pastore GM (2004) Biosurfactant production by *Bacillus subtilis* using cassavaprocessing effluent. Appl Biochem Biotechnol 112:163–172. https://doi.org/10.1385/ABAB:112:3:163

Niu Y, Wu J, Wang W, Chen Q (2019) Production and characterization of a new glycolipid, mannosylerythritol lipid, from waste cooking oil biotransformation by *Pseudozyma aphidis* ZJUDM34. Food Sci Nutr 7:937–948

Ohno A, Ano T, Shoda M (1995) Production of a lipopeptide antibiotic, surfactin, by recombinant *Bacillus subtilis* in solid state fermentation. Biotechnol Bioeng 47:209–214

Olasanmi IO, Thring RW (2019) Evaluating rhamnolipid-enhanced washing as a first step in remediation of petroleum-contaminated soils and drill cuttings. J Adv Res 21:79–90

Park J, Chen Y, Chen J, Yang J (2002) Removal of phenanthrene from soil by additive-enhanced electrokinetics. Geosci J 6(1):1–5

Parthipan P, Preetham E, Machuca LL, Rahman PK, Murugan K, Rajasekar A (2017) Biosurfactant and degradative enzymes mediated crude oil degradation by bacterium *Bacillus subtilis* A1. Front Microbiol 8:193

Peng W, Chang L, Li P, Han G, Huang Y, Cao Y (2019) An overview on the surfactants used in ion flotation. J Mol Liq 286:110955

Peypoux F, Bonmatin JM, Wallach J (1999) Recent trends in the biochemistry of surfactin. Appl Microbiol Biotechnol 51:553–563

Pi Y, Bao M, Liu Y, Lu T, He R (2017) The contribution of chemical dispersants and biosurfactants on crude oil biodegradation by *Pseudomonas* sp. LSH-7′. J Clean Prod 153:74–82

Qingmei L, Hang Y, Jun W, Guohong G, Wei Z, Yonghong F, Li W, Jianming Y, Zengliang Y (2006) A mutant of *Bacillus subtilis* with high-producing surfactin by ion beam implantation. Plasma Sci Technol 8:491–496

Radzuan MN, Banat JM, Winterburn J (2018) Biorefining palm oil agricultural refinery waste for added value rhamnolipid production via fermentation. Ind Crop Prod 116:64–72

Rocha Junior RB, Meira HM, Almeida DG, Rufino RD, Luna JM, Santos VA, Sarubbo LA (2018) Application of a low-cost biosurfactant in heavy metal remediation processes. Biodegradation 30(4):1–19

Rufino RD, Luna JM, Marinho PHC, Farias CBB, Ferreira SRM, Sarubbo LA (2013) Removal of petroleum derivative adsorbed to soil by biosurfactant Rufisan produced by *Candida lipolytica*. J Pet Sci Eng 109:117–122

Sajna KV, Sukumaran RK, Gottumukkala LD, Pandey A (2015) Crude oil biodegradation aided by biosurfactants from *Pseudozyma* sp. NII 08165 or its culture broth. Bioresour Technol 191:133–139

Salam JA, Das N (2013) Enhanced Biodegradation of lindane using oil-in-water biomicroemulsion stabilized by biosurfactant produced by a new yeast strain, *Pseudozyma* VITJzN01. J Microbiol Biotechnol 23(11):1598–1609

Salmani Abyaneh A, Fazaelipoor MH (2016) Evaluation of rhamnolipid (RL) as a biosurfactant for the removal of chromium from aqueous solutions by precipitate flotation. J Environ Manag 165:184–187

Sarubbo LA, Rocha RB, Luna JM, Rufino RD, Santos VA, Banat IM (2015) Some aspects of heavy metals contamination remediation and role of biosurfactants. Chem Ecol 31(8):707–723

Sen R (2008) Biotechnology in petroleum recovery: the microbial EOR. Prog Energy Combust Sci 34:714–724

Simiqueli APR, Andrade CJ, Fai AEC (2017) Current status and trends in mannosylerylthritol lipids: production, purification and potential applications. In: Upton CR (ed) Biosurfactants: occurrences, applications and research. Nova Science Publishers, New York, pp 149–171

Singh P, Cameotra SS (2004) Enhancement of metal bioremediation by use of microbial surfactants. Biochem Biophys Res Commun 319(2):291–297

Singh R, Singh SK, Rathore D (2019) Analysis of biosurfactants produced by bacteria growing on textile sludge and their toxicity evaluation for environmental application. J Dispers Sci Technol 2019:1–13

Slizovskiy IB, Kelsey JW, Hatzinger PB (2011) Surfactant-facilitated remediation of metal-contaminated soils: Efficacy and toxicological consequences to earthworms. Environ Toxicol Chem 30(1):112–123

Souza EC, Vessoni-Penna TC, Oliveira RPS (2014) Biosurfactant-enhanced hydrocarbon bioremediation: an overview. Int Biodeterior Biodegrad 89:88–94

Spoeckner S, Wray V, Nimtz M, Lang S (1999) Glycolipids of the smut fungus *Ustilago maydis* from cultivation on renewable resources. Appl Microbiol Biotechnol 51:33–39

Tahseen R, Afzal M, Iqbal S et al (2016) Rhamnolipids and nutrients boost remediation of crude oil-contaminated soil by enhancing bacterial colonization and metabolic activities. Int Biodeterior Biodegrad 115:192–198

Tang J, He J, Liu T, Xin X, Hu H (2017) Removal of heavy metal from sludge by the combined application of a biodegradable biosurfactant and complexing agent in enhanced electrokinetic treatment. Chemosphere 189:599–608

Venkatesh NM, Vedaraman N (2012) Remediation of soil contaminated with copper using Rhamnolipids produced from *Pseudomonas aeruginosa* MTCC 2297 using waste frying rice bran oil. Ann Microbiol 62(1):85–91

Walia NK, Cameotra SS (2015) Lipopeptides: biosynthesis and applications. J Microb Biochem Technol 7(2):103–107

Wan J, Meng D, Long T et al (2015) Simultaneous removal of lindane, lead and cadmium from soils by rhamnolipids combined with citric acid. PLoS One 10(6):1–14

Xia W, Du Z, Cui Q, Dong H, Wang F, He P, Tang YC (2014) Biosurfactant produced by novel *Pseudomonas* sp. WJ6 with biodegradation of n-alkanes and polycyclic aromatic hydrocarbons. J Hazard Mater 276:489–498. https://doi.org/10.1016/j.jhazmat.2014.05.062

Yang Z, Shi W, Yang W et al (2018) Combination of bioleaching by gross bacterial biosurfactants and flocculation: a potential remediation for the heavy metal contaminated soils. Chemosphere 206:83–91

Yu M, Liu Z, Zeng G, Zhong H, Liu Y, Jiang Y, Li M, He X, He Y (2015) Characteristics of mannosylerythritol lipids and their environmental potential. Carbohydr Res 407:63–72

Zeng Z, Liu Y, Zhong H et al (2018) Mechanisms for rhamnolipids-mediated biodegradation of hydrophobic organic compounds. Sci Total Environ 634:1–11

Zhang Y, Miller RM (1992) Enhanced octadecane dispersion and biodegradation by a *Pseudomonas* rhamnolipid surfactant (biosurfactant). Appl Environ Microbiol 58(10):3276–3282

Zhao F, Han S, Zhang Y (2020) Comparative studies on the structural composition, surface/interface activity and application potential of rhamnolipids produced by *Pseudomonas aeruginosa* using hydrophobic or hydrophilic substrates. Bioresour Technol 295 (September):122269

Zhen M, Chen H, Liu Q, Song B, Wang Y, Tang J (2019) Combination of rhamnolipid and biochar in assisting phytoremediation of petroleum hydrocarbon contaminated soil using Spartina anglica. J Environ Sci 85:107–118

Zhong H, Liu G, Jiang Y et al (2017) Transport of bacteria in porous media and its enhancement by surfactants for bioaugmentation: a review. Biotechnol Adv 35(4):490–504

Zhu Z, Zhang G, Luo Y, Ran W, Shen Q (2013) Production of lipopeptides by *Bacillus amyloliquefaciens* XZ-173 in solid state fermentation using soybean flour and rice straw as the substrate. Bioresour Technol 112:254–260. https://doi.org/10.1016/j.biortech.2012.02.057

Biosurfactant Mediated Remediation of Heavy Metals: A Review

4

Ruchira Malik and Savita Kerkar

Abstract

Heavy metal contamination has become a serious issue in recent decades. These heavy metals are lethal even at trace amounts. They can bio-accumulate for a long time and can become strongly inhibitory to all the living forms. Various remediation strategies have been developed over the past few decades. However, there is still an ongoing search for alternate tools that are equally effective as well as eco-friendly. This review lays particular emphasis on the use of biosurfactants as a tool for heavy metal removal. Biosurfactants are amphiphilic molecules produced extracellularly by different microorganisms. These molecules have gained interest in the last few decades due to its biodegradable and eco-friendly nature. The properties like emulsification, solubilization, and complex formation with metal ions make it an excellent tool for heavy metal remediation. This chapter explores the various classes of biosurfactants produced by microorganisms and their applications in heavy metal remediation.

Keywords

Biosurfactants · Bioremediation · Heavy metals · Microbes

4.1 Introduction

Heavy metals are naturally occurring elements classified by their higher atomic weight and atomic number and are found throughout the earth's crust. They are known to have high density, i.e. above 5 g/cm^3. Some of these metals are essential in minute quantities as nutrients for microorganisms, plants, animals, and humans.

R. Malik · S. Kerkar (✉)
Department of Biotechnology, Goa University, Taleigao plateau, Goa, India

© The Author(s), under exclusive licence to Springer Nature Singapore Pte Ltd. 2021

V. Kumar et al. (eds.), *Rhizobiont in Bioremediation of Hazardous Waste*,
https://doi.org/10.1007/978-981-16-0602-1_4

They function as cofactors in a wide array of enzymatic and metabolic pathways, however, are capable of being toxic in increased concentration or in specific molecular structures. Some heavy metals are poisonous even at very low concentrations (Mishra et al. 2019). They accumulate in the soft tissues and can develop into emphatically inhibitory to the entire living forms. They can originate from both natural and anthropogenic processes. Under certain environmental circumstances, natural emissions of heavy metals occur, which include volcanic eruptions, forest fires, rock weathering, and many more. The anthropogenic activities include agricultural waste, livestock waste, industrial waste, pesticides, fertilizers, mining, automobile exhaust, smelting, and burning of fossil fuels. Once the metals are released from their endemic spheres they penetrate into different environmental compartments such as soil, water, and air and ultimately enter the food chain. Moreover, these can penetrate into the living system through the air, water, or food and bio-accumulate for quite a while (Tchounwou et al. 2012; Selvi et al. 2019). An elevated amount of metals in loam can cause damaging effects on the quality and lushness of the soil. In the human body, the accumulation of these toxic metals causes extreme health impacts such as growth deformities, carcinogenesis, damaged liver and kidneys, abnormalities, infertility, and pregnancy (Jaishankar et al. 2014; Ayangbenro and Babalola 2018). Nowadays rapid urbanization and industrialization are resulting in unprecedented heavy metal contamination in the environment, thus, their exclusion has become obligatory in favor of environmental well-being. This has given rise to discover and develop innovative approaches that are equally effectual at the same time eco-friendly. One such strategy explicitly attaining importance is using biosurfactant for remediation.

4.2 Biosurfactants

Biosurfactants are structurally diverse groups of surface-active agents produced by diverse microorganisms, for instance, bacteria, fungi, and yeasts on the cell surface or excreted extracellularly. They are naturally amphiphilic, i.e. they have both hydrophilic (water-loving) and hydrophobic (water-hating) moieties. They possess an ability to accrue between liquid segments, capable of lowering surface and interfacial tension. Biosurfactants are produced by inexpensive raw materials which increase its effectiveness towards the increasing demand. In recent years they are widely used for various applications from household detergents to pharmaceuticals. Also, biosurfactants can be customized based on the applications by modifying the genes or by optimizing the production conditions (Thernmozhi et al. 2011).

Table 4.1 List of biosurfactants produced by different microorganisms

Class	Source	References
Glycolipids		
Rhamnolipids	*Pseudomonas* sp., *Pseudomonas aeruginosa*	Guerra-Santos et al. (1986), Hisatsuka et al. (1971), Koch et al. (1988), Rashedi et al. (2005), Robert et al. (1989), Suzuki et al. (1965)
Trehalose lipids	*Rhodococcus erythropolis, Nocardia erythropolis, Arthrobacter sp., Mycobacterium sp.*	Abu-Ruwaida et al. (1991), Bryant (1990), Cooper et al. (1981), MacDonald et al. (1981), Robert et al. (1989), Rosenberg et al. (1979)
Sophorolipids	*Candida bombicola, Candida apicola, Rhodotorula mucilaginosa, and Candida rugosa*	Daverey and Pakshirajan (2009), De Oliveira et al. (2014), Desai and Banat (1997), Deshpande and Daniels (1995)
Mannosylerythritol lipids	*Pseudozyma* (*Candida*) *sp, Ustilago sp*	Arutchelvi et al. (2008), Morita et al. (2015), Yu et al. (2015)
Lipopeptides		
Surfactin/iturin/ fengycin	*Bacillus subtilis*	Arima et al. (1968), Bernheimer and Avigad (1970), Cooper et al. (1981), Rosenberg et al. (1988), Wei et al. (2004)
Viscosin	*Pseudomonas fluorescens*	Neu and Poralla (1990)
Lichenysin	*Bacillus licheniformis*	Grangemard et al. (2001), Madslien et al. (2013), Nerurkar (2010)
Serrawettin	*Serratia marcescens*	Matsuyama et al. (1991), Thies et al. (2014)
Subtilisin	*Bacillus subtilis*	Bernheimer and Avigad (1970)
Gramicidins	*Bacillus brevis*	Marahiel et al. (1977)
Polymyxins	*Bacillus polymyxa*	Suzuki et al. (1965)
Arthrofactin	*Arthrobacter* sp.	Morikawa et al. (1993)
Bamylocin A	*Bacillus amyloliquefaciens*	Lee et al. (2007)
Fengycin S	*Bacillus amyloliquefaciens*	Lee et al. (2010)
Phospholipids/fatty acids/neutral lipids		
Phospholipids	*Acinetobacter sp., Corynebacterium lepus, Thiobacillus thio-oxidans*	Beeba and Umbreit (1971), Dehghan-Noudeh et al. (2007), Kaeppeli and Finnerty (1979), Knoche and Shiveley (1972), Rosenberg and Ron (1999), Rosenberg et al. (1988), Zosim et al. (1982)
Fatty acids	*Corynebacterium lepus*	Chandran and Das (2011), MacDonald et al. (1981)
Neutral lipids	*Nocardia erythropolis*	MacDonald et al. (1981)
Corynomicolic acid	*Corynebacterium insidibasseosum*	Nitschke and Costa (2007)

(continued)

Table 4.1 (continued)

Class	Source	References
Polymeric surfactants		
Emulsan	*Acinetobacter calcoaceticus*	Cirigliano and Carman (1984), Cirigliano and Carman (1985)
Biodispersan	*Acinetobacter calcoaceticus*	Nitschke and Costa (2007)
Liposan	*Candida lipolytica*	Bernheimer and Avigad (1970), Bryant (1990)
Particulate biosurfactants		
Vesicles	*Acinetobacter calcoaceticus*	Gutnick and Shabtai (1987), Kaeppeli and Finnerty (1979)
Whole microbial cells	*Cyanobacteria,* variety of bacteria	Fattom and Shilo (1985), Nitschke and Costa (2007), Rosenberg et al. (1988)

4.3 Classification of Biosurfactants

They are classified following their molecular structure and microbial source (Table 4.1). In general, they are composed of a hydrophilic moiety (polysaccharides or peptides or amino acids) and hydrophobic moiety (saturated or unsaturated fatty acids) (Desai and Banat 1997). They can also be classified as based on the molecular mass. Glycolipids, lipopeptides, and phospholipids are low molecular mass surfactants while polymeric and particulate surfactants are high molecular mass surfactants (Rosenberg and Ron 1999). Biosurfactants are moreover anionic or neutral (Nitschke and Costa 2007).

4.4 Properties of Biosurfactant

4.4.1 Self-Aggregation

As biosurfactants are amphiphilic in nature with hydrophilic and hydrophobic moieties they have self-aggregation properties. In the solution, they form molecular aggregates termed as micelles beyond critical concentration which gives it excellent detergency and solubilization properties. They can be used as detergents, emulsifiers, wetting agents, dispersants, and foaming agents. Micelles act as emulsifiers allowing a compound to dissolve which are usually insoluble. They are an important component of pharmaceutical chemistry and have several applications. Biosurfactants increase the bioavailability of the compounds or act as a mobilizing agent which can be used in the removal of the hydrocarbon contaminants by pseudo-solubilization.

4.4.2 Specificity

They are multifarious organic molecules with precise functional groups, which frequently make them more specific in their action which would be quite persuasive in detoxification of contaminants (Kosaric 2001).

4.4.3 Biodegradability

Biosurfactants are biodegradable as they are produced from natural sources. So they have an advantage over synthetic surfactants that are lethal to the environment owing to their recalcitrant and persistent nature.

4.4.4 Stability

They are stable over a range of temperature, pH, and salinity.

4.4.5 Low Toxicity

They are less toxic in comparison to synthetic surfactants (Juwarkar et al. 2007).

4.5 Role of Biosurfactants in the Remediation of Heavy Metals

Several studies have been executed to evaluate the possibility of metal removal by biosurfactants from the soil as well as from aqueous solutions due to their anionic characteristics and properties like emulsification, solubilization, and complex formation with metal ions. Biosurfactants are capable of modifying the metal surfaces and form aggregate at interphases that favor the separation of metals from contaminated soils. Bacterial cell and exopolymers are capable of remediating metals from waste streams such as industrial effluents, mine water, and sewage sludge. Nonetheless, metal–cell and metal–exopolymer complexes would be filtered out by the soil during washing or flushing due to the large size of bacterial cells and exopolymers (Aşçı et al. 2007). Also, numerous aspects that influence and edge bioremediation efficiency using microbes include pH, temperature, nutritional status, redox potential, moisture, and composition of heavy metals (Shukla et al. 2013). The utilization of microorganisms unaided has revealed limited efficiency due to several aspects including poor competitiveness and excessive heavy metal concentrations. Therefore, biosurfactants have a discrete advantage over the use of the entire cell and exopolymers, as they are small in size and stable over a wide range of temperature, pH, and salinity.

4.6 Mechanism of Action

- In solid phases, desorption of heavy metals endorsed according to Le Chatelier's principle, which occurs in the course of electrostatic interactions or formation of the metal complex with biosurfactants, decreasing the activity of the metal in aqueous phase (Miller 1995).
- Accumulation of biosurfactants at the interface will possibly allow undeviating contact between the biosurfactant and the metal to form a metal–biosurfactant complex. The bonds between metal and biosurfactant are stronger than the bond between metal and soil. Under conditions of decreased interfacial tension, these complexes are further desorbed from the soil matrix to the soil solution succeeding in its removal by flushing. (Gomaa and El-Meihy 2019).
- In aqueous solutions, biosurfactants will adsorb heavy metals and will chelate with the heavy metals to form an insoluble metal—biosurfactant co-precipitate (Das et al. 2009).

4.7 Biosurfactants Used in the Remediation of Heavy Metals

4.7.1 Rhamnolipids

Among biosurfactant classes, rhamnolipids are the most characterized biosurfactant for its potential to remove heavy metals. They are anionic in nature so they are useful to remediate cationic metal ions, such as cadmium, nickel, lead, copper, zinc, and iron (Dahrazma and Mulligan 2007). They are said to be the successive generation of biosurfactants to achieve the market. Rhamnolipids are produced by *Pseudomonas aeruginosa* and are classified as mono and di-rhamnolipids (Parra et al. 1989; Rashedi et al. 2005; Robert et al. 1989; Siegmund and Wagner 1991). They comprise of β-hydroxy fatty acid and a rhamnose sugar molecule attached by carboxyl end. They are also produced by *Pseudomonas fluorescens, Pseudomonas chlororaphis, Pseudomonas plantarii, and Pseudomonas putida* (Sekhon Randhawa and Rahman 2014). They have a wide array of applications in various industries. Though so far, the bioremediation potential of rhamnolipids has been extensively studied and is the major topic for publication.

In 2007, Juwarkar et al. reported remediation of Cd and Pb from artificially contaminated soil using rhamnolipid biosurfactant produced by *Pseudomonas aeruginosa* strain BS2. The study showed that the remediating efficiency reached 92% of Cd and 88% of Pb after 36 h. when the soil was washed with the rhamnolipid. Also, the treatment with rhamnolipid solution enabled the soil to regain its fertility and soil microflora which were lost due to the inhibitory and toxic effect of heavy metals. Thus the study showed that biosurfactant technology is an efficient method for bioremediation. The feasibility of rhamnolipid foam to remediate nickel (Ni) and cadmium (Cd) from sandy soil was evaluated by Wang and Mulligan (2004). The rhamnolipid solution (0.5%) was able to generate foam which removed 73.2% of Cd and 68.1% of Ni with an initial pH value of 10.

Rhamnolipid-mediated desorption of heavy metals from representative soil components was also examined. In 2007, Asci et al. assessed the potential of rhamnolipid to remove Cd(II) from kaolin (soil component). Herein study, the effects of pH and rhamnolipid concentration on desorption efficiency were also evaluated. The maximum removal of Cd(II) was observed to be 71.9% with 80 mM concentration of the rhamnolipid at pH 6. An additional study by Asci et al. reported the removal of zinc from Na-feldspar (a soil component). It was found that the utmost removal efficiency was 98.83% of the sorbed Zn (II) from Na-feldspar using 25 mM rhamnolipid concentration at optimal pH 6.8. The recovery of Cd(II) from sepiolite and K-feldspar (soil components) using rhamnolipid was also accounted for by Asci et al. (2008). The desorption efficiency from K-feldspar was approximately 96%, whereas only 10.1% from sepiolite.

In 2011, Venkatesh and Vedaraman found that 2% of rhamnolipids produced by Pseudomonas aeruginosa MTCC 2297 were able to remove 71% of 474 ppm copper and 74% of 4484 ppm copper from the soil using batch washing experiment. Akintunde et al. (2015) reported remediation of Fe using rhamnolipid from aqueous solution. In this study potential of the biosurfactant to remove iron was investigated. The rhamnolipid was able to remove 60.34% of iron indicating it as an efficient iron remediating agent.

4.7.2 Lipopeptides

Lipopeptides are the most popular biosurfactants as they have a broad range of applications in de-emulsification, food-processing, and crude oil recovery. They also exhibit antimicrobial antiviral, anti-adhesive, and antitumor activities (Cao et al. 2009; Lee et al. 2010; Donio et al. 2013; Pereira et al. 2013; Varadavenkatesan and Ramachandra 2013; Alvarez et al. 2015). They consist of a peptide moiety in combination with fatty acid. The isoform differs from the peptide moiety, the length of the fatty acid chain with the linkage among the two groups (Mnif and Ghribi 2015). *Bacillus sp*. is reported to produce lipopeptide surfactants which have wide applications. Surfactin produced by *Bacillus subtilis* on the whole is the most potent lipopeptide type biosurfactant among the lipopeptides (Wei et al. 2004; Wei et al. 2003; Yeh et al. 2005). It consists of four isomers, Surfactin A–D which displays various physiological activities (Arima et al. 1968). Due to its anionic character, they are capable of forming a complex with the positively charged metal which makes them a metal sequestering candidate for remediating heavy metals.

The efficiency of a biosurfactant in removing heavy metals from solutions was detailed by Das et al. (2009). Biosurfactant derived from a marine bacterium was able to remove 42.74% and 76.6% of 100 ppm of cadmium and lead at a 0.5× critical micelle concentration (CMC). At the same time as the concentration of biosurfactant was increased to 5× CMC, there was an almost complete removal of cadmium and lead. The efficiency of metal removal depended on the concentration of biosurfactant and that of the metal. In 2013, Singh and Cameotra studied the ability to remediate heavy metals from contaminated soil using fengycin and

surfactin produced from *Bacillus subtilis* A21. Heavy metals such as zinc cadmium, iron, copper, lead, cobalt, and nickel were present in high concentrations in the soil. Washing of the soil was carried out with a mixture of surfactin and fengycin at a concentration of 50 CMC. It was able to remove copper (26.2%), lead (40.3%), cadmium (44.2%), zinc (32.07%), nickel (32.2%), and cobalt (35.4%) in a period of 24 h. Further biosurfactant washed soil was for mustard seed germination to check its ability for plant growth. The soil treated with biosurfactant showed 100% germination of seed as compared to the soil washed only with water where no germination was seen.

Bioreduction of Cr (VI) using surfactin was also reported by Swapna et al. (2016). Chromium solution (100 ppm) was treated with surfactin (10 mg/ml) over the period of 72 h. There was 38% removal of Cr (VI) at 12 h which was increased to 74% on incubation up to 72 h.

The advantage of biosurfactants is that they can be produced by using cheap raw materials which can be cost-effective. Hisham et al. (2019) accounted production of biosurfactant by *Bacillus* sp. HIP3 using used cooking oil. The produced lipopeptide biosurfactant was able to remove 12.71% lead, 2.91% zinc, 1.68% chromium, 0.7% cadmium, and 13.57% copper, respectively, from artificially contaminated water, stressing its bioremediation prospective.

4.7.3 Sophorolipids

Sophorolipids consist of disaccharide sophoroses linked to a long-chain hydroxy fatty acid. They are produced by yeasts such as *Candida bombicola*. They are a mixture of 6–9 different hydrophobic sophorosides (Desai and Banat 1997). They can be classified as anionic (acidic) or non-ionic (lactonic). Among all the biosurfactants, the yield of sophorolipids is reported to be the highest. They are considered among promising biosurfactants and are used for commercial production and applications.

The potential sophorolipids from *Torulopsis bombicola* were utilized in the metal ion remediation such as copper and zinc from contaminated sediments. The study confirmed that 4% of sophorolipids were able to remove zinc (60%) and copper (25%) with a single washing (Mulligan et al. 2001). The efficiency of sophorolipids in the removal of lead and cadmium from artificially contaminated soil was also deliberated by using sophorolipids derived from *Starmerella bombicola* CGMCC 1576. Crude acidic sophorolipid was able to remediate 44.8% of lead and 83.6% of cadmium at a concentration of 8%. The removal efficiency of sophorolipids was better than the synthetic surfactants. Moreover, the study also showed that the efficiency of acidic sophorolipid to remediate heavy metals was higher than the lactonic sophorolipid (Qi et al. 2018).

4.7.4 Other Biosurfactants

Heavy metal bioremediation was explored using biosurfactant produced from *Rahnella* sp. RM isolated from chromium-contaminated subsurface soil. The biosurfactant was able to remove 74.3%, 72.5%, and 70.1% of 100 mg/L of Cu, Cr, Pb, respectively, at 48 h. The study showed the purified biosurfactant can be used as a potential candidate in the removal of the metals from contaminated environments (Govarthanan et al. 2017). The biosurfactant extracted from *Candida guilliermondii* UCP 0992 was able to remove 98.6% Fe, 99.9% Zn, and 93.8% Pb from the soil comprising of initial metal concentrations of 1470, 1877, and 3038 mg/l of Zn, Fe, and Pb, respectively. Further, the toxicity of this biosurfactant was also studied on the germination of seeds of cabbage (*Brassica oleracea*). The study showed that the biosurfactant had no toxic effect on seed germination. (Sarubbo et al. 2018).

Recently, Gomaa and El-Meihy (2019) described the efficiency of biosurfactant derived from *Citrobacter freundii* MG812314.1 to remediate heavy metals from the wastewater. The biosurfactant was able to remove 80% aluminum, 67% lead, 66% zinc, 55% cadmium, 45% iron, 44% copper, and 41% manganese, respectively, from wastewater with a concentration of 10% (w/v) after 3 days. Interestingly, the results also showed that when wastewater was treated with 5% biosurfactant with increasing contact time the removal efficiency was increased.

4.8 Conclusions and Future Perspectives

The biosurfactant industry has revealed significant growth over the past few decades. Through recent years numerous studies have shown a wide range of microorganisms capable of producing different types of biosurfactants. The properties like biodegradability and lower toxicity significantly reduce the environmental impact and offer an advantage over their synthetic counterparts. They have an ample range of uses in a range of industries and are on the verge of replacing synthetic surfactants. Despite the immense potential of biosurfactants, their use remains limited, owing to their high production and purification cost. Research needs to focus on the production of biosurfactants on a large scale at a minimum operational cost, which will step forward to a new age of biosurfactants. Even though several studies have accounted for the bioremediation efficacy of biosurfactants, many questions are yet to answer. Generally, studies illustrated are performed under laboratory conditions. There is a requirement for structuring more effective as well as cost-efficient bioremediation strategies using biosurfactants.

References

Abu-Ruwaida AS, Banat IM, Haditirto S, Khamis A (1991) Nutritional requirements and growth characteristics of a biosurfactant producing *Rhodococcus* bacterium. World J Microbiol Biotechnol 7:53–61

Akintunde TA, Abioye OP, Oyeleke SB, Boboye BE, Ijah UJJ (2015) Remediation of iron using rhamnolipid-surfactant produced by *Pseudomonas aeruginosa*. Res J Environ Sci 9(4):169–177

Alvarez VM, Jurelevicius D, Marques JM, De Souza PM, De Araújo LV, Barros TG, De Souza ROMA, Freire DMG, Seldin L (2015) *Bacillus amyloliquefaciens* TSBSO 3.8, a biosurfactant-producing strain with biotechnological potential for microbial enhanced oil recovery. Colloids Surf B Biointerfaces 136:14–21

Arima K, Kakinuma A, Tamura G (1968) Surfactin, a crystalline peptide lipid surfactant produced by *Bacillus subtilis*: isolation, characterization and its inhibition of fibrin clot formation. Biochem Biophys Res Commun 31:488–494

Arutchelvi JI, Bhaduri S, Uppara PV, Doble M (2008) Mannosylerythritol lipids: a review. J Ind Microbiol Biotechnol 35:1559–1570

Aşçı Y, Nurbaş M, Açıkel YS (2007) Sorption of cd (II) onto kaolin as a soil component and desorption of cd (II) from kaolin using rhamnolipid biosurfactant. J Hazard Mater 139(1):50–56

Asci Y, Nurbas M, Sag AY (2008) Removal of zinc ions from a soil component Na-feldspar by a rhamnolipid biosurfactant. Desalination 223(1–3):361–365. https://doi.org/10.1016/j.desal.2007.01.205

Ayangbenro AS, Babalola OO (2018) Metal (loid) bioremediation: strategies employed by microbial polymers. Sustainability 10(9):3028

Beeba JL, Umbreit WW (1971) Extracellular lipid of *Thiobacillus thiooxidans*. J Bacteriol 108:612–615

Bernheimer AW, Avigad LS (1970) Nature and properties of a cytological agent produced by *Bacillus subtilis*. J Gen Microbiol 61:361–369

Bryant FO (1990) Improved method for the isolation of biosurfactant glycolipids from *Rhodococcus sp*. strain H13A. Appl Environ Microbiol 56:1494–1496

Cao XH, Liao ZY, Wang CL, Yang WY, Lu MF (2009) Evaluation of a lipopeptide biosurfactant from *Bacillus Natto* Tk-1 as a potential source of anti-adhesive, antimicrobial and antitumor activities. Braz J Microbiol 40:373–379

Chandran P, Das N (2011) Characterization of sophorolipid biosurfactant produced by yeast species grown on diesel oil. Int J Sci Nat 2(1):63–71

Cirigliano MC, Carman GM (1984) Isolation of a bioemulsifier from *Candida lipolytica*. Appl Environ Microbiol 48:747–750

Cirigliano MC, Carman GM (1985) Purification and characterization of liposan, a bioemulsifier from *Candida lipolytica*. Appl Environ Microbiol 50:846–850

Cooper DG, MacDonald CR, Duff SJB, Kosaric N (1981) Enhanced production of surfactin from *B. subtilis* by continuous product removal and metal cation additions. Appl Environ Microbiol 42:408–412

Dahrazma B, Mulligan CN (2007) Investigation of the removal of heavy metals from sediments using rhamnolipid in a continuous flow configuration. Chemosphere 69:705–711

Das P, Mukherjee S, Sen R (2009) Biosurfactant of marine origin exhibiting heavy metal remediation properties. Bioresour Technol 100:4887–4890

Daverey A, Pakshirajan K (2009) Production of sophorolipids by the yeast *Candida bombicola* using simple and low cost fermentative media. Food Res Int 42:499–504

De Oliveira MR, Doumit CN, Baldo C, Magri A, Celligoi MAPC (2014) Biosynthesis and production of Sophorolipids. Int J Sci Technol Res 3(11):133–146

Dehghan-Noudeh G, Moshafi MH, Sharififar F, Masoumi MA (2007) Studies on biosurfactant production by *Acinetobacter calcoaceticus* (PTCC 1318). Jundishapur J Nat Pharm Prod 2 (2):116–123

Desai JD, Banat IM (1997) Microbial production of surfactants and their commercial potential. Microbiol Mol Biol Rev 61(1):47–64

Deshpande M, Daniels L (1995) Evaluation of sophorolipid biosurfactant production by *Candida bombicola* using animal fat. Bioresour Technol 54:143–150

Donio MBS, Ronica SFA, Viji VT, Velmurugan S, Jenifer JA, Michaelbabu M, Citarasu T (2013) Isolation and characterization of halophilic *Bacillus* sp. BS3 able to produce pharmacologically important biosurfactants. Asian Pac J Trop Med 6(11):876–883

Fattom A, Shilo M (1985) Production of emulcyan by *Phormidium* J-1: its activity and function. FEMS Microbiol Ecol 31:3–9

Gomaa EZ, El-Meihy RM (2019) Bacterial biosurfactant from Citrobacter freundii MG812314. 1 as a bioremoval tool of heavy metals from wastewater. Bull Natl Res Centre 43(1):69. https://doi.org/10.1186/s42269-019-0088-8

Govarthanan M, Mythili R, Selvankumar T, Kamala-Kannan S, Choi D, Chang YC (2017) Isolation and characterization of a biosurfactant-producing heavy metal resistant Rahnella sp. RM isolated from chromium-contaminated soil. Biotechnology Biotechnol. Bioprocess Eng. 22 (2):186–94.

Grangemard I, Wallach J, Maget-Dana R, Peypoux F (2001) Lichenysin: a more efficient cationchelator than surfactin. Appl Biochem Biotechnol 90(3):199–210

Guerra-Santos LH, Kappeli O, Flechter A (1986) Dependence of *Pseudomonas aeruginosa* continuous culture biosurfactant production on nutritional and environmental factors. Appl Microbiol Biotechnol 24:443–448

Gutnick DL, Shabtai Y (1987) Exopolysaccharide bioemulsifiers. In: Kosaric N, Cairns WL, Gray NCC (eds) Biosurfactants and biotechnology. Marcel Dekker, New York, pp 211–246

Hisatsuka K, Nakahara T, Sano N, Yamada K (1971) Formation of rhamnolipid by *Pseudomonas aeruginosa*: its function in hydrocarbon fermentations. Agric Biol Chem 35:686–692

Hisham MB, Hanisah N, Ibrahim MF, Ramli N, Abd-Aziz S (2019) Production of biosurfactant produced from used cooking oil by *Bacillus* sp. HIP3 for heavy metals removal. Molecules 24 (14):2617

Jaishankar M, Tseten T, Anbalagan N, Mathew BB, Beeregowda KN (2014) Toxicity, mechanism and health effects of some heavy metals. Interdiscip Toxicol 7(2):60–72. https://doi.org/10.2478/intox-2014-0009

Juwarkar AA, Nair A, Dubey KV, Singh SK, Devotta S (2007) Biosurfactant technology for remediation of cadmium and lead contaminated soils. Chemosphere 68(10):1996–2002. https://doi.org/10.1016/j.chemosphere.2007.02.027

Kaeppeli O, Finnerty WR (1979) Partition of alkane by an extracellular vesicle derived from hexadecane-grown *Acinetobacter*. J Bacteriol 140:707–712

Knoche HW, Shiveley JM (1972) The structure of an ornithine containing lipid from *Thiobacillusthiooxidans*. J Biol Chem 247:170–178

Koch AK, Reiser J, Kappeli O, Fiechter A (1988) Genetic construction of lactose-utilizing strains of *P. aeruginosa* and their application in biosurfactant production. Bio/Technology 6:1335–1339

Kosaric N (2001) Biosurfactants and their application for soil bioremediation. Food Technol. Biotechnol. 39(4):295–304.

Lee SC, Kim SH, Park IH, Chung SY, Chandra MS, Choi YL (2010) Isolation, purification and characterization of novel Fenzycin S from *Bacillus amyloliquefaciens* LSC04 degrading-crude oil. Biotechnol Bioeng 15:246–253

Lee SC, Kim SH, Park IH, Chung SY, Choi YL (2007) Isolation and structural analysis of bamylocin a, novel lipopeptide from *Bacillus amyloliquefaciens* LP03 having antagonistic and crude oil-emulsifying activity. Arch Microbiol 188:307–312

MacDonald CR, Cooper DG, Zajic JE (1981) Surface-active lipids from *Nocardiaerythropolis* grown on hydrocarbons. Appl Environ Microbiol 41:117–123

Madslien EH, Ronning HT, Lindbäck T, Hassel B, Andersson MA, Granum PE (2013) Lichenysin is produced by most *Bacillus licheniformis* strains. J Appl Microbiol 115(4):1068–1080

Marahiel M, Denders W, Krause M, Kleinkauf H (1977) Biological role of gramicidin S in spore functions. Studies on gramicidin-S negative mutants of *Bacillus brevis* 9999. Eur J Biochem 99:49–52

Matsuyama T, Sogawa M, Yano I (1991) Direct colony thin-layer chromatography and rapid characterization of *Serratiamarcescens* mutants defective in production of wetting agents. Appl Environ Microbiol 53:1186–1188

Miller RM (1995) Biosurfactant-facilitated remediation of metal-contaminated soils. Environ Health Perspect 103:59. https://doi.org/10.2307/3432014

Mishra S, Bharagava RN, More N, Yadav A, Zainith S, Mani S, Chowdhary P (2019) Heavy metal contamination: an alarming threat to environment and human health. In: Environmental biotechnology: for sustainable future. Springer, Singapore, pp 103–125

Mnif I, Ghribi D (2015) Review lipopeptides biosurfactants: mean classes and new insights for industrial, biomedical, and environmental applications. Pept Sci 104(3):129–147

Morikawa M, Daido H, Takao T, Murata S, Shimonishi Y, Imanaka T (1993) A new lipopeptide biosurfactant produced by *Arthrobacter* sp. strain MIS38. J Bacteriol 175(20):6459–6466

Morita T, Fukuoka T, Imura T, Kitamoto D (2015) Mannosylerythritol lipids: production and applications. J Oleo Sci 64(2):133–141

Mulligan CN, Yong RN, Gibbs BF (2001) Heavy metal removal from sediments by biosurfactants. J Hazard Mater 85(1-2):111–125

Nerurkar AS (2010) Structural and molecular characteristics of lichenysin and its relationship with surface activity. Adv Exp Med Biol 672:304–315

Neu TR, Poralla K (1990) Emulsifying agent from bacteria isolated during screening for cells with hydrophobic surfaces. Appl Microbiol Biotechnol 32:521–525

Nitschke M, Costa SGVAO (2007) Biosurfactants in food industry, trends food Sci. Tech 18:252–259

Parra JL, Guinea J, Manresa MA, Robert M, Mercade ME, Comelles F, Bosch MP (1989) Chemical characterization and physicochemical behaviour of biosurfactants. J Am Oil Chem Soc 66:141–114

Pereira JFB, Gudiña EJ, Costa R, Vitorino R, Teixeira JA, Coutinho JAP, Rodrigues LR (2013) Optimization and characterization of biosurfactant production by *Bacillus subtilis* isolates towards microbial enhanced oil recovery applications. Fuel 111:259–268

Qi X, Xu X, Zhong C, Jiang T, Wei W, Song X (2018) Removal of cadmium and Lead from contaminated soils using Sophorolipids from fermentation culture of Starmerella bombicola CGMCC 1576 fermentation. Int J Environ Res Public Health 15(11):2334

Rashedi H, Jamshidi E, Mazaheri AM, Bonakdarpour B (2005) Isolation and production of biosurfactant from *Pseudomonas aeruginosa* isolated from Iranian southern wells oil. Int J Environ Sci Tech 2(2):121–127

Robert M, Mercade ME, Bosch MP, Parra JL, Espuny MJ, Manresa MA, Guinea J (1989) Effect of the carbon source on biosurfactant production by *Pseudomonas aeruginosa* 44T. Biotechnol Lett 11:871–874

Rosenberg E, Ron EZ (1999) High- and low molecular-mass microbial surfactants. Appl Microbiol Biotechnol 52:154–162

Rosenberg E, Rubinovitz C, Legmann R, Ron EZ (1988) Purification and chemical properties of *Acinetobacter calcoaceticus* A2 biodispersan. Appl Environ Microbiol 54:323–326

Rosenberg E, Zuckerberg A, Rubinovitz C, Gutnick DL (1979) Emulsifier *Arthrobacter* RAG-1: isolation and emulsifying properties. Appl Environ Microbiol 37:402–408

Sarubbo L, Brasileiro P, Silveira G, Luna J, Rufino R (2018) Application of a low cost biosurfactant in the removal of heavy metals in soil. Chem Eng Trans 64:433–438

Sekhon Randhawa KK, Rahman PKSM (2014) Rhamnolipid biosurfactants—past, present, and future scenario of global market. Front Microbiol 5:454. https://doi.org/10.3389/fmicb.2014.00454

Selvi A, Rajasekar A, Theerthagiri J, Ananthaselvam A, Sathishkumar K, Madhavan J, Rahman PKSM (2019) Integrated remediation processes toward heavy metal removal/recovery from

various environments-a review. Front Environ Sci 7:66. https://doi.org/10.3389/fenvs.2019.00066

Shukla KP, Sharma S, Singh NK, Singh V, Bisht S, Kumar V (2013) Rhizoremediation: a promising rhizosphere technology. In: Applied bioremediation-active and passive approaches. IntechOpen, New York

Siegmund I, Wagner F (1991) New method for detecting rhamnolipids exerted by *Pseudomonas* species grown on mineral agar. Biotechnol Tech 5:265–268

Singh AK, Cameotra SS (2013) Efficiency of lipopeptide biosurfactants in removal of petroleum hydrocarbons and heavy metals from contaminated soil. Environ Sci Pollut Res 20 (10):7367–7376

Suzuki TK, Hayashi K, Fujikawa TK (1965) The chemical structure of polymyxin E. the identities of polymyxin E1 with colistin a and polymyxin E2 with colistin B. J Biochem 57:226–227

Swapna TH, Papathoti NK, Khan MY, Reddy G, Hameeda B (2016) Bioreduction of Cr (VI) by biosurfactant producing marine bacterium *Bacillus subtilis* SHB 13. J Sci Ind Res 75:432–438

Tchounwou PB, Yedjou CG, Patlolla AK, Sutton DJ (2012) Heavy metal toxicity and the environment. Exp Suppl 101:133–164. https://doi.org/10.1007/978-3-7643-8340-4_6

Thernmozhi R, Sornalaksmi A, Praveenleumar D, Nagasathya A (2011) Characterization of biosurfactant produced by bacterial isolates from engine oil contaminated soil. Adv Environ Biol 5(8):2402–2408

Thies S, Santiago-Schübel B, Kovaci F, Rosenauc F, Hausmannd R, Jaeger KE (2014) Heterologous production of the lipopeptide biosurfactant serrawettin W1 in *Escherichia coli*. J Biotechnol 181:27–30

Varadavenkatesan T, Ramachandra VM (2013) Production of a lipopeptide biosurfactant by a Novel *Bacillus sp*. and its applicability to enhanced oil recovery. Microbiology 2013:621519

Venkatesh NM, Vedaraman N (2011) Remediation of soil contaminated with copper using Rhamnolipids produced from Pseudomonas aeruginosa MTCC 2297 using waste frying rice bran oil. Ann Microbiol 62(1):85–91. https://doi.org/10.1007/s13213-011-0230-9

Wang S, Mulligan CN (2004) Rhamnolipid foam enhanced remediation of cadmium and nickel contaminated soil. Water Air Soil Pollut 157:315–330

Wei YH, Wang LF, Chang JS (2004) Optimizing iron supplement strategies for enhanced surfactin production with *Bacillus subtilis*. Biotechnol Prog 20:979–983

Wei YH, Wang LF, Chang JS, Kung SS (2003) Identification of induced acidification in iron-enriched cultures of *Bacillus subtilis* during biosurfactant fermentation. J Biosci Bioeng 96:174–178

Yeh MS, Wei YH, Chang JS (2005) Enhanced production of surfactin from *Bacillus subtilis* by addition of solid carriers. Biotechnol Prog 21:1329–1334

Yu M, Liu Z, Zeng G, Zhong H, Liu Y, Jiang Y, Li M, He X, He Y (2015) Characteristics of mannosylerythritol lipids and their environmental potential. Carbohydr Res 407:63–72

Zosim Z, Gutnick DL, Rosenberg E (1982) Properties of hydrocarbon-in-water emulsions stabilized by *Acinetobacter* RAG-1 emulsan. Biotechnol Bioeng 24:281–292

Surface-Active Agents from *Pseudomonas* Emulsify *n*-Hexadecane: Past, Present, and Future Trends

5

Sivamurugan Vajiravelu, K. C. Ramya Devi, R Rachel Veronica, and K. Mary Elizabeth Gnanambal

Abstract

This chapter highlights the importance and the devastating irreparable damage it could have on the various ecosystems, especially in the marine realm. In the past, various ways have been adopted to counter the effect of oil pollution by both chemical and physical means, however, they themselves pose either harm to the ecosystem or are highly expensive/involve high-end infrastructure for the operations. Hence a most inexpensive and an ecofriendly approach using microorganisms have been thought of to reduce or mitigate the effects of oil pollution for the last five decades. The chapter concentrates on the non-marine as well marine-sourced bacterial groups those were/are employed for bioremediation purpose and the importance of bioemulsifiers in such operations. The chapter details the remediation strategies for hexadecane, a 16-C aliphatic hydrocarbon and the usage of bioemulsifiers for such purpose. Work from the authors' laboratory gives insights into the isolation of a bacterium, *Pseudomonas guguanensis* and the role of its bioemulsifier in hexadecane removal. A detailed pathway is proposed for the biosynthesis of the emulsifier by the bacterium and how that is being used to emulsify hydrocarbon so that a link is established between the feed and the product. Conclusive statements on the future of use of this organism for hexadecane removal and the possible approaches are listed.

S. Vajiravelu
PG and Research Department of Chemistry, Pachaiyappa's College, Chennai, Tamil Nadu, India

K. C. Ramya Devi · Rachel Veronica R · K. Mary Elizabeth Gnanambal (✉)
Department of Biotechnology, Faculty of Biomedical Sciences, Technology and Research, SRI Ramachandra Institute of Higher Education and Research (SRIHER), Deemed to be University (DU), Chennai, Tamil Nadu, India
e-mail: drelizabethrajesh@sriramachandra.edu.in

© The Author(s), under exclusive licence to Springer Nature Singapore Pte Ltd. 2021

V. Kumar et al. (eds.), *Rhizobiont in Bioremediation of Hazardous Waste*,
https://doi.org/10.1007/978-981-16-0602-1_5

Keywords

Bioemulsifier · Bioremediation · Microbes · Petroleum hydrocarbons

5.1 Introduction

One of the major resources in this modern industrial world is oil and its products. Hence it is certain that there is a huge danger of oil spillage as long as oil is being used. Oil spills impose serious concerns in the environment (Kingston 2002). Oil spillage is a type of pollution wherein as a result of accidents or anthropogenic actions, there is a release of liquid petroleum into the surroundings, mainly in the marine environment (Briggs and Briggs 2018). Oceanic oil spills became a serious environmental problem in the 1960s (Fig. 5.1).

There are four major sources for oil pollution: 1. urban runoff, 2. atmospheric fall outs, 3. natural seeps, and 4. oil spills. In the urban areas, oil from the vehicles build-up on the roads is washed off due to rains or melting of snow and enters the sewer systems and the water sources. The U.S. Environmental Protection Agency (EPA) states the major causes of runoff oil pollution to be vehicular leaks, fuel station spills, and oil which is not disposed properly. During rains or melting of snow, the oil which floats on the water is forced to flow out of the city and thus enters the rural areas polluting its water resources and natural elements. Oil from vehicles and planes which pollutes the air is called atmospheric fallout. In the long run, this oil tends to drop down from the air and settles on oceans or on land. Based on the site and the pollution load in the air, the fallout can be heavy or light. For instance, as vehicles run, a part of the oil is burned which produces not only energy but also emit gases into the atmosphere. Thus, this oil travels in the air or drops down from the air. The oil is pushed from the air and settles onto the water or land to cause pollution during rains or snow. Natural seep is a type of pollution which occurs naturally and is unavoidable. The oil oozes from the ground and causes pollution in the surrounding area. La Brea Tar Pits in California seepage of oil and gas forming tar maybe

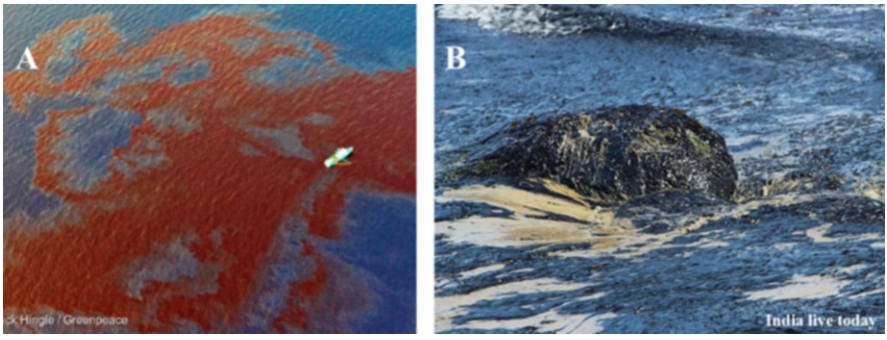


Fig. 5.1 Oil spill (**a**) April 2010, Gulf of Mexico and (**b**) January 2017 Ennore, Tamilnadu

considered as one of the well-known natural seeps. Oil spill is the most serious type of oil pollution out of all the types mentioned above. This may occur due to several reasons such as damage to an oil ship or any transport issues, equipment malfunctions at oil refineries. Among these, oil spills mostly take place during the transportation of oil. For example, an oil spill occurred on April 20, 2010 in the Gulf of Mexico due to an explosion which caused 205 million gallons of oil to be spilled into the sea as reported by "The Huffington Post" (Mayank 2019; www.newindianexpress.com). Around 0.33 million tonnes of petroleum lubricant spilled into the sea when two cargo ships collided in the Ennore coast in Chennai (Tamil Nadu, India) on January 28, 2017. These oil spills resulted in serious damage to the beaches and the marine environment. More recently, there was an oil spill in Russia on May 29, 2020 when a fuel tank collapsed and released around 21,000 tonnes of diesel oil into the Ambarnaya River, turning it crimson red, which now has a risk of spreading into the Arctic Ocean (BBC News 2020).

5.2 Biological Impact of Oil Pollution

Oil pollution damages the ecosystems and causes contamination of water. The oil coats the marine animals and also the birds' feathers and fur (Fig. 5.2).

The animals cannot protect themselves from the cold water and the birds experience trouble flying once they are covered in oil. The animals ingest some of the oil during the process of cleaning themselves. Due to the thick oil deposit on the water surface, fishes can be suffocated, and also prolonged exposure to oil can result in liver, reproductive and growth-related disorders in bottom-dwelling fishes (NOAA 2020). Oil pollution can harm the plants which grow in or near the water. Sunlight needed for the plants to carry out photosynthesis can be blocked by an oil spill and as a result the plants growing in oil spilled water cannot survive and hence a huge loss in primary productivity in localized areas may occur. Oil spills can cause closure of beaches and harbors. Certain areas are more susceptible than the others to oil pollution. For instance, when compared to the sandy beaches and sea-grass beds, the more easily affected areas are the coral reefs, mangroves, and marshes (ITOPF 2011a). The oil at times can be carried off for a long distance from the site of the spill by the water and wind currents and along the way causes harm to the plants, birds and marine animals.

5.3 Oil Pollution Clean-up Methods

Depending upon the kind and the quantity of the spilled oil, the location of the water source and the weather conditions of that area, there are various clean-up strategies that can be recommended. The recovery period can vary from weeks to decades. Recovery may occur within several weeks along the bedrock shorelines due to the high-energy waves. Usually, exposed beaches recover in a few months. Although, recovery could take several years or even decades in marshes and salt flats. Recovery

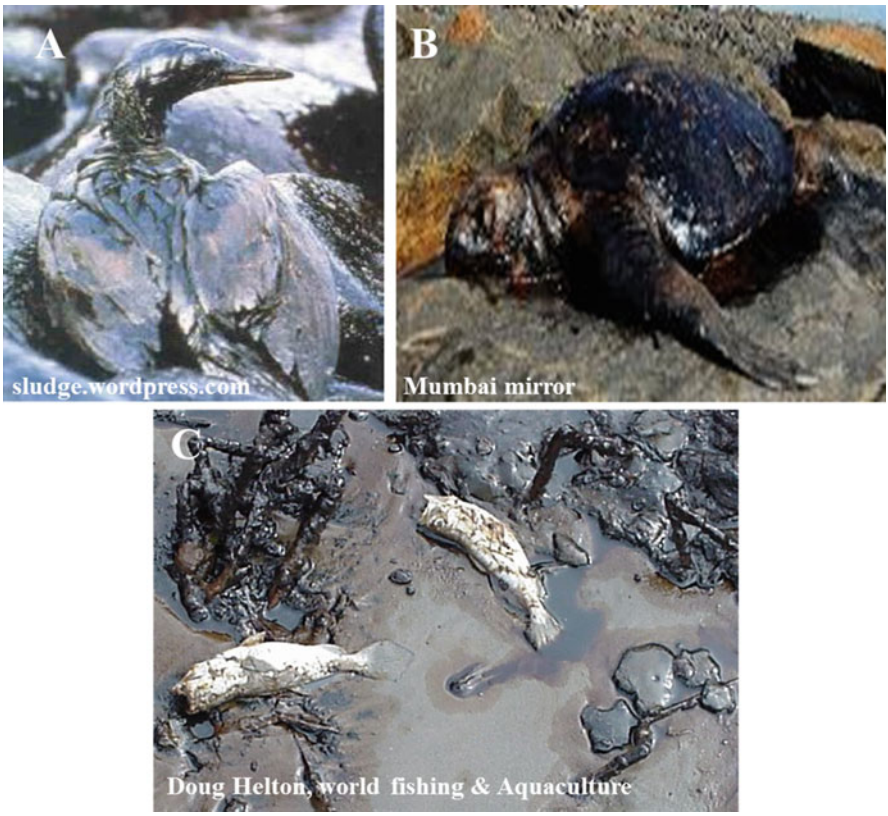


Fig. 5.2 (**a**) Birds soaked in oil after Exxon Valdez oil spill, Alaska, (**b**) dead turtle after Ennore oil spill, and (**c**) dead fish in an oil spill

can take up to 50 years in the Mangroves, which are claimed to be the most productive yet sensitive coastal regions in the tropics and subtropics.

A list of commonly used clean-up methods to treat oil spilled areas is summarized below (Safe Drinking Water Foundation 2017).

5.3.1 Booms

One of the most commonly used tools is the booms as they contain the oil and prevent the spread. There are three common kinds of booms extant: hard, sorbent and fire booms (NOAA 2019c). Booms are highly efficient when the oil slicks are thin and light. There are four basic characteristics a boom possesses: a freeboard which is above the water and this helps in containing the oil; a device for floatation; a skirt that is below the water surface which helps in containing the oil and reduces the quantity of oil which goes under the boom; a longitudinal support which goes along

the skirt bottom and this helps the boom to withstand wind and wave action offering stability. Once the oil is contained, the boom is fastened to a vessel at the end points in order to form a pocket which is U- or J-shaped in which the oil is collected. This confined oil is pumped out into storage tanks and taken for appropriate disposal to the shore (US EPA 1999b; ITOPF 2011b).

5.3.2 Chemical Dispersants

The usage of chemical dispersants in the clean-up of oil spills has been successful. These are chemicals which are applied by a low-flying plane to the water surface. Many a times, hydrocarbons can also breakdown naturally. Chemical dispersants are those which speed up this natural process. Once the dispersants are applied, the oil is dispersed in the water, that is, the oil and the dispersant are bound and have moved down the water column. The concentration of the oil is diluted by the water so that there is less danger to the marine life (US EPA 1999a; ITOPF 2011c).

5.3.3 Skimmers

The oil can be skimmed from the surface of water with the aid of boats called skimmers (NOAA 2019a). The physicochemical properties of oils are not quite changed by the skimmers. Thus, the oil can be refined if it is relatively fresh, whereas, in other instances, the oil is burned. The kind and the denseness of the oil spill, the debris load in the water, the site and its weather conditions decide the success rate of skimming (calm weather is best suitable for skimming) (US EPA 1999b).

5.3.4 Sorbents

Sorbents are also applied as powders to the surface of water as it has the ability to absorb small quantities of oil. Thus the final step of clean-up is mostly sorbents. Natural as well as synthetic organic materials are used as sorbents. Peat moss and sawdust are some of the natural organic materials and polypropylene, polyester foam or polystyrene are some of the synthetic organic materials that are commonly used as sorbents. Generally, these are applied manually, and nets and rakes are used for recovery (US EPA 1999b; ITOPF 2012).

5.3.5 Burning

Burning is a frequently used method for the removal of oil from the surface of water. Following the deployment of skimmers for the removal of oil from the surface of water, the oil can be burned. Although the removal of oil from the water surface

occurs rapidly and efficiently by burning, there is release of oxides of nitrogen and sulfur due to burning of oil which leads to acid rain and causes further pollution (NOAA 2019b; National Research Council 2013).

5.3.6 Beach Clean-Up

Manual clean-up with the help of shovels and trucks is often carried out in oil contaminated beaches and shores. The oiled beach sand and gravel can be removed manually from the beach and transported to another location to carry out treatment. The oil may be vacuumed off the beach with the help of vacuum trucks. Oil can then be washed off of the beaches with the help of pressurized hoses into the water. Here, the oil will be dispersed and diluted (NOAA 2019a; US EPA 1999c).

These methods have various disadvantages, for example, booms are efficient only in cleaning of thin oils, burning of oil causes acid rain and dispersants per se cause detergent pollution. Not only that, all of these methods increase the Chemical Oxygen Demand (COD) and the Biological Oxygen Demand (BOD) thereby lowering the amount of available Dissolved Oxygen (DO). Higher aquatic organisms are affected by the chemical substances by inhalation through respiratory tracts. It can either be external gills or regions of specialized cells on the body surface as in the case of invertebrates such as crustaceans or epithelial membranes as in the higher organisms such as fish. When exposed to emulsifiers there may be destabilization of the epithelial membranes which causes changes in membrane permeability, cellular lysis and cellular respiration impairment (Dicks 1998). Thus on top of oil pollution the recovery methods also pose significant challenges to the biota and hence there has been a shift from chemical to biological way of cleaning up oil spills, which may be eco-friendly.

5.4 Biosurfactants and Bioemulsifiers Could Be an Eco-Sustainable Solution?

Contaminants from the water and soil are efficiently removed by the microorganisms. Certain microorganisms which occur in the environment are able to break down many toxic chemicals, especially hydrocarbons, such as gasoline and oil. In order to enhance the rate at which the microorganisms work, often, there is an addition of nutrients like nitrogen or phosphorus. The process by which a contaminated site is cleaned up or remediated with the help of microorganism is called bioremediation. The oil which is difficult to remove is broken down by this biological process. Sensitive areas such as coral reefs and mangroves are also cleaned up by this process. Bioemulsifiers are amphiphilic compounds that contain both hydrophobic and hydrophilic moieties and make emulsions by dispersing oil in water or water in oil. This can be achieved by reducing the surface-active forces of both the oil as well as water thus making both the aqueous and non-aqueous phases either fully or partially miscible.

5.4.1 Bioemulsifiers

Microorganisms which produce bioemulsifiers are omnipresent. They are present both in aquatic and terrestrial environments and also in extreme environments (for example, in hypersaline sites and in oil reservoirs as well). They are able to survive in a broad range of temperatures, pH and salinities. Bioemulsifier produced by microorganisms solubilizes the hydrophobic compounds in the surroundings and helps in its utilization as sources of energy and nutriment (Floodgate 1978; Margesin and Schinner 2001; Olivera et al. 2003). At times, a bioemulsifier is produced on substrates which are water-soluble by few microorganisms (Turkovskaya et al. 2001; Gunther et al. 2005). This indicates that the bioemulsifier molecules present on the cell surface of the microorganism tends to increase the cell's hydrophobicity and aids for its survival in the hydrophobic setting (Abraham et al. 1998; Perfumo et al. 2009). The bioemulsifier produced may either be localized on the surface or released extracellularly into the environment. In the case when the bioemulsifier is in association with the cell, the cell membrane of microorganism acts as a bioemulsifier and controls the property of adherence to the substrates which are insoluble in water (Maneerat and Dikit 2007). The isolation and characterization of microorganisms which produce bioemulsifier has mostly been carried out from the polluted (petroleum or its byproduct and oils) marine and terrestrial environments. Different types of bioemulsifiers with various molecular structures are produced by a broad range of genera which are linked with the marine environment.

5.4.2 A Short Review on Bioemulsifiers from Marine and Non-Marine Microbes

Bioemulsifiers which are produced by marine microbes, in addition to having properties such as tolerance to temperatures (20–100 °C), pH (3–12), and salinities (0.5–2.0%), have certain other unusual properties as well. Due to the lack of infrastructure to culture marine bacteria, there is very limited bioemulsifiers produced from marine microbes. *A. calcoaceticus* RAG-1 when cultured on hexadecane produces bioemulsifier (Rosenberg and Ron 1997). An anionic glucose lipid was produced by *Alcanivorax borkumensis* that contained a tetrameric oxyacyl side chain (Abraham et al. 1998), while an *Alcaligenes* sp. produced a glucose lipid (Poremba et al. 1991). An extracellular polysaccharide bioemulsifier was produced from *Rhodococcus rhodochrous* and has been characterized in Japan (Noriyuki et al. 2002). A complex of lipid, carbohydrate, and protein which was isolated from *Yarrowia lipolytica* was identified to function as a bioemulsifier at National Chemical Laboratory (NCL), Pune, India (Zinjarde and Pant 2002). A commercial bioemulsifier was produced by *Acinetobacter* sp. which is a predominant group of Gram-negative bacteria in the marine environment (Haleem 2003). A flavolipid bioemulsifier was produced by *Flavobacterium* sp. strain MTN11 of Arizona, Texas and its structure and some of its selected properties have been identified and reported for the first time (Bodour et al. 2004). *Pseudomonas aeruginosa* produced

rhamnolipid bioemulsifier in larger quantities (Wei et al. 2005). Lipoproteins such as Ornithine lipids with bioemulsifier like function were isolated from *Myroides* sp. SM1 in the coasts of Okayama, Japan (Maneerat et al. 2006). A glycolipid bioemulsifier was partially characterized (Thavasi et al. 2008) at the Centre for Advanced Study in Marine Biology, Parangipettai, Tamil Nadu. The preliminary characterization of the bioemulsifier products was performed for the isolates *B. megaterium, C. kutscheri* and *P. aeruginosa* and it was identified to be glycolipid, glycolipopeptide, and lipopeptide, respectively (Thavasi et al. 2010). A marine Actinobacterium, *Brevibacterium aureum* MSA13 produced a lipopeptide which was optimized to bioemulsifier production at the Bharathidasan University, Tiruchirappalli, Tamil Nadu, India (Kiran et al. 2010).

From the petroleum contaminated sites and oil reservoirs, the bacteria producing bioemulsifiers have been isolated (Batista et al. 2006). There are numerous emulsifiers produced by terrestrial bacteria and fungi. *Bacillus* strain FE-2 produced a lysozyme-sensitive bioemulsifier (Patel and Gopinathan 1986). *Acinetobacter radioresistens* KA-53 produced an anionic alanine-containing heteropolysaccharide—protein bioemulsifier called Alasan. *A. junii* SC14 produced a proteoglycan bioemulsifier (Patil and Chopade 2004). An extracellular polymer bioemulsifier was produced through continuous fermentation by *Corynebacterium hydrocarboclastus* when the carbon source used was kerosene (Shilo et al. 1993). *Pseudomonas putida* ML2 was reported to produce a bioemulsifer and an extracellular polysaccharide with emulsifying and flocculating activity (Bonilla et al. 2005). In the fungal groups, a liposan emulsifier was produced by *Candida lipolytica* and a mannoprotein type of bioemulsifier was produced by *Saccharomyces cerevisiae.* An extracellular polysaccharide was isolated and characterized from *Penicillium citrinum* (Morais et al. 2003). *Pseudozyma* sp. or *Ustilago* sp., *Pseudomonas aeruginosa* and *Bacillus subtilis* YB7 produced mannosylerythritol lipids, glycolipid, and cyclic lipopeptide, respectively (Arutchelvi et al. 2009; Arutchelvi and Doble 2010).

5.4.3 Bioemulsifier Classification

The classification of emulsifiers is on the basis of their hydrophilic—lipophilic balance (HLB). Predominantly, an emulsifier is lipophilic when its HLB is low and has a water-soluble property when its HLB is high. A biosurfactant has two major components: a hydrophobic tail and a hydrophilic head, wherein the hydrophilic region consists of amino acids/peptides; mono, di/polysaccharides while the hydrophobic part consists of either unsaturated or saturated fatty acids which may be hydroxylated, in most of the cases. Glycolipids, lipoprotein, lipopeptides, phospholipids, fatty acids and polymeric bioemulsifiers are the major classes of bioemulsifiers (Desai and Banat 1997). This chapter generally confines to the glycolipid-type of emulsifiers because similar compounds were isolated by us.

5.4.3.1 Glycolipid Bioemulsifier

These are basically low molecular weight bioemulsifiers. Their structure includes carbohydrates and a long chain composed of aliphatic hydroxyl/aliphatic acids. Rhamnolipid, trehalolipid, and sophorolipid are the well-studied glycolipid bioemulsifiers. *Arthrobacter paraffineus* when grown on hydrocarbon substrates produced a trehalose lipid which was confined to the emulsion layer of the culture broths (Suzuki et al. 1969). *Rhodococcus erythropolis* is generally known to produce trehalose dimycolates (Wagner et al. 1983). It is said to have interfacial activities which could be widely applied for enhanced oil recovery (Kim et al. 1990). The trehalose lipid bioemulsifiers produced by *R. erythropolis* are mostly cell bound (Kretschmer et al. 1982). Extracellular sophoroselipids which consists of two glucose units each linked with 6` hydroxyl moieties are produced by different species of yeast. *Torulopsis bombicola* when grown on glucose and oil produced sophoroselipids which was obtained from the extracellular fluid (Itoh and Inoue 1982). Sophoroselipids are produced by *T. bombicola* ATCC 22214 when substrates such as glucose and vegetable oil were used in the medium. Because of the lower surface tension, sophorose lipids are not considered as very potent emulsifying agents (Cooper and Paddock 1983).

5.4.3.2 Rhamnolipid Bioemulsifier

The glycolipid bioemulsifier "Rhamnolipids" stands apart amongst the different categories of bioemulsifiers. *Pseudomonas* sp., produces these rhamnolipids predominantly which are classified as mono and dirhamnose containing lipids. It has been reported that *P. chlororaphis*, *P. aeruginosa, P. putida, P. plantarii,* and *P. fluorescens* are those species in this genus which produce rhamnolipids. Some of these bacteria are recognized producers of mono-rhamnolipids, while some produce both mono and di-rhamnolipids together. By the production method, the ratio of mono and di-rhamnolipids can be manipulated. The conversion of mono-rhamnolipids into di-rhamnolipids are mediated strictly by certain enzymes.

Rhamnolipid was initially discovered on 1946 (Bergström et al. 1946) and it was reported that *P. aeruginosa* when grown on glucose produced a glycolipid which was named as pyolipic acid. The production of glycolipids which contain rhamnose from *Pseudomonas aeruginosa* and the structure of rhamnolipid was elucidated (Jarvis and Johnson 1949). In general, two β-hydroxydecanoic acid groups are bound to two rhamnose groups with glycosidic linkages. When two of the β-hydroxy fatty acids are joined by ester linkages, the disaccharide portion possessed 1,3-glycosidic bonds. However, the bond between the two rhamnose groups was identified as an α-1,2-glycosidic, the linkage was predominantly ascertained by periodate oxidation and subsequent methylation (Edwards and Hayashi 1965). Thus, 2-*O*-α-1,2-*L*-rhamnopyranosyl-α-L-rhamnopyranosyl-*β*-hydroxydecanoyl-*β*-hydroxydecanoate was the chemical description given for this rhamnolipid (Fig. 5.3).

After this discovery, α-*L*-rhamnopyranosyl-*β*-hydroxydecanoyl-*β*-hydroxydecanoate, a monorhamnolipid was isolated from *P. aeruginosa* when grown on *n*-paraffin. It was also hypothesized that this monorhamnolipid is the

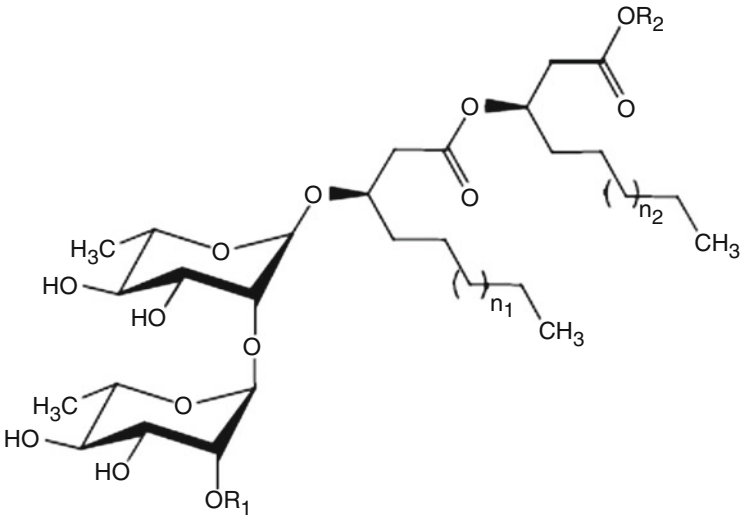


Fig. 5.3 A di-rhamnolipid from *Pseudomonas aeruginosa*

major precursor for di-rhamnolipid (Itoh et al. 1971). Two additional rhamnolipid congeners were produced by *Pseudomonas* sp. DSM 2874 when cultivated on glycerol. It was found that these two are very similar to the previously identified rhamnolipid with the difference being that it has only one β-hydroxydecanoic acid side chain (Syldatk et al. 1985). Different compositions of the rhamnolipid produced in the batch culture of *Cellulomonas cellulans* were reported by Arino et al. (1998). It was identified to be a mixture of 67% of di-rhamno-di-lipid, 22% of mono-rhamno-di-lipid and slightly lesser amounts of di-rhamno-mono-lipid (9%) and still a lesser amount of mono-rhamno-mono-lipid (3%).

In 1980s, a set of four other rhamnolipid congeners were identified. Two unusual di-lipidic rhamnolipids were produced by a *Pseudomonas* sp. when the sole carbon source used was *n*-paraffin. Acylation reaction with a 2-decenoyl group at the 2-hydroxyl moieties of the rhamnose molecules and a clear description of the congeners was also reported (Yamaguchi et al. 1978; Lang and Wagner 1987). These two congeners have been reported only by a very few teams since then. This may be an indication of their strain-specificity (Yamaguchi et al. 1978; Ishigami et al. 1987). Two novel rhamnolipids were found to methyl esters of the free carboxylic ends of two di-lipidic rhamnolipids were also identified previously. The only known nonionic rhamnolipids are these two methylated congeners (Hirayama and Kato 1982). The isolated rhamnolipids were found to include rhamnolipid homologues such as, RL1, RL2, RL3 and RL4 (Abdel-Mawgoud et al. 2010).

A clinical isolate of *P. aeruginosa* produced five new di-rhamnolipid congeners which was found to have aliphatic chains of variable lengths (C_8-C_{10}, C_{10}-C_8, C_{10}-C_{12}, C_{12}-C_{10}, and C_{10}- $C_{12:1}$) (Rendell et al. 1990). A total of 28 rhamnolipids, the di-rhamnolipid congeners which contain C_8-C_{10}, C_8-$C_{12:1}$, $C_{12:1}$-C_8, $C_{12:1}$-C_{10},

$C_{12:1}$-C_{12}, C_{10}-$C_{14:1}$, C_{12}-C_{12}, C_8, $C_{12:1}$, and C_{12} moieties, and also certain new monorhamnolipid congeners with C_8-C_8, $C_{12:1}$-C_{10}, C_8, and C_{12} moieties which was secreted by *P. aeruginosa* when nourished with mannitol or for that matter even naphthalene (Deziel et al. 1999; Deziel et al. 2000). New monorhamnolipid congeners ($C_{8:2}$ and $C_{12:2}$) which are polyunsaturated with β-hydroxy-fatty acid chains was identified from *P. aeruginosa* cultures (Abalos et al. 2001). *P. aeruginosa* (AT10) also produced the same congeners in significant amounts (Haba et al. 2003). In the cultures of *Pseudomonas chlororaphis*, a monorhamnolipid with C_{10}-$C_{14:1}$, C_{12}-$C_{12:1}$, and C_{10}-C_{14} were detected (Gunther et al. 2006). Other monosaturated di-rhamnolipid congeners were also identified (Sharma et al. 2007). *P. aeruginosa* LBI produced new monorhamnolipids containing C_8-$C_{10:1}$, C_{10}-$C_{10:1}$, and $C_{12\text{-}C12}$ chain lengths (Nitschke et al. 2010). Monorhamnolipid congeners containing $C_{14:2}$ and $C_{10:1}$-C_8 moieties were produced by a *P. aeruginosa* mutant (MIG-N146) (Guo et al. 2009).

Apart from *P. aeruginosa*, other *Pseudomonas* spp. reported to produce rhamnolipids are the following: *P. alcaligenes* (Oliveira et al. 2009), *P. cepacian* (Onbasli and Aslim 2009), *P. chlororaphis* (Gunther et al. 2006), *P. fluorescens* (Onbasli and Aslim 2009; Wilson and Bradley 1996; Vasileva-Tonkova et al. 2006; Husain 2008; Abouseoud et al. 2008), *P. luteola* (Onbasli and Aslim 2009), *P. putida* (Tuleva et al. 2002; Martinez-Toledo et al. 2006; Onbasli and Aslim 2009), *P. stutzeri* (Onbasli and Aslim 2009; Janiyani et al. 1992; Celik et al. 2008). Mono and di-rhamnolipids production in *P. clemancea*, *P. collierea,* and *P. teessidea* has been identified (Rahman et al. 2009).

5.4.3.3 Rhamnolipids from Non-Pseudomonads

Non-*Pseudomonas* sp. also has the ability to produce rhamnolipid bioemulsifiers. A rhamnolipid was isolated from *Acinetobacter calcoaceticus* (Rooney et al. 2009). Although *Pseudomonas* and *Acinetobacter* belong to different families, they come under the same Phylum: Gammaproteobacteria. Examples include *Pseudoxanthomonas* sp. (Nayak et al. 2009), *Enterobacter* sp., and *Pantoea* sp. (Vasileva-Tonkova and Gesheva 2007; Rooney et al. 2009).

The rhamnolipid synthesizing bacteria those do not come under the class Gammaproteobacteria have also been found. A new di-rhamnolipid which was produced by a *Pseudomonas glumae* was identified (Pajarron et al. 1993) and the organism was renamed thereafter as *Burkholderia glumae* (Urakami et al. 1994). Congeners with C_{14}-C_{14}, C_{12}-C_{14}, C_{14}-C_{12}, C_{14}-C_{16} and C_{16}-C_{14} have been discovered. Yet another species of *Burkholderia* that produced dirhamnolipids is *B. pseudomallei* (Haussler et al. 1998; Howe et al. 2006). Dirhamno-C_{14}-C_{14} congener and a few other rhamnolipid congeners with *β*-hydroxytetradecanoic acid: Dirhamno-C_{14} and Dirhamno-C_{14}-C_{14}-C_{14} (unpublished datum) was secreted by *Burkholderia plantarii* (Andra et al. 2006). *Burkholderia thailandensis* when cultivated on glycerol or vegetable oil and different combinations of fatty acids was found to produce new mono- and di-rhamnolipid homologues. *B. pseudomallei* produced a range of di-rhamnolipid congeners which was found to carry the same

mixtures of C_{12}, C_{14}, and C_{16} fatty acids as found in *B. thailandensis* (Dubeau et al. 2009).

Myxotyrosides, an unusual glycolipid which contains rhamnose (rhamnoside) was produced by *Myxococcus* sp. (class Deltaproteobacteria). It consists of a core structure which is tyrosine-derived. The basic skeletal structure is glycosylated and acylated with rhamnose and unusual fatty acids, respectively, such as (Z)-15-methyl-2-hexadecenoic and (Z)-2-hexadecenoic acid. Although these are not the usual rhamnolipids, the authors claim that the rhamnolipids and the similarly acylated amino acids are the only molecules related to myxotyrosides (Ohlendorf et al. 2008).

Interestingly, bacteria such as *Cellulomonas cellulans* (Arino et al. 1998), *Nocardioides* sp. (Vasileva-Tonkova and Gesheva 2005), and *Renibacterium salmoninarum* (Christova et al. 2004) which belong to a different phylum other than *Pseudomonas* have the ability to produce rhamnolipids. These bacteria come under the phylum *Acetinobacteria*. *Tetragenococcus koreensis,* belonging to the Phylum-Firmicutes. New congeners are still being reported regularly (Lee et al. 2005).

5.5 How Difficult is Hexadecane Biodegradation?

Hexadecane (which is also known as cetane) is a hydrocarbon (Chemical formula: $C_{16}H_{34}$). It contains a 16 carbon chain wherein the three hydrogen atoms form bonds with two carbon atoms at the ends and two hydrogen atoms to each of the remaining 14 carbon atoms. Pollution caused by petroleum oil and its by-products pose a widespread ecological hazard (Kumar et al. 2018). Thus, the breakdown of hydrocarbons by microorganisms, in general, bacterial groups remain as a top priority among many researchers (Cameotra and Singh 2009). Hexadecane is also one of the constituents of crude oil which is categorized as water-immiscible. To evaluate the biodegradation and bioavailability of aliphatic compounds, most importantly and to understand the metabolic pathways, hexadecane (*n*-C16) is generally used as a reference standard (Dombrowski et al. 2016). Fuels which are used in most combustion engines, such as gasoline and diesel contain more amounts of aliphatic than aromatic compounds (Chenier et al. 2003; ITRC 2014; TOXNET 2016). In hydrocarbon-polluted sites, microbial degradation has been utilized as an alternative remediation technique. Based on the biochemical and microbiological aspects of a specific site, the rate of petroleum degradation takes place (Varjani and Upasani 2017). Soil polluted by hexadecane has notably known to pose danger to the terrestrial and marine ecosystems. Production of biosurfactants is a key mechanism, a process which is greatly exploited by organisms that degrade hydrocarbons, especially bacteria to use and assimilate such substrates. In natural ecosystems, the process of biodegradation of hexadecane is much complex owing to the long duration which is mainly because of its bulk size. Generally speaking, hexadecane or for that matter any hydrocarbon is utilized by a variety of microbial process as a carbon source which results in the breakdown of higher molecular weight compounds to lesser ones during the process of biodegradation. On the basis of

Table 5.1 Bioremediation of hexadecane by marine bacteria reported from the beginning till date

S. No	Microorganisms	Studies carried out in vitro	References
1	*Acinetobacter calcoaceticus subsp. anitratus*	Ethanol precipitation; stability studies; emulsification activity; emulsifies hexadecane	Phetrong et al. (2008)
2	*Acinetobacter calcoaceticus* (BS); *Alcanivorax dieselolei* (PG 12)	Crude oil removal assay −82% and 71%; n-alkanes (C9-C25) degradation by these two organisms C16 degradation - 48% and 100%; biosurfactant production: Drop collapse, oil displacement; emulsification activity; bacterial adhesion to hydrocarbons; surface tension reduction assays; presence of alkB gene	Hassanshahian et al. (2012)
3	*Phormidium* sp	Biodisks of Phormidium sp. in 150 ml of media with hexadecane (0.3%) and diesel (0.5%); ethanol extraction; gas chromatography; emulsification index; hexadecane removal - 45%	Morales and Paniagua-Michel (2013)
4	*Bacillus amyloliquefaciens*, *Staphylococcus epidermidis*, *Micrococcus luteus*, *Nitratireductor aquimarinus*, and *Bacillus pumilus*	Hexadecane biodegradation screening; biodegradation analysis; biodegradation index above 97%	Ferrari et al. (2019)
5	*Bacillus cereus* (J3), *Staphylococcus haemolyticus* (J5) and *Pseudomonas aeruginosa* (J12)	Hemolytic activity, oil spreading, emulsification activity, surface tension measurement; crude oil removal assay −66%, 53%, and 43%; J3 degrades C9-C25 n-alkanes. In consortia, n-alkane degradation increases. Removal of 60% of n-alkanes in crude oil residues	Tanzadeh et al. (2020)

the details known from alkane oxidation, generally these reactions are enhanced by alkane mono/di-oxygenases and invariably these reactions produced the respective alcohols. Thereafter further oxidation happens with a formation of an aldehyde and its associated fatty acid by respective alcohol and aldehyde dehydrogenases. In general, primary alcohols and fatty acids of the similar chain lengths for the bacterial cultures grown on *n*-hexadecane is a clear-cut indication that there happens oxidative attack specifically at the methyl groups of such hydrocarbons.

A thorough review is being done here to understand which non-marine and marine bacterial species could utilize hexadecane as their carbon source and listed in Tables 5.1 and 5.2. From both the tables it is very clear that only a hand full of bacteria could utilize hexadecane both from marine (Phetrong et al. 2008;

Table 5.2 Bioremediation of hexadecane by non-marine bacteria reported from the beginning till date

S. No	Microorganisms	Studies carried out in vitro	Studies carried out ex-situ	Type of biosurfactants	References
1	*Flavobacterium sp.* strain MTN11 isolated from soil	Reduces surface tension; strong and stable emulsifier; solubilizing agent and enhances hexadecane mineralization		Flavolipid	Bodour et al. (2004)
2	*Pseudomonas aeruginosa* isolated from oil contaminated soil	70% hexadecane degradation		Rhamnolipid	Cameotra and Singh (2009)
3	*Acinetobacter beijerinckii* ZRS isolated from an oil-contaminatedsoil sample	Emulsification activity—diesel, hexadecane, aromatic hydrocarbons; optimization of medium for BE production; stability studies; extraction and characterization of BE	Oil spill bioremediation simulated experiment: The beach-simulating tank system; crude oil degradation—58.3%	Glycolipoprotein complex	Zhao et al. (2016)
4	*P. aeruginosa* PG1 isolated from hydrocarbon contaminated garage soil	Degradation of crude oil (and n-alkanes - C16); degrades 81.8% of total petroleum hydrocarbons (TPH); biosurfactant production, extraction, characterization; emulsification activity -emulsifies hexadecane; reduces surface tension		Rhamnolipid	Patowary et al. (2017)
5	*Bacillus* sp. L30 isolated from contaminated groundwater	Degradation of n-alkanes (C10-C27) in diesel; biosurfactant production: Drop collapse test; emulsification activity - for hexadecane 19.4 ± 1.91; presence of alkane hydroxylase alkB gene (group III)			Lima et al. (2019)

Hassanshahian et al. 2012; Morales and Paniagua-Michel 2013; Ferrari et al. 2019; Tanzadeh et al. 2020) and non-marine sources (Bodour et al. 2004; Cameotra and Singh 2009; Zhao et al. 2016; Patowary et al. 2017; Lima et al. 2019) and almost all the works are limited to in vitro experiments only. Among the bacterial groups only *Bacillus, Pseudomonas* and *Acinetobacter* could effectively utilize hexadecane. The mostly stated biosurfactant types are rhamnolipids followed by a lipoprotein and a flavolipid. In the following section works from our laboratory with respect to screening of hexadecane consumers and the potent bioemulsifiers produced are discussed.

5.6 Works from Our Laboratory

5.6.1 Isolation and Evaluation of Bacteria for Bioemulsifier Production

While in the previous section an extensive review has been made emphasizing the role of the genus: *Pseudomonas* and its species in producing biosurfactants and utilization of aliphatic hydrocarbons, this section will focus on a particular species, *guguanensis*. A wide range of sampling sites were chosen and microbiological screening was huge isolation programme was conducted at six different locations in the Indian coast, particularly in the Southeast border: 1. Tuticorin, 2. Olaikuda boat jetty, 3. Fishing boat jetty at Gulf of Mannar and three points of Chennai harbor, ie., 4. Signal station, 5. Container and 6. Sailing regions. The first three sites are designated as "highly biodiversified areas" under the Gulf of Mannar Biosphere Reserve. Hence it can always be hypothesized that bacterial species prevalent in these areas to be highly competent owing to the rich biodiversity. Three types of media: Minimal Salt medium, Bushnell and Haas Medium, and ZoBell Marine Medium were used for isolation process. Different hydrocarbons like, crude oil, tributyrin, diesel, and *n*-hexadecane were supplemented to the aforementioned media for recovery of maximum isolates as shown in Fig. 5.4. More than 849 bacterial isolates were isolated and all of them were put to rigorous screening for hydrocarbon utilizing capacities by employing assays, such as hydrocarbon dispersion (Morikawa et al. 1993) and Emulsification Index$_{24}$ [EI_{24}] (Cooper and Goldenberg 1987). As a preliminary check, the expended medium of the bacterial isolates alone were used for these assays. Both oil spread and emulsification assays showed only 0.0023% of the total isolates to be positive, i.e., only two isolates. They were identified as *Pseudomonas aeruginosa* and *Pseudomonas guguanensis.* Since there are numerous reports to quote the oil degrading properties of *P. aeruginosa,* the latter was chosen to mention in detail in this section.

The identity of *P. guguanensis* was established by 16S rRNA gene sequencing and the blast sequences were submitted to GenBank with the accession number: KU302611]. The results of the *e*mulsification activities on the different types of hydrocarbons by the spent broths of *P. guguanensis* are illustrated as Fig. 5.5. In a large-scale cultivation of this potent bacterium in a 40 L fermentation vessel, it was

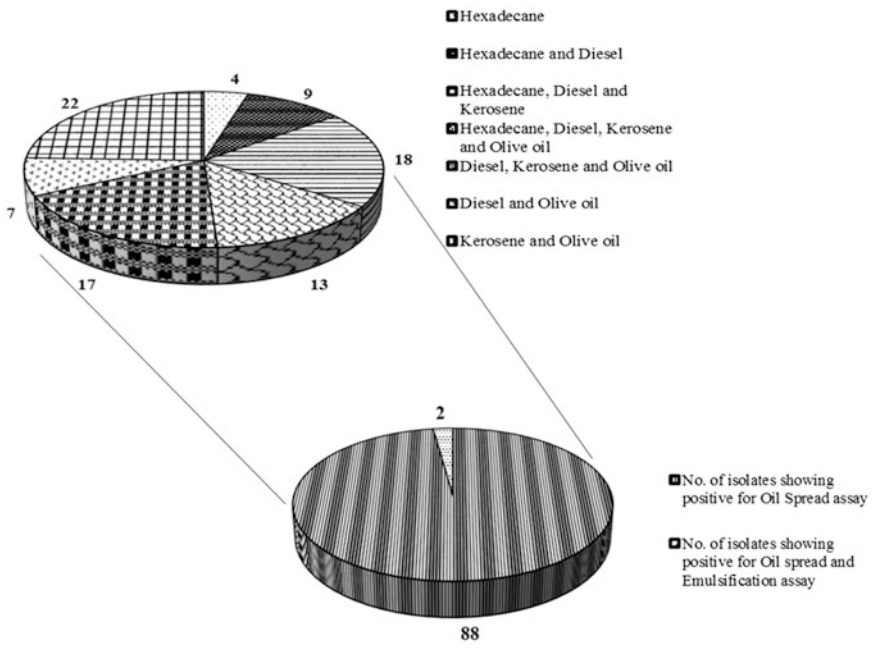


Fig. 5.4 Bacterial population [90 amongst 849 isolates] possessing oil spreading [up] and oil emulsifying (2.2% of oil spreaders) [down] abilities

found that the yield of the bioemulsfier was only 2 g and that too at day 7. The emulsifier was categorized as a rhamnolipid that possessed three compounds, i.e., a rhamnose sugar and two aliphatic hydrocarbon chains. The molecular weight of this compound was higher than 1000 Da (close to 1250 Da) and hence it is better named emulsifier and not as surfactant. The following section will give information on the chemical and biological properties of this bioemulsifier.

5.6.2 Chemical Properties of the Bioemulsifier from *P. guguanensis*

The emulsifier was identified as an unusual mono-rhamnolipid which is composed of three compounds: The combination of all the three molecules synergistically possessed emulsification activity. In contrast, the individual or combination of two compounds not showed the emulsion activity. The chemical structures of compounds 1–3 are given as Fig. 5.6.

The compound 1 appeared as dark yellowish waxy oil and isolated in 24 mg. The FT-IR analysis of compound 1 indicated the intramolecularly bound alcoholic hydroxyl (-OH) groups, C-H stretching vibration from long alkyl chains and also the presence of aliphatic ester carbonyl and C-O stretching vibration. The structure of palmitic acid-glycerol ester has been identified with the support of fragmentation pattern of mass spectrum obtained from GC-MS. In addition, ^{1}H and ^{13}C NMR

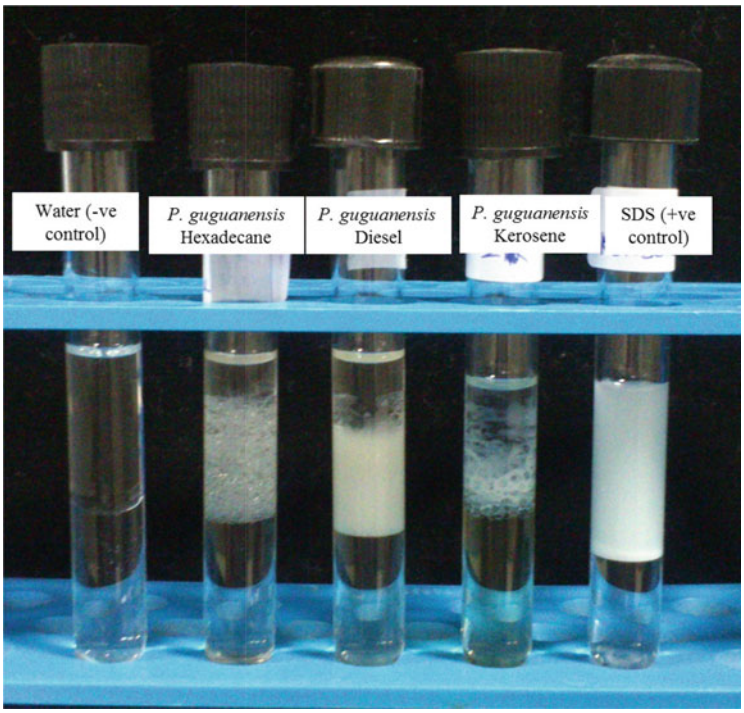
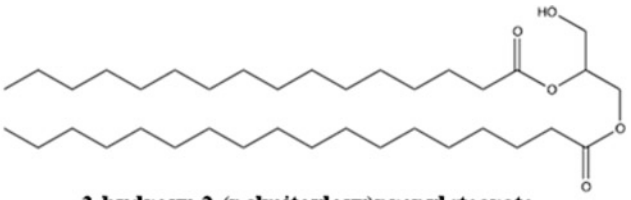


Fig. 5.5 Bioemulsifier containing expended media [≈1 OD at Abs660] of *P. guguanensis* emulsify different types of hydrocarbons

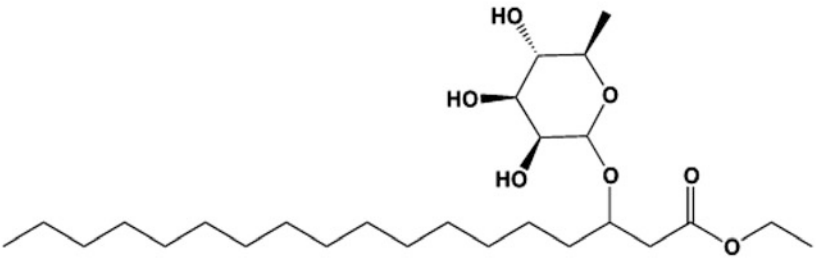
studies confirmed the presence of long hydrocarbon chain of fatty acid, ester group as well as glycerol ester groups in the compound 1. Hence, compound 1 is named as 3 hydroxy-2-(palmitoyloxy) propyl stearate with a molecular formula $C_{37}H_{72}O_5$ and molecular weight of 596.96 g. mol^{-1}.

Compound 2 was isolated as yellow oily shiny soft crystalline semi-solid and the yield was found to be 41 mg. In FT-IR spectrum, the presence of broad peaks in 3500–3000 cm^{-1} range revealed hydrogen bonding of the alcoholic groups present in Rhamnose sugar. The study revealed the presence of alkyl chain C-H vibration and ester carbonyl groups from the respective FT-IR peaks. Further, the structure of compound 2 is ascertained to be a rhamnose sugar attached with 3-hydroxy hexadecanoic acid ethyl ester. Further, the study also revealed rhamnose sugar connected to hydroxy group of hexadecanoic acid. The carbon skeleton of Compound 2 contained an ester carbonyl, hydroxy carbon and C=O was confirmed by 13C NMR while the presence of fatty acid and rhamnose sugar was confirmed using ^{1}H NMR. Based on the spectral studies, compound 2 was confirmed to be a ethyl ester of 3-((Rhamnosyl)-2-oxy)octadecanoate.

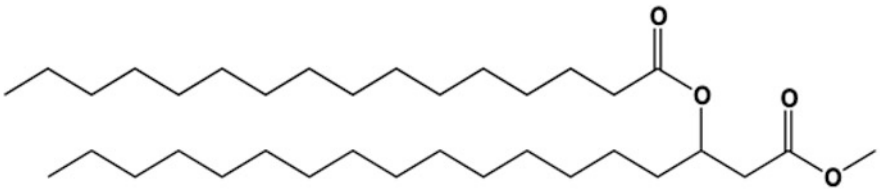
Compound 3 was purified as an oily substance with dark yellowish-brown color weighing 8 mg. The compound was subjected to FT-IR study which showed the



3-hydroxy-2-(palmitoyloxy)propyl stearate
Chemical Formula: $C_{37}H_{72}O_5$
Molecular Weight: 596.96
m/z: 596.54 (100.0%), 597.54 (41.0%), 598.54 (8.8%), 599.55 (1.5%)



ethyl 3-(((3*S*,4*S*,5*S*,6*R*)-3,4,5-trihydroxy-6-methyltetrahydro-2*H*-pyran-2-yl)oxy)octadecanoate
Chemical Formula: $C_{26}H_{50}O_7$
Exact Mass: 474.36
Molecular Weight: 474.67



Methyl 3-(palmitoyloxy)octadecanoate
Chemical Formula: $C_{35}H_{68}O_4$
Exact Mass: 552.51
Molecular Weight: 552.91

Fig. 5.6 Structural details of compounds 1, 2 and 3 of the rhamnolipids of *P. guguanensis*

presence of alcoholic hydroxyl groups, alkyl chain and ester carbonyl functional groups. Mass fragmentation pattern confirmed the presence of palmitic acid and α-hydroxy palmitic acid. Additionally, the confirmation of fatty acid chain, ester group, and other alkyl chains connected alcoholic group of palmitic acid was obtained using ^{1}H NMR and ^{13}C NMR. Thus compound 3 was identified to be a methyl 3-(palmitoyloxy) octadecanoate.

5.6.3 Biological Properties of the Bioemulsifier

Among the hydrocarbons, n-hexadecane preferentially emulsified by the extracellularly secreted monorhamnolipids with Emulsification Index (EI_{24}): 56 ± 1.42% using 2 mL of the used medium. The ethyl acetate partitioned extract possessed an EI_{24} value of about 65%, while the purified rhamnolipid product showed 78% and the concentration of the samples used were 12.5 mg/mL concentration. It is interesting to observe that individual or combination of any two components not showed any emulsifying activity on n-hexadecane in water but mixture of all the three components showed emulsifying activity.

Surface-active property of the isolated mono-rhamnolipid from *P. guguanensis*, the reference compound (*n*-hexadecane) (to which it showed maximum emulsification), control (water) and reference control (SDS) were all estimated by GBX 3S tensiometer [Dublin, Ireland] by employing Wilhelmy plate technique (Wilhelmy 1863). Water as well as the used up broth had surface tension of 70–72 mN/m, whereas the purified mono-rhamnolipids of *P. guguanensis* was at 32.98 ± 0.3 mN/m, indicating better surface-active property.

Scanning Electron Micrographs of the bacterial cultures revealed an increasing pattern of extracellular secretion of mono-rhamnolipids that reached maximum on the sixth day (as observed in Fig. 5.7) of the investigation period. When the bioprocess parameters for obtaining maximal emulsification efficiencies were standardized, the sixth day yet again showed maximum results which is concordant with the SEM results. There was a striking difference between the amount of *n*-hexadecane present in the uninoculated and inoculated culture tubes at the end of the experimentation period as seen by the peak area obtained from GC-MS analysis (data not shown). We were able to observe a 77.2% removal of hexadecane and degradation of C_{10}-C_{18} fatty acids as compared with library of references, preloaded in the software. These fragments overlap with the components of the monorhamnolipids produced by this bacterium which suggest that these fragments may be used in the production of rhamnolipids and this idea is discussed below.

5.6.4 Biosynthesis of Rhamnolipids of *P. guguanensis* as Compared with *P. aeruginosa*

Hexadecane is opted as a reference substrate to investigate crude oil degradation and diesel (Schoefs et al. 2004). Based on the analytical results, we recommend the possible pathway on synthesizing mechanism of the reported three compounds present in *P. guguanensis,* which together worked as an emulsifier. We have arrived at a biosynthetic pathway for the production of this emulsifier based on the spectral and chromatographic on the substrate and the products formed (as given in Fig. 5.8). We have observed that the degradation begins with conversion of the methyl group of n-hexadecane to give hexadecan-1-ol as reported in *Pseudomonas aeruginosa* previously (Meng et al. 2017; Nie et al. 2017). Further, the hexadecan-1-ol is oxidized to palmitic acid, which supported by other reports (Meng et al. 2017;

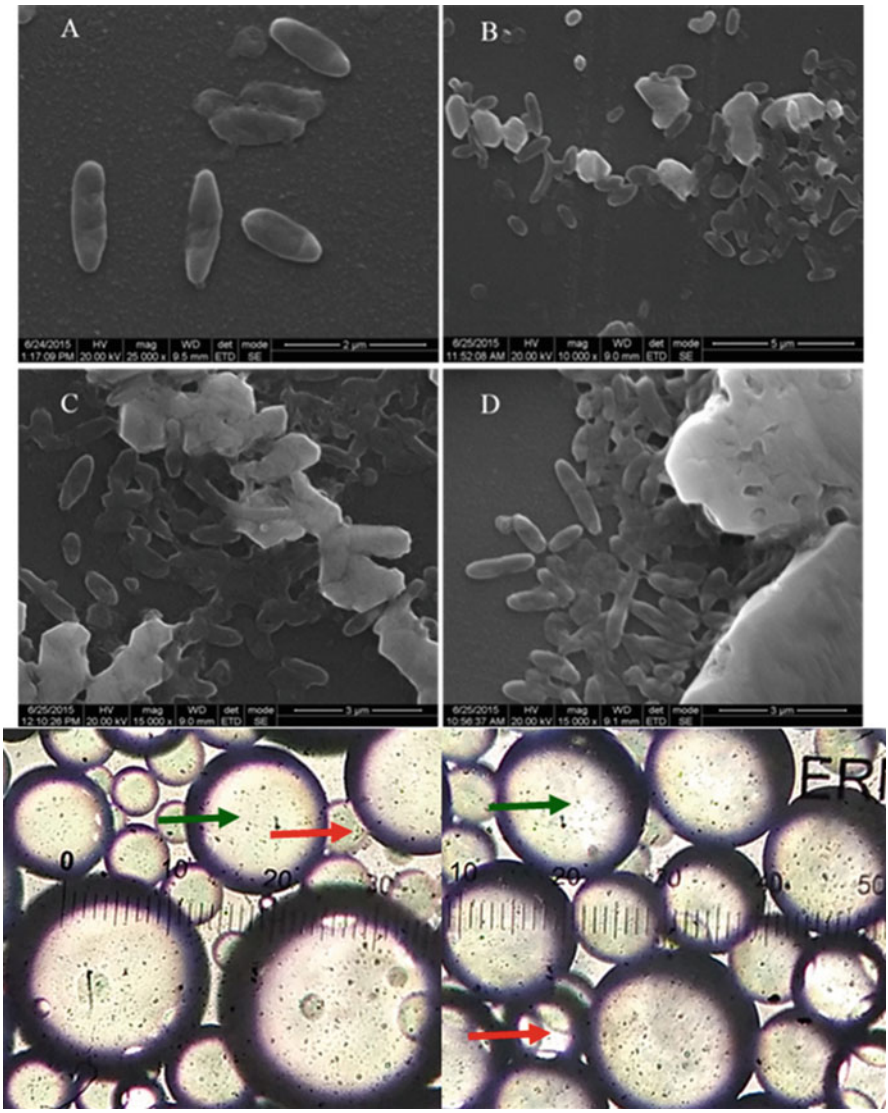


Fig. 5.7 Oiled cultures of *P. guguanensis* showing extracellular secretion of monorhamnolipids on the 2nd [B], 4th [C], and 6th day [D] of the experimental trials as against unprovoked controls [A] given as Scanning Electron Micrographs (SEMs). Micrographs of water-hexadecane emulsions formed by mono-rhamnolipids (left) and SDS (right) both at 5 mg/mL concentration as exactly viewed in 10X magnification in an optical Nikon Eclipse 200 binoculars (green and red arrows indicate water and hexadecane droplets, respectively)

Zhu and Rock 2008). Oxidative transformations promoted by alkane hydroxylase and hexdecan-1-ol dehydrogenase usually occur in the extracellular region to aid the uptake of the available carbon by the bacterial consortium. The palmitic acid

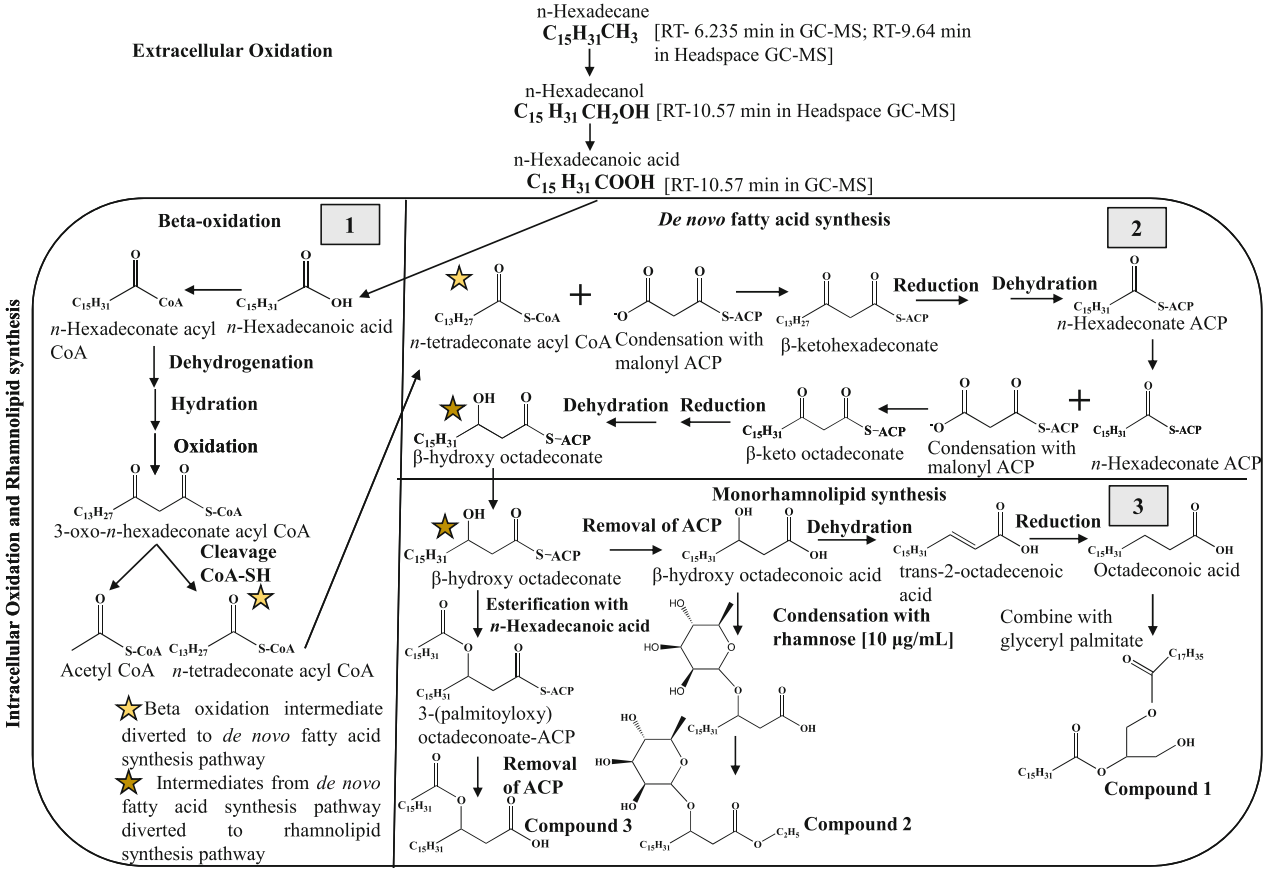


Fig. 5.8 Proposed de novo synthetic pathway of monorhamnolipids in *Pseudomonas guguanensis*

transported through the bacterial membranes inward the cell to form a conjugate with coenzyme A (CoA). A study using isotope tracing method and assays of gene expression reported that *n*-tetradeconate acyl CoA undergoes fatty acid synthesis de novo that led to the production of rhamnolipid precursors (Yuan et al. 2012), which was catalyzed by β-ketoacyl ACP synthase (Zhang et al. 2012). Further, the reduction of the keto group to alcoholic group formed 3-hydroxystearic acid and subsequent elimination of water to form trans-2-hexadecenoyl ACP. Similar cycle has been repeated to form β-hydroxyoctadeconate. The precursors obtained for the biosynthesis of compounds, 1, 2, and 3 obtained from three different routes to attribute a synergistic role to the bioemulsifer are proposed herein.

De-esterification of β-hydroxyoctadeconate led to β-hydroxyoctadeconoic acid (HAA) followed by the removal of water to give trans-2-octadecenoic acid and conversion to stearic acid is by hydrogenation reactions. Thus, compound 1 can be formed by esterification of octadecanoic acid with glyceryl palmitate. The mechanism of compound 2 formation followed the condensation of β-hydroxyoctadeconoic acid with a rhamnose sugar containing octadecenoate. Further, it may be also possible that due to the presence of hydroxyl group in β-hydroxy octadeconate, formation of 3-(palmitoyloxy) octadecenoate (compound 3) is achieved because of the availability of free fatty acids in the cell, followed by the removal of ACP. Based on our studies, the most plausible synthetic route for the bioemulsifiers is thus proposed.

5.7 Conclusion

Generally, it is believed that only a narrow niche of bacterial species produce biosurfactants because of a few reasons: 1. It is hard to utilize bulk hydrocarbons as they do not diffuse easily through the cell walls. 2. Production of biosurfactants is a cumbersome and energy expending in principle. Both these factors put together during a hydrocarbon stress, give the organisms all the more difficulty to get evolved and be fit enough to express those genes that are particularly involved in the biosynthetic pathway of biosurfactants. Moreover, biosurfactants are produced in minimal amounts and released out of the cell in a time and concentration-dependent manner and hence large-scale cultivation of biosurfactant producers depend on a lot of factors, including temperature, pH, salinity, nutrients supplied, and many other culture conditions. However, permutation studies involving computerized reactions using a variety of software for the purpose, most importantly, Response Surface Methodology (RSM), can certainly increase the yield of biosurfactants. *P. guguanensis* listed in this section was permuted for various bioprocess factors like carbon and nitrogen sources, pH, and time courses, all of which were validated using RSM tools. When the results obtained from the permutation experiments were used as the base for fixing the conditions for cultivation and growth of the bacterium under laboratory conditions, close to a three-fold more rhamnolipid production was reported by the authors. Despite the small amounts of production of biosurfactants in nature, certainly these amphiphilic molecules are considered as better choices than

chemical dispersants. The price of a 10 g quantity of any rhamnolipid (90% purity) is around Rs. 10,000/− and there is a huge market for the same. Hence let us look forward to biological means of hydrocarbon degradation by way of relying on microorganisms, especially bacterial systems, which offers a steadfast and a safe way to bioremediation.

Permissions Sought

Figures 5.4 and 5.7 are reproduced fully from Ramya Devi et al. (2018) and Figs. 5.5, 5.6, and 5.8 are reproduced completely from Ramya Devi et al. (2019). Respective permissions were sought from the authors/publishers.

References

Abalos A, Pinazo A, Infante MR, Casals M, Garcia F, Manresa A (2001) Physicochemical and antimicrobial properties of new rhamnolipids produced by *Pseudomonas aeruginosa* AT10 from soybean oil refinery wastes. Langmuir 17:1367–1371

Abdel-Mawgoud AM, Lépine F, Déziel E (2010) Rhamnolipids: diversity of structures, microbial origins and roles. Appl Microbiol Biotechnol 86:1323–1336

Abouseoud M, Maachi R, Amrane A, Boudergua S, Nabi A (2008) Evaluation of different carbon and nitrogen sources in production of biosurfactant by *Pseudomonas fluorescens*. Desalination 223(1–3):143–151

Abraham WR, Meyer H, Yakimov M (1998) Novel glycine containing glucolipids from the alkane using bacterium *Alcanivorax borkumensis*. Biochim Biophys Acta 1393:57–62

Andrä J, Rademann J, Howe J, Koch MHJ, Heine H, Zähringer U, Brandenburg K (2006) Endotoxin-like properties of a rhamnolipid exotoxin from *Burkholderia* (*Pseudomonas*) *plantarii*: immune cell stimulation and biophysical characterization. Biol Chem 387:301–310

Arino S, Marchal R, Vandecasteele JP (1998) Production of new extracellular glycolipids by a strain of *Cellulomonas cellulans* (*Oerskovia xanthineolytica*) and their structural characterization. Can J Microbiol 44:238–243

Arutchelvi J, Bhaduri S, Uppara PV, Doble M (2009) Production and characterization of biosurfactant from *Bacillus subtilis* YB7. J Appl Sci 9(17):3151–3155

Arutchelvi J, Doble M (2010) Characterization of glycolipid biosurfactant from *Pseudomonas aeruginosa* CPCL isolated from petroleum-contaminated soil. Lett Appl Microbiol 51(1):75–82

Batista SB, Mounteer AH, Amorim FR, Totola MR (2006) Isolation and characterization of biosurfactant/bioemulsifier producing bacteria from petroleum contaminated sites. Bioresour Technol 97:868–875

BBC News (2020) Russian Arctic oil spill pollutes big lake. https://www.bbc.com/news/world-europe-52977740

Bergström S, Theorell H, Davide H (1946) Pyolipic acid. A metabolic product of *Pseudomonas pyocyanea* active against *Mycobacterium tuberculosis*. Arch Biochem Biophys 10:165–166

Bodour AA, Guerrero-Barajas C, Jiorle BV, Malcomson ME, Paull AK, Somogyi A, Trinh LN, Bates RB, Maier RM (2004) Structure and characterization of flavolipids, a novel class of biosurfactants produced by *Flavobacterium* sp. strain MTN11. Appl Environ Microbiol 70 (1):114–120

Bonilla M, Olivaro C, Corona M, Vazquez A, Soubes M (2005) Production and characterization of a new bioemulsifier from *Pseudomonas putida* ML2. J Appl Microbiol 98:456–463

Briggs IL, Briggs BC (2018) Petroleum industry activities and human health. In: Ndimele PE (ed) The political ecology of oil and gas activities in the Nigerian aquatic ecosystem. Academic Press, Cambridge, MA, pp 143–147. https://doi.org/10.1016/b978-0-12-809399-3.00010-0

Cameotra SS, Singh P (2009) Synthesis of rhamnolipid biosurfactant and mode of hexadecane uptake by Pseudomonas species. Microb Cell Factories 8:16

Celik GY, Aslim B, Beyatli Y (2008) Enhanced crude oil biodegradation and rhamnolipid production by *Pseudomonas stutzeri* strain G11 in the presence of Tween-80 and triton X-100. J Environ Biol 29:867–870

Chénier MR, Beaumier D, Roy R, Driscoll BT, Lawrence JR, Charles WG (2003) Impact of seasonal variations and nutrient inputs on nitrogen cycling and degradation of hexadecane by replicated river biofilms. Appl Environ Microbiol 69:5170–5177

Christova N, Tuleva B, Lalchev Z, Jordanova A, Jordanov B (2004) Rhamnolipid biosurfactants produced by *Renibacterium salmoninarum* 27BN during growth on n-hexadecane. Z Nat CJ Biosci 59:70–74

Cooper DG, Goldenberg BG (1987) Surface-active agents from two *Bacillus* species. Appl Environ Microbiol 53(2):224–249

Cooper DG, Paddock DA (1983) *Torulopsis petrophilum* and surface activity. Appl Environ Microbiol 46(6):1426–1429

Desai JD, Banat IM (1997) Microbial production of surfactant and their commercial potential. Microbial Mol Bio Rev 61:47–64

Déziel E, Lepine F, Dennie D, Boismenu D, Mamer OA, Villemur R (1999) Liquid chromatography/mass spectrometry analysis of mixtures of rhamnolipids produced by *Pseudomonas aeruginosa* strain 57RP grown on mannitol or naphthalene. Biochim Biophys Acta 1440:244–252

Déziel E, Lépine F, Milot S, Villemur R (2000) Mass spectrometry monitoring of rhamnolipids from a growing culture of *Pseudomonas aeruginosa* strain 57RP. Biochim Biophys Acta 1485:145–152

Dicks B (1998) The Environmental Impact of Marine Oil Spills- Effects, Recovery and Compensation. International Seminar on Tanker Safety, Pollution, Spill Response and Compensation. Rio de Janeiro, Brasil, 6th November, 1998

Dombrowski N, Donaho JA, Gutierrez T, Seitz KW, Teske AP, Baker BJ (2016) Reconstructing metabolic pathways of hydrocarbon-degrading bacteria from the Deepwater horizon oil spill. Nat Microbiol 1:16057

Dubeau D, Déziel E, Woods D, Lépine F (2009) *Burkholderia thailandensis* harbors two identical *rhl* gene clusters responsible for the biosynthesis of rhamnolipids. BMC Microbiol 9:263–275

Edwards JR, Hayashi JA (1965) Structure of a rhamnolipid from *Pseudomonas aeruginosa*. Arch Biochem Biophys 111:415–421

Ferrari VB, Cesar A, Cayô R et al (2019) Hexadecane biodegradation of high efficiency by bacterial isolates from Santos Basin sediments. Mar Pollut Bull 142:309–314

Floodgate D (1978) The formation of oil emulsifying agents in hydrocarbonclastic bacteria. In: Loutit MW, Miles JAR (eds) Microbial Ecology. Springer-Verlag, New York, pp 82–85

Gunther NW, Nunez A, Fett W, Solaiman DKY (2005) Production of rhamnolipids by *Pseudomonas chlororaphis*, a nonpathogenic bacterium. Appl Environ Microbiol 71:2288–2293

Gunther NW, Nunez A, Fortis L, Solaiman DKY (2006) Proteomic based investigation of rhamnolipid production by *Pseudomonas chlororaphis* strain NRRL B-30761. J Ind Microbiol Biotech 33:914–920

Guo YP, Hu YY, Gu RR, Lin H (2009) Characterization and micellization of rhamnolipidic fractions and crude extracts produced by *Pseudomonas aeruginosa* mutant MIG-N146. J Colloid Interface 331(2):356–363

Haba E, Abalos A, Jauregui O, Espuny MJ, Manresa A (2003) Use of liquid chromatography-mass spectroscopy for studying the composition and properties of rhamnolipids produced by different strains of *Pseudomonas aeruginosa*. J Surfactant Deterg 6:155–161

Haleem AED (2003) *Acinetobacter:* environmental and biotechnological applications. Afr J Biotechnol 2:71–74

Hassanshahian M, Emtiazi G, Cappello S (2012) Isolation and characterization of crude-oil-degrading bacteria from the Persian Gulf and the Caspian Sea. Mar Poll Bull 64(1):7–12

Häussler S, Nimtz M, Domke T, Wray V, Steinmetz I (1998) Purification and characterization of a cytotoxic exolipid of *Burkholderia pseudomallei*. Infect Immun 66:1588–1593

Hirayama T, Kato I (1982) Novel methyl rhamnolipids from *Pseudomonas aeruginosa*. FEBS Lett 139:81–85

Howe J, Bauer J, Andra J, Schromm AB, Ernst M, Rossle M, Zahringer U, Rademann J, Brandenburg K (2006) Biophysical characterization of synthetic rhamnolipids. FEBS J 273:5101–5112

Husain S (2008) Effect of surfactants on pyrene degradation by *Pseudomonas fluorescens* 29L. World J Microbiol Biotechnol 24:2411–2419

Ishigami Y, Gama Y, Yamaguchi M, Nakahara H, Kamata T (1987) Surface active properties of rhamnolipids as microbial biosurfactants. J Jpn Oil Chem Soc 36:791–796

Itoh S, Honda H, Tomita F, Suzuki T (1971) Rhamnolipids produced by *Pseudomonas aeruginosa* grown on *n*-paraffin (mixture of C12, C13 and C14 fractions). J Antibiot 24:855–859

Itoh S, Inoue S (1982) Sophorolipids from *Torulopsis bombicola* as microbial surfactants in alkane fermentations. Appl Enviro Microbiol 43:1278–1283

ITOPF (2011a) Effects of oil pollution on the marine environment. Technical information paper 13. International Tanker Owners Pollution Federation Limited

ITOPF (2011b) Use of booms in oil pollution response. Technical information paper 3. International Tanker Owners Pollution Federation Limited

ITOPF (2011c) Use of dispersants to treat oil spills. Technical information paper 4. International Tanker Owners Pollution Federation Limited

ITOPF (2012) Use of sorbent materials in oil spill response. Technical information paper 8. International Tanker Owners Pollution Federation Limited

ITRC (2014) Interstate technology and regulatory council

Janiyani KL, Wate SR, Joshi SR (1992) Surfactant production by *Pseudomonas stutzeri*. J. Microb Biotechnol 7:18–21

Jarvis FG, Johnson MJ (1949) A glyco-lipid produced by *Pseudomonas aeruginosa*. J Am Chem Soc 71:4124–4126

Kim JS, Powalla M, Lang S, Wagner F, Lunsdorf H, Wray V (1990) Microbial glycolipid production under nitrogen limitation and resting cell conditions. J Biotechnol 13:257–266

Kingston PF (2002) Long-term environmental impact of oil spills. Spill Sci. Technol B 7 (1–2):53–61

Kiran GS, Anto Thomas T, Selvin J, Sabarathnam B, Lipton AP (2010) Optimization and characterization of a new lipopeptide biosurfactant produced by marine *Brevibacterium aureum* MSA13 in solid state culture. Bioresour Technol 101:2389–2396

Kretschmer A, Bock H, Wagner F (1982) Chemical and physical characterization of interfacial-active lipids from *Rhodococcus erythropolis* grown on *n*-alkanes. Appl Environ Microbiol 44 (4):864–870

Kumar V, Kumar M, Prasad R (2018) Microbial action on hydrocarbons. Springer, Singapore

Lang S, Wagner F (1987) Structures and properties of biosurfactants. In: Kosaric N, Cairns WL, Gray NCC (eds) Biosurfactants and biotechnology. Marcel Dekker, New York, pp 21–45

Lee M, Kim MK, Vancanneyt M, Swings J, Kim SH, Kang MS, Lee ST (2005) *Tetragenococcus koreensis* sp. nov., a novel rhamnolipid producing bacterium. Int J Syst Evol Microbiol 55:1409–1413

Lima SD, Oliveira AF, Golin R, Lopes VCP, Caixeta DS, Lima ZM, Morais EB (2019) Isolation and characterization of hydrocarbon-degrading bacteria from gas station leaking-contaminated groundwater in the southern Amazon, Brazil. Brazilian J Biol 80(2):354–361. https://doi.org/10.1590/1519-6984.208611

Maneerat S, Bamba T, Harada K, Kobayashi A, Yamada H, Kawai F (2006) A novel crude oil emulsifier excreted in the culture supernatant of a marine bacterium, *Myroides* sp strain SM1. Appl Microbiol Biotechnol 70:254–259

Maneerat S, Dikit P (2007) Characterization of cell-associated bioemulsifier from *Myroides* sp. SM1, a marine bacterium. Songklanakarin J Sci Technol 29(3):769–779

Margesin R, Schinner F (2001) Bioremediation (natural attenuation and biostimulation) of diesel-oil-contaminated soil in an alpine glacier skiing area. Appl Environ Microbiol 67(7):3127–3133
Martinez-Toledo A, Rios-Leal E, Vazquez-Duhalt R, Gonzalez-Chavez Mdel C, Esparza-Garcia JF, Rodriguez-Vazquez R (2006) Role of phenanthrene in rhamnolipid production by *P. putida* in different media. Environ Technol 27:137–142
Mayank J. (2019) Types of oil pollution. https://sciencing.com/types-oil-pollution-8084758.html
Meng L, Li H, Bao M, Sun P (2017) Metabolic pathway for a new strain *Pseudomonas synxantha* LSH-7′: from chemotaxis to uptake of n-hexadecane. Sci Rep 7:39068
Morais CM, Ramos SAF, Pimentel MCB, Morais MA Jr, Lima Filho JL (2003) Production of an extracellular polysaccharide with emulsifier properties by *Penicillium citrinum*. World J Microbiol Biotechnol 19:191–194
Morales AR, Paniagua-Michel J (2013) Bioremediation of hexadecane and diesel oil is enhanced by Photosynthetically produced marine biosurfactants. J Bioremed Biodegr S4:005
Morikawa M, Daido H, Takao T (1993) A new lipopeptide biosurfactant produced by *Arthrobacter* sp. strain MIS38. J Bacteriol 175:6459–6466
National Oceanic and Atmospheric Administration (NOAA) (2019a) How do spills happen? office of response and restoration. https://response.restoration.noaa.gov/training-and-education/education-students-and-teachers/how-do-spills-happen.html Accessed 05 Feb 2019
National Oceanic and Atmospheric Administration (NOAA) (2019b) In situ burning. Office of response and restoration. https://response.restoration.noaa.gov/oil-and-chemical-spills/oil-spills/resources/in-situ-burning.html. Accessed 08 Feb 2019
National Oceanic and Atmospheric Administration (NOAA) (2019c) Spill containment methods. Office of response and restoration. https://response.restoration.noaa.gov/oil-and-chemical-spills/oil-spills/spill-containment-methods.html. Accessed 24 April 2019
National Oceanic and Atmospheric Administration (NOAA) (2020) How does oil impact marine life? National Ocean Service website. https://oceanservice.noaa.gov/facts/oilimpacts.html. Accessed 03 Nov 2020
National Research Council (2013) Oil Spill Response Technologies. In: An ecosystem services approach to assessing the impacts of the deepwater horizon oil spill in the Gulf of Mexico. The National Academies Press, Washington, DC. https://doi.org/10.17226/18387
Nayak AS, Vijaykumar MH, Karegoudar TB (2009) Characterization of biosurfactant produced by *Pseudoxanthomonas* sp PNK-04 and its application in bioremediation. Int Biodeterior Biodegrad 63:73–79
Nie H, Nie M, Xiao T, Wang Y, Tian X (2017) Hexadecane degradation of *Pseudomonas aeruginosa* NY3 promoted by glutaric acid. Sci Total Environ 575:1423–1428
Nitschke M, Costa S, Contiero J (2010) Structure and applications of a rhamnolipid surfactant produced in soybean oil waste. Appl Biochem Biotechnol 160(7):8707–8708
Noriyuki I, Sunairi M, Urai M, Itoh C, Anzai H, Nakajima M, Harayama S (2002) Extracellular polysaccharides of *Rhodococcus rhodochrous* S-2 stimulate the degradation of aromatic components in crude oil by indigenous marine Bacteria. Appl Environ Microbiol 68 (5):2337–2343
Ohlendorf B, Lorenzen W, Kehraus S, Krick A, Bode HB, König GM (2008) Myxotyrosides A and B, unusual rhamnosides from *Myxococcus* sp. J Nat Products 72:82–86
Oliveira FJS, Vazquez L, de Campos NP, de Franca FP (2009) Production of rhamnolipids by a *Pseudomonas alcaligenes* strain. Process Biochem 44:383–389
Olivera NL, Commendatore MG, Delgado O, Esteves JL (2003) Microbial characterization and hydrocarbon biodegradation potential of natural bilge waste microflora. J Ind Microbiol Biotechnol 30(9):542–548
Onbasli D, Aslim B (2009) Biosurfactant production in sugar beet molasses by some *Pseudomonas* spp. J Environ Biol 30(1):161–163
Pajarron AM, Dekoster CG, Heerma W, Schmidt M, Haverkamp J (1993) Structure identification of natural rhamnolipid mixtures by fast-atom-bombardment tandem mass-spectrometry. Glycoconj J 10:219–226

Patel MN, Gopinanthan KP (1986) Lysozyme sensitive bioemulsifier for immiscible organophosphorus pesticides. Appl Environ Microbiol 52:1224–1226

Patil JR, Chopade BA (2004) Bioemulsifier production by Acinetobacter strain isolated from healthy human skin. US Patent 20,040,138,429 (to CSIR India), 15 July 2004

Patowary K, Patowary R, Kalita MC, Deka S (2017) Characterization of biosurfactant produced during degradation of hydrocarbons using crude oil as sole source of carbon. Front Microbiol 8:279

Perfumo A, Smyth TJP, Marchant R, Banat IM (2009) Production and roles of biosurfactants and bioemulsifiers in accessing hydrophobic substrates. In: Timmis Kenneth N (ed) Microbiology of hydrocarbons, oils, lipids and derived compounds. Springer, Berlin, pp 1502–1512

Phetrong K, H-kittikun A, Maneerat S (2008) Production and characterization of bioemulsifier from a marine bacterium, *Acinetobacter calcoaceticus* subsp. *anitratus* SM7. Songklanakarin J Sci Technol 30(3):297–305

Poremba K, Gunkel W, Lang S, Wagner F (1991) Marine biosurfactants, III. Toxicity testing with marine microorganisms and comparison with synthetic surfactants. Z Nat 46:210–216

Rahman P, Lungut A, Idowu J, Olea M (2009) Biosurfactant production using novel bacteria from Northeast England. In: Building business on bioscience sustainable innovation conference. Heriot-Watt University, Edinburgh

Ramya Devi KC, Lakshmi Sundaram R, Asha D, Sivamuruga V, Vasudevan V, Gnanambal Krishnan ME (2018) Demonstration of bioprocess factors optimization for enhanced mono-rhamnolipid production by a marine *Pseudomonas guguanensis*. Int J Biol Macromol 108:531–540

Ramya Devi KC, Lakshmi Sundaram R, Sivamurugan V, Vasudevan V, Gnanambal Krishnan ME (2019) Structure elucidation and proposed *de novo* synthesis of an unusual mono-rhamnolipid by *Pseudomonas guguanensis* from Chennai Port area. Sci Rep 9:5992

Rendell NB, Taylor GW, Somerville M, Todd H, Wilson R, Cole PJ (1990) Characterization of *Pseudomonas* Rhamnolipids. Biochim Biophys Acta 1045:189–193

Rooney AP, Price NP, Ray KJ, Kuo TM (2009) Isolation and characterization of rhamnolipid-producing bacterial strains from a biodiesel facility. FEMS Microbiol Lett 295:82–87

Rosenberg E, Ron EZ (1997) Bioemulsan: microbial polymeric emulsifiers. Curr Opinion Biotechnol 8:313–316

Safe Drinking Water Foundation (2017) Oil spills. https://www.safewater.org/fact-sheets-1/2017/1/23/oil-spills

Schoefs O, Perrier M, Samson R (2004) Estimation of contaminant depletion in unsaturated soils using a reduced-order biodegradation model and carbon dioxide measurement. Appl Microbiol Biotechnol 64:53–61

Sharma A, Jansen R, Nimtz M, Johri BN, Wray V (2007) Rhamnolipids from the rhizosphere bacterium *Pseudomonas* sp. GRP(3) that reduces damping-off disease in Chilli and tomato nurseries. J Nat Prod 70:941–947

Shilo M, Fattom A, Hagalil M (1993) Polymeric substance and method of separating and culturing bacteria. US Patent 525020

Suzuki T, Tanaka K, Matsubara I, Kinoshita S (1969) Trehalose lipid and a-branched−/3-hydroxy fatty acid formed by bacteria grown on n-alkanes. Agric Biol Chem 33:1619–1627

Syldatk C, Lang S, Wagner F, Wray V, Witte L (1985) Chemical and physical characterization of four interfacial-active rhamnolipids from *Pseudomonas* sp. DSM 2874 grown on n-alkanes. Z Nat C 40:51–60

Tanzadeh J, Ghasemi M, Anvari M, Issazadeh K (2020) Biological removal of crude oil with the use of native bacterial consortia isolated from the shorelines of the Caspian Sea. Biotechnol Biotechnological Equip 34:361–374

Thavasi R, Jayalakshmi S, Balasubramanian T, Banat IM (2008) Production and characterization of a glycolipid biosurfactant from *Bacillus megaterium* using economically cheaper sources. World J Microbiol Biotechnol 24(7):917–925

Thavasi R, Jayalakshmi S, Banat IM (2010) Biosurfactants from marine bacterial isolates. In: Méndez-Vilas A (ed) Current research, technology and education topics in applied microbiology and microbial biotechnology. Formatex Research Center, Badajoz, Spain, pp 1367–1373
TOXNET (2016) Hexadecane. U.S. National Library of Medicine. https://toxnet.nlm.nih.gov/cgi-bin/sis/search2/f?./temp/~6T57cw:3
Tuleva BK, Ivanov GR, Christova NE (2002) Biosurfactant production by a new *Pseudomonas putida* strain. Z Nat Forsch C J Biosci 57:356–360
Turkovskaya OV, Dmitrieva TV, Yu Muratova A (2001) A biosurfactant-producing *Pseudomonas aeruginosa* strain. Appl Biochem Microbiol 37(1):71–75
Urakami T, Ito-Yoshida C, Araki H, Kijima T, Suzuki KI, Komagata K (1994) Transfer of *Pseudomonas plantarii* and *Pseudomonas glumae* to *Burkholderia* as *Burkholderia* spp. and description of *Burkholderia vandii* sp. nov. Int J Syst Bacteriol 44:235–245
US EPA (1999a) Alternative countermeasures for oil spills. In: Understanding oil spills and oil spill response. EPA, Washington, DC, pp 13–16
US EPA (1999b) Mechanical containment and recovery of oil following a spill. In: Understanding oil spills and oil spill response. EPA, Washington, DC, pp 9–12
US EPA (1999c) Shoreline cleanup of oil spills. In: Understanding oil spills and oil spill response. EPA, Washington, DC, pp 17–20
Varjani S, Upasani V (2017) A new look on factors affecting microbial degradation of petroleum hydrocarbon pollutants. Int Biodeterior Biodegrad 120:71–83
Vasileva-Tonkova E, Galabova D, Stoimenova E, Lalchev Z (2006) Production and properties of biosurfactants from a newly isolated *Pseudomonas fluorescens* HW-6 growing on hexadecane. Z Nat Forsch C J Biosci 61:553–559
Vasileva-Tonkova E, Gesheva V (2005) Glycolipids produced by Antarctic *Nocardioides* sp during growth on *n*-paraffin. Process Biochem 40:2387–2391
Vasileva-Tonkova E, Gesheva V (2007) Biosurfactant production by antarctic facultative anaerobe *Pantoea* sp during growth on hydrocarbons. Curr Microbiol 54:136–141
Wagner F, Behrendt V, Bock H, Kretschmer A, Lang S, Syldatk C (1983) Production and chemical characterization of surfactants from Rhodococcus erythropolis and Pseudomonas sp. MUB grown on hydrocarbons. In: Zajic JE, Cooper DG, Jack TR, Kosaric N (eds) Microbial enhanced oil recovery. PennWell Publishing Company, Tulsa, pp 55–60
Wei YH, Chou JL, Chang JS (2005) Rhamnolipid production by an indigenous isolate *Pseudomonas aeruginosa* J4 originating from petrochemical wastewater. Biochem Eng J 27(2):146–154
Wilhelmy L (1863) Uber die Abhanigkeit der Capillaritats-Constanten des Alkols vonSubstanz und Gestalt des benetztenfestenKorpers. Ann Physik Lpz 119(1863):177–217
Wilson NG, Bradley G (1996) The effect of immobilization on rhamnolipid production by *Pseudomonas fluorescens*. J Appl Bacteriol 81:525–530
Yamaguchi M, Sato A, Dazai M, Takahara Y (1978) Report of ferment. Res Inst 51:51–53
Yuan Y, Leeds JA, Meredith TC (2012) *Pseudomonas aeruginosa* directly shunts β-oxidation degradation intermediates into de novo fatty acid biosynthesis. J Bacteriol 194:5185–5196
Zhang L, Veres-Schalnat TA, Somogyi A, Pemberton JE, Maier RM (2012) Fatty acid co-substrate provides β-oxidation precursors for Rhamnolipid biosynthesis in *Pseudomonas aeruginosa*: evidence from isotope tracing and gene expression. Appl Environ Microbiol 24:8611–8622
Zhao YH, Chen LY, Tian ZJ, Sun Y, Liu JB, Huang L (2016) Characterization and application of a novel bioemulsifier in crude oil degradation by *Acinetobacter beijerinckii* ZRS. J Basic Microbiol 56(2):184–195
Zhu K, Rock CO (2008) RhlA converts b-Hydroxyacyl-acyl carrier protein intermediates in fatty acid synthesis to the b-Hydroxydecanoylb-Hydroxydecanoate component of Rhamnolipids in *Pseudomonas aeruginosa*. J Bacteriol 190:3147–3154
Zinjarde SS, Pant A (2002) Emulsifier from tropical marine yeast, *Yarrowia lipolytica* NCIM 3589. J Bas Microbiol 42:67–73

Application of Bio-Nanoparticles in Biotechnological Process Focusing in Bioremediation

6

Paula Paterlini, Cintia Mariana Romero, and Analía Alvarez

Abstract

Environmental contamination is a problem that currently faces the world-wide population due to extensive industrialization, urbanization, and new agricultural practices. Several and different pollutants profoundly alter water, soil, and air, producing biodiversity extinction, the decline in soil condition, and harming human health. Hence, various environmental remediation systems have been investigated, using biological and physicochemical approaches. This chapter examines new techniques for the remediation of contaminated systems using nanotechnology. General concepts about nanoparticles such as, types, methods of production, properties, and distinctive characteristics. It focuses in particular on the use of green synthesis nanoparticles for the bioremediation of soils and water.

Keywords

Bioremediation · Bio-nanoparticles · Synthesis mechanism · Microbes

P. Paterlini · A. Alvarez (✉)
Planta Piloto de Procesos Industriales Microbiológicos (PROIMI-CONICET), Tucumán, Argentina

Facultad de Ciencias Naturales e IML, Universidad Nacional de Tucumán, Tucumán, Argentina

C. M. Romero
Planta Piloto de Procesos Industriales Microbiológicos (PROIMI-CONICET), Tucumán, Argentina

Facultad de Bioquímica, Química y Farmacia, Universidad Nacional de Tucumán, Tucumán, Argentina

© The Author(s), under exclusive licence to Springer Nature Singapore Pte Ltd. 2021

V. Kumar et al. (eds.), *Rhizobiont in Bioremediation of Hazardous Waste*,
https://doi.org/10.1007/978-981-16-0602-1_6

6.1 Introduction

Environmental contamination is a problem that currently faces the world-wide population due mainly to technological progress and demographic growth. Especially contamination with heavy metals is of great concern due to their high toxicity. Mercury (Hg), lead (Pb), arsenic (As), nickel (Ni), cadmium (Cd), zinc (Zn), copper (Cu), and chromium (Cr) are among the most common pollutants (Hansda et al. 2014).

Even though it is natural to find metals in the ground, when the values are above a certain limit they are seen as sources of environmental pollution. Metals are considered important even in trace concentrations since they cannot degrade and consequently cause physiological effects in living organisms. Contamination of the soil by heavy metals can cause disorder in their structure. Besides, metals accumulate in plants, joining finally, into the cycle of the food. Thence it is of great importance to protect soil and ensure its stability. The tendency of heavy metal accumulation in the soil is growing and its impact will be evidenced after years (Esmaeilzadeh et al. 2019). Numerous methods have been used to approach this problem, for example, ion exchange, chemical precipitation, reverse osmosis, dialysis, and solvent extraction (Xu et al. 2017). Nevertheless, such techniques have high costs and low efficiency, in addition to showing adverse effects on the soil structure, changing their natural composition (Azimi et al. 2017). To get over these inconveniences, alternative ecological methods have been developed (Uqab et al. 2016). Researches are increasingly promoted for the development of green strategies to speed up decontamination of soil and water, in addition, to cheapen pollutant removal. Biologically based methods known together as bioremediation have shown great potential (Philp and Atlas 2005).

Bioremediation is able to eliminate smaller concentrations of pollutants in comparison with environmental clean-up physical or chemical methods. These methods offer a profitable remediation technique and environmentally friendly (El-Kassas et al. 2016).

Amongst the newer methods, the use of nanomaterials and their field applications have been the objective of several laboratory studies, mainly in North America and Europe.

The combination of bioremediation with nanomaterials has a huge potential because of efficiency and sustainability (Cecchin et al. 2016).

The fundamental component of nanomaterials is nanoparticles (NPs). They are particles from 1 to 100 nm which most important characteristic lies in the high surface area (Bhardwaj and Kaushik 2017). Amongst the different existing NPs, metallic NPs composed of pure metal atoms (zinc, silver, gold, cerium, thallium, and iron) or their compounds (oxides, hydroxides, sulfides, phosphates, fluorides, and chlorides) stand out. So far, they are the most promising types of nanomaterials due to their diverse applications, highlighting those related to the field of bioremediation (Salvadori et al. 2018).

There are different forms to synthesize NPs. The most innovative and eco-friendly of such methods use biomolecules from microorganisms or plants to

reduce a metallic precursor, resulting in the obtention of NPs (Singh et al. 2016c). The use of biosynthesized NPs in the area of bioremediation implies the combination of two green technologies as a sustainable alternative for cleaning different polluted environments.

6.2 Nanotechnology

Nanotechnology is considered a multidisciplinary science responsible for the understanding and manipulation of materials involved in the manufacture, development, and study of nanomaterials. In recent years, nanotechnology has acquired great global interest because their development represents important progress in different areas such as optics, mechanics, foods, environmental, space industries, biomedicine, healthcare, tissue engineering, among others (Sudha et al. 2018). This will make possible to achieve important scientific advances oriented to the manufacture of new materials with extraordinary properties or, to the development of those already existing, with a significant improvement of their characteristics (weight, density, conductivity, resistance, hardness, etc.) (Saratale et al. 2018).

6.2.1 Nanoparticles

The fundamental component of nanomaterials is nanoparticles (NPs). Nanoparticles can be defined as any particle from 1 to 100 nm, and that behaves as a unit in terms of structural properties, functionality, transport, and interaction with other species and with the environment (Bhardwaj and Kaushik 2017).

One of the most important characteristics of NPs which makes them more advantageous compared to their precursor material lies in their high surface-volume ratio. The shape and structure of NPs are important parameters that must be taken into account for possible applications in the area of nanotechnology. These distinctive features are responsible for their various electronic, optical, electrical, magnetic, chemical, biological, and mechanical properties. Thus, spherical, cylindrical, flat, cubic, icosahedral, triangular, etc., NPs can be found (Khan et al. 2019).

6.2.2 Organic Nanoparticles

Conforming to the chemical nature, NPs are classified into two main groups. Organic NPs involve organic polymers such as lipids, proteins, and membranes, among other biological materials. Micelles, dendrimers, ferritins, liposomes are some of the organics NPs that can be mentioned. This kind of NPs is characterized as being non-toxic, biodegradable, being sensitive to thermal and electromagnetic radiation such as heat and light (Ealias and Saravanakumar 2017). Organic NPs are one of the most used in the biomedical area, for example, in the system of directed

administration of medications, since they can be injected into specific parts of the body, reaching good drug stability (Moeinzadeh and Esmaiel 2017).

6.2.3 Inorganic Nanoparticles

Inorganic NPs are composed of pure or combined atoms forming a crystalline structure when they are interacting. This type of NP is characterized by excellent chemical and physical properties, which convert them into very important candidates for the manufacture of optical, electronic, and magnetic devices. Inorganic NPs are also recognized for their great catalytic power, which allows classifying them into two groups: non-metallic and metallic. Non-metallic NPs are generally based on carbon atoms. This atom is very versatile for the formation of different structures due to its allotropic character (Moeinzadeh and Esmaiel 2017).

The metal NPs are composed of pure metal atoms (zinc, silver, gold, cerium, thallium, and iron) or their compounds (oxides, hydroxides, sulfides, phosphates, fluorides, and chlorides). From a practical point of view, metal NPs are very important at present, since they represent the most promising kinds of nanomaterials because of their electrical, magnetic, optical, catalytic, and thermal properties, antimicrobial activity, and applications in bioremediation (Slavin et al. 2017). Some examples of metallic NPs are:

-quantum dots: semiconductor NPs that are generally used as imaging probes, since they have high quantum yields of fluorescence, high photostability, and a fluorescent emission that can be variable according to their size (Namdari et al. 2017).

Iron oxide nanoparticles (FeO NPs): biocompatible and easily biodegradable. They are widely used for the purification of contaminated water. They also have great potential in biomedicine given their intrinsic ability to be monitored in vivo by nuclear magnetic resonance techniques (Ali et al. 2016).

6.3 Nanoparticles Synthesis

The development of methods to obtain NPs with controlled chemical composition, shapes, and sizes became a field of great interest for research. The numerous methods of synthesis of NPs that have been proposed involve two types of strategies: the “top-down” or the “bottom-up” paths (Hu and Shaw 1999). The term “top-down” refers to the obtaining of NPs from micromaterials, such as the mechanical crushing of the microcellulose by a grinding process to obtain nanocellulose. In the “bottom-up” strategy, structures are constructed atom by atom. An example is the chemical production of AuNPs or ZnNPs by reducing agents. The selection of the procedure is related to the specific characteristics of the desired NPs and their chemical composition (Al-Kassas et al. 2017).

The NPs obtention can be carried out by different physical, chemical, or biological methods.

6.3.1 Physical Methods

Physical methods consist of the use of high radiation or mechanical pressure, electrical or thermal energy for NPs obtention. This causes the abrasion, fusion, evaporation, or condensation of the material, thus generating the NPs (Ealias and Saravanakumar 2017). Generally, these methods follow a "top-down" strategy and have certain advantages such as avoiding the use of solvents and producing uniform monodispersed NPs. On the other hand, the abundant residues produced during the synthesis make these methods more expensive (Abbasi et al. 2016). Some examples of physical synthesis to highlight are electrospraying, laser ablation, laser pyrolysis, physical vapor deposition, and ash spray pyrolysis (Ealias and Saravanakumar 2017).

6.3.2 Chemical Methods

Techniques such as hydrolysis, condensation, precipitation, emulsification, among others, together with chemical reducing agents and organic and inorganic solvents are used. Some reducing agents currently used are polyethylene glycol, ascorbate, sodium citrate, N, N-dimethylformamide, sodium borohydride, elemental hydrogen, etc. (Ealias and Saravanakumar 2017). This type of synthesis has advantages with respect to physical methods such as greater control in the morphology and structure of the NPs, higher speed of production, and greater control of the process. However, chemical methods have unfavorable characteristics because of the use of harmful chemicals as stabilizing and/or reducing agents for the NPs produced and the extremely stringent conditions of pH, temperature, and pressure that must be taken into account to synthesize certain NPs.

Some of the most commonly used chemical methods are hydrothermal synthesis, sol–gel method, chemical vapor synthesis, and microemulsification (Abbasi et al. 2016).

6.3.3 Biological Methods

It has been explained that different plants and organisms can perform as "bio-nano-factories" for the fabrication of metal oxide and pure NPs using biomimetic methods. It has been recognized that biomolecules from these organisms (microorganisms, bacteria, and fungi) and plants perform an operating role in NPs production with different sizes and shapes (Sharma et al. 2019). Bio-NPs are synthesized when metal particles are reduced by means of the bioreductors synthesized by the cells themselves (Gour and Jain 2019).

Microorganisms can detoxify heavy metals because they have a variety of biomolecules, among which are different reductase enzymes with the capacity of reducing metal salts and form metal NPs with low polydispersity. Proteins, metal-resistant genes, enzymes, peptides, organic materials, and reducing cofactors act as

reducing agents and provide a natural capping to the synthesized NPs, giving additional stability (Singh et al. 2016c).

Biological methods have a great number of advantages over traditional chemical methods. They are environmentally friendly, energy saving, and cheaper. The synthesized NPs does not demand extra stabilizing agents because the biomolecules from plants and microorganism act as capping agents (Makarov et al. 2014).

In comparison with NPs obtained by chemical methods, this layer that covers its surface makes them biocompatible (Tripp et al. 2002; Hakim et al. 2005). The NPs biocompatibility offers notable applications in the biomedicine ground (Huang et al. 2015). For instance, when biological NPs interact with complex biological fluids, adsorb biomolecules gradually and selectively on its surface, developing a corona that participates in interactions with biological systems. The corona coat offers extra effectiveness over comparing with naked NPs (Monopoli et al. 2012; Mukherjee et al. 2012). The biogenic procedures allow the obtention of NPs with diverse sizes and interesting morphologies (Schröfel et al. 2014). Besides, green methods of synthesis can reduce significantly the toxicity of NPs and their synthesis process consumes a shorter time in comparison with physicochemical methodologies (Gour and Jain 2019). Biosynthesis of NPs applied in processes of bioremediation is a technique that promises to cope with the increasing demands for wastes treatment, particularly in relation to the activity of the heavy metal industry (Salvadori et al. 2018).

6.4 Bio-Nanoparticles Producing Organisms

6.4.1 Microorganisms and Algae

There are many examples of microorganisms, such as bacteria (Raliya et al. 2014; Wypij et al. 2017) fungi (Raliya and Tarafdar 2013; Bhargava et al. 2016), and algae (Arockiya Aarthi Rajathi et al. 2012; Zhang et al. 2016) acting as microbial-nanofactories of NPs.

Gold NPs of uniform size were obtained using *Penicillium rugulosum*, a bacterium frequently used in several industrial processes (Mishra et al. 2012). Platinum NPs of regular size and shape have been synthesized with the cell-soluble protein extract of sulfate-reducing bacteria (Riddin et al. 2010). In both cases, yields of NPs fabricated by enzymatic processes surpassed those obtained by traditional chemical methods.

The culture of *Verticillium* sp. in the presence of an aqueous solution of Ag^+ ions resulted in the synthesis of AgNPs. NPs were observed to be produced on the surface of the mycelia due to the electrostatic interaction between the carboxylate groups of negatively charged enzymes present in the cell wall and the Ag^+ ions. (Mukherjee et al. 2001).

The biosynthesis of NPs using algae is an emergent area of research. Different morphotypes of algae are being used as models for the synthesis of NPs, especially useful in bioremediation (Patel et al. 2015).

Fawcett et al. (2017) communicated that different bioactive chemicals, such as proteins and polysaccharides, present in the cell membrane of marine algae can play a role not just as reducing, but also as capping agents. The formation of stable, polycrystalline, spherical Au and Ag NPs was carried out using extracts of the brown macroalgae *Palmaria decipiens* and *Desmarestia menziesii* (González-Ballesteros et al. 2018).

6.4.2 Plant-Mediated Biosynthesis

Plant biomass submerged in water can be used for the synthesis of NPs (Gour and Jain 2019). Different parts of the plant (fruits, leaves, roots, stems, and their biomolecules) have been utilized to obtain metal NPs (Murugan et al. 2015; Naseem and Farrukh 2015). Although the mechanisms are not yet fully elucidated, it was suggested that organic acids, amino acids, vitamins, proteins, and secondary metabolites, like alkaloids, polysaccharides, flavonoids, heterocyclic compounds, polyphenols, and terpenoids, have an important function in the reduction of metal salts to obtain NPs.

Additionally, plant biomolecules may have a role as protection and stabilizing agents for the synthesized NPs (Duan et al. 2015). Nanoparticles of Au and Ag have been produced successfully employing leaf extract and root of the medicinal plant *Panax ginseng* (Singh et al. 2016a, b). Studies suggest that the different mechanisms used for the plant to synthesize NPs depend on the plant species (Baker et al. 2013). For example, cyperoquinone and remirin present in mesophytic plants are convenient, in general, to synthesize metal NPs. Emodin, a purgative resin present in xerophyte plants is specifically responsible for the synthesis of AgNPs (Makarov et al. 2014). Dicotyledonous plants have a great number of secondary metabolites that can participate in the NPs synthesis (Singh et al. 2016c).

6.4.3 Mechanisms of Nanoparticles Biosynthesis

As a result of the development of different defense mechanisms that microorganisms use to decrease environmental toxicity, appear diverse ways of NPs production (Bansal et al. 2012). Nevertheless, independent of the biosynthesis mechanism, it is imperative to optimize the conditions of NPs production to achieve monodispersity and to control the particle size. These are important considerations for its subsequent use in biotechnology (Jain et al. 2015).

6.4.3.1 Intracellular Synthesis

First, metallic ions are absorbed into the cell wall as a consequence of the attraction to the negatively charged functional groups along the cell surface (Erasmus et al. 2014). The second process comprises the passage of the metal ions into the cell through ATP-dependent pumps. Cellular enzymes reduce metallic ions and occasionally cap them, and consequently, the synthesis of NPs begins. Then, capping

proteins neutralize NPs surface charge, binding to these through open amine groups and cysteine residues (Dávila Costa et al. 2020). Furthermore, these capping proteins prevent the agglomeration, playing an essential role as a site for bio-conjugation with other molecules (El-deeb et al. 2013). Stability decreases the toxicity of the NPs, making them more environmentally friendly (Stark et al. 2013).

6.4.3.2 Extracellular Synthesis

This synthesis of NPs can happen in two ways. The first one might be comparable to the intracellular mechanism: oxide-reduction enzymes perform the production of NPs when metal ions pass into the cell as described above. The capping and reducing proteins bind to the NPs during the reductive process. NPs are transported to the outside of the cell after configuring their size and shape. (Bansal et al. 2012). The second way consists of the expulsion of the reducing proteins to the solution of the exterior. This process is a result of the change in pH because of the presence of the metallic ions. At the moment that this signal is received, the cell activates the secretion of oxidoreductase enzymes that produce the reduction reaction and form NPs (Huang et al. 2015).

6.5 Methods for NPs Characterization

A very important step after the biosynthesis of NPs is their characterization. Because NPs of varied shapes and sizes can be obtained, which in turn will define their possible applications, various techniques are used to characterize them in depth. Some important parameters that can be known in this way are the morphology, size, elemental composition, and dispersion of the NP.

Ultraviolet-visible (UV-vis) spectrophotometer, energy dispersive X-ray spectroscopy (EDX), transmission electron microscopy (TEM), atomic force microscopy (AFM), scanning electron microscopy (SEM), and Fourier transform infrared spectroscopy (FTIR) are some of the most used methods for the characterization of NPs.

Surface plasmon resonance is what dominates the optical absorption spectra of metallic NPs. The wavelength at which the characteristic peak of the plasmon resonance is presented depends on each NP (Vaghari et al. 2016). For example, a peak near 400 nm indicates the presence of AgNPs. Also, the position and shape of the peak can give us an idea of the NPs concentration (Mahmoudi et al. 2009; Xu and Sun 2013).

UV spectroscopy is a type of absorption spectroscopy in which the light from the UV region (200–400 nm) is absorbed by the molecule. It produces the excitation of electrons from the fundamental state to a state of greater energy. The energy of the UV radiation that is absorbed is equal to the difference in energy between the fundamental state and the higher energy states.

Complete UV-visible absorption happens at a determinate wavelength in each molecular structure (Xu et al. 2014). In the NPs field, UV-visible spectrometry is a widely used technique. It is a consistent and very simple method to know the shape, size, and polydispersity of the NPs.

FTIR is a simple, adequate, convenient, non-invasive, and cost-effective technique, frequently used to detect biomolecules associated with the NPs surface and possibly involved in their synthesis and stabilization (Dávila Costa et al. 2020).

SEM, TEM, and AFM are imaging methods by which morphology, size distribution, dispersion, and aggregation of a NPs sample can be identified (Liu 2006). The ability to perform analytical measurements and give a better spatial resolution are two of the advantages that TEM has over SEM (Chauhan et al. 2016). AFM can be used to characterize the interaction of nanomaterials with compatible lipid bilayers in real-time and measurements can be performed in aqueous fluids. The downside is that particles not attached to a substrate will float and leading to imaging artifacts (Al Juraifani and Azzah 2015).

The NPs elemental composition can be analyzed by the blend of two techniques: SEM and X-ray spectroscopy (EDX). This can also provide important information about the degree of the particles aggregation and purity. XRD is utilized to determine the crystal structure of the NPs (Shi et al. 2015).

Dynamic light scattering (DLS) is a widely used technique employed to quantify size distribution and surface charges of NPs on a simple solvent or biological environment (Wen et al. 2016). Measurements are non-invasive and very fast when a sample is in its native colloidal state (Xue et al. 2016).

6.6 Nanoparticles Applications.

The applications of NPs have become very important in all areas of science (Singh et al. 2016c). Biomedical, agricultural, environmental, and physicochemical are just some of them (Pereira et al. 2015). For example, AuNPs have been used for drug delivery, tumor and genetic disease detection, photoimage, and photothermal therapy. AgNPs have been utilized for anti-cancer, antimicrobial, wound treatment, and anti-inflammatory purposes (Ahamed et al. 2010). Because of their non-toxic, self-cleaning, biocompatible, antimicrobial, and dermatological behavior, zinc and titanium NPs have been applied in cosmetic and biomedical areas (Ambika and Sundrarajan 2015). Palladium and copper NPs have been used in polymers, batteries, optical limiting devices, and plastic plasmon waveguides (Momeni and Nabipour 2015).

Amongst the most innovative and promising applications of NPs, those related to the recovery of contaminated environments are highlighted. Nano-remediation is a novel potential solution to clean up the environment. Nanoparticles play an important paper in the prevention, sensing, supervising, and remediation of polluted systems (Rajan 2011). The properties of the nanoparticles allow both catalysis and chemical reduction to attenuate the contaminants of interest. Nanoparticles can penetrate very tiny nooks in the subsoil and remain suspended in the groundwater, allowing them to travel faster than macro-size particles achieving wider distribution. Besides, the elevated relation surface/volume of NPs is beneficial for technologies that depend on reactions at the water–solid and gas–solid interfaces. Such is the case of the adsorption mechanisms used to treat wastewaters, exhaust gases, or

photocatalytic processes for the degradation of pollutants. In the case of ex-situ remediation, NPs can be easily maintained in suspension reactors to treat contaminated soil and sediment. Alternatively, to improve water treatment, they can be anchored in a solid matrix such as carbon (Bhandari 2018).

6.6.1 Bioremediation

Contamination with heavy metals produces world-wide concern due to their high toxicity and great dispersion capacity. Consequently, bioremediation of heavy metals using biogenic NPs is a topic of great interest. One of the most hazardous metals is Pb since it is quickly accumulated by fishes (Ribeiro et al. 2010) entering into the cycle of the food (Crist et al. 1992). El-Kassas et al. (2016) biosynthesized iron oxide NPs (Fe_3O_4-NPs) to remove Pb by employing a fully green method. Seaweed extracts of the algae *Padina pavonica* and *Sargassum acinarium* were employed for the reduction of a ferric chloride solution, resulting in the synthesis of Fe_3O_4-NP. Biosynthesized Fe3O4-NP was stabilized on calcium alginate beads and utilized in experiments of adsorption of Pb. The authors observed the NPs biosynthesized through *P. pavonica* removed 91% of Pb while NPs from *S. acinarium* removed 78% of Pb, after 75 min. The utilization of FeNPs to remove chlorinated solvents (PCE, TCE, DCE), arsenic, pesticides (lindane, DDT), and for the transformation of other organic compounds such as nitrates from water and soil have also been reported (Karn et al. 2009). Kanel et al. (2005, 2006) informed the elimination of As(III) and As(V) using FeNPs. These are two of the most toxic and predominant species of arsenic in groundwater.

Another example of the use of biogenic NPs for bioremediation is the case of AuNPs. López-Miranda et al. (2019) were able to synthesize AuNPs of fairly homogeneous size (40–60 nm) using aqueous extracts of *Aloysia triphylla*. When evaluating their catalytic properties to degenerate organic dyes (Congo red and Methylene blue), short degradation periods were obtained. These results suggest that AuNPs produced by *A. triphylla* can be used for remediation of water.

Different studies show that the use of NPs as white rot fungi (WRF) supports can have a synergistic effect, improving the stability of WRFs in the bioremediation of wastewaters. Nanoparticles could contribute by increasing the practical yield of the WRF biomass or acting as supports in the immobilization of enzymes from WRF that participate in the removal processes (i.e., laccases) (Chen et al. 2013; Xu et al. 2013; Hu et al. 2016).

Because of their single qualities, biogenic NPs are suitable for the design of nanobiosensors (Peng and Miller 2011). Nanosensors were used for the determination of mycobacteria, algae, mercury toxins in drinking water (Selid et al. 2009). As well, nanosensors can be useful to detect viruses, crop pests, stress factors, and soil nutrient levels, and hormonal regulation. For example, Koren et al. (2015) detected levels of oxygen and auxin distributed in the seagrass rhizosphere using optical O_2 nanosensors with built-in NPs.

Biogenic AgNPs were used for the manufacturing of a cost-effective fiber optic-based sensor for H2O2 detection that can be applied in different industrial processes (Tagad et al. 2013).

6.7 Conclusions

The environmental damage produced because of the exponential increase in industrialization is a reason for great preoccupation. In this context, nanotechnology is presented as an alternative with an enormous prospect to improve actual technologies used in different areas. Regarding the remediation of polluted systems, nanotechnology can provide ecological and effective solutions. In this chapter, updated data about the biological synthesis of metallic NPs and some of the most used techniques for their characterization are presented in summary form. In addition, some of its main applications are described, emphasizing its use in bioremediation processes.

Nano-bioremediation is an efficient and sustainable focus to provide a remedy for global contaminated sites. It can proportionate profitable and timesaving cleanup procedures for extensive contaminated places.

Because of its great potential, it is estimated that NPs uses will enhance in the future and they would be key to a sustainable development. For this reason, more researches on aspects fundamental and practical of nano-bioremediation are needed.

References

Abbasi E, Milani M, Aval SF, Kouhi M, Akbarzadeh A, Nasrabadi HT, Nikasa P, Joo SW, Hanifehpour Y, Nejati-Koshki K, Samiei M (2016) Silver nanoparticles: synthesis methods, bio-applications and properties. Crit Rev Microbiol 42:173–180. https://doi.org/10.3109/1040841X.2014.912200

Ahamed M, AlSalhi MS, Siddiqui MKJ (2010) Silver nanoparticle applications and human health. Clin Chim Acta 411:1841–1848. https://doi.org/10.1016/j.cca.2010.08.016

Al Juraifani AAA, Azzah AG (2015) Biosynthesis of silver nanoparticles by Aspergillus Niger, *Fusarium oxysporum* and *Alternaria solani*. Afr J Biotechnol 14:2170–2174. https://doi.org/10.5897/ajb2015.14482

Ali A, Zafar H, Zia M, Haq IU, Phull AR, Ali JS, Hussain A (2016) Synthesis, characterization, applications, and challenges of iron oxide nanoparticles. Nanotechnol Sci Appl 9:49–67. https://doi.org/10.2147/NSA.S99986

Al-Kassas R, Bansal M, Shaw J (2017) Nanosizing techniques for improving bioavailability of drugs. J Control Release 260:202–212. https://doi.org/10.1016/j.jconrel.2017.06.003

Ambika S, Sundrarajan M (2015) Green biosynthesis of ZnO nanoparticles using *Vitex negundo* L. extract: spectroscopic investigation of interaction between ZnO nanoparticles and human serum albumin. J Photochem Photobiol B Biol 149:143–148. https://doi.org/10.1016/j.jphotobiol.2015.05.004

Arockiya Aarthi Rajathi F, Parthiban C, Ganesh Kumar V, Anantharaman P (2012) Biosynthesis of antibacterial gold nanoparticles using brown alga, *Stoechospermum marginatum* (kützing). Spectrochim Acta Part A Mol Biomol Spectrosc 99:166–173. https://doi.org/10.1016/j.saa.2012.08.081

Azimi A, Azari A, Rezakazemi M, Ansarpour M (2017) Removal of heavy metals from industrial wastewaters: a review. Chem Bio Eng Rev 4:37–59. https://doi.org/10.1002/cben.201600010

Baker S, Rakshith D, Kavitha KS, Santosh P, Kavitha HU, Rao Y, Satish S (2013) Plants: emerging as nanofactories towards facile route in synthesis of nanoparticles. Bio Impacts 3:111–117. https://doi.org/10.5681/bi.2013.012

Bansal V, Bharde A, Ramanathan R, Bhargava SK (2012) Inorganic materials using "unusual" microorganisms. Adv Colloid Interf Sci 179–182:150–168. https://doi.org/10.1016/j.cis.2012.06.013

Bhandari G (2018) Environmental nanotechnology: applications of nanoparticles for bioremediation. In: Prasad R, Aranda E (eds) Approaches in bioremediation. Nanotechnology in the life sciences. Springer, Cham, pp 301–315. https://doi.org/10.1007/978-3-030-02369-0_13

Bhardwaj V, Kaushik A (2017) Biomedical applications of nanotechnology and nanomaterials. Micromachines 8:298. https://doi.org/10.3390/mi8100298

Bhargava A, Jain N, Khan MA, Pareek A, Dilip RV, Panwar J (2016) Utilizing metal tolerance potential of soil fungus for efficient synthesis of gold nanoparticles with superior catalytic activity for degradation of rhodamine B. J Environ Manag 183:22–32. https://doi.org/10.1016/j.jenvman.2016.08.021

Cecchin I, Reddy KR, Thomé A, Tessaro EF, Schnaid F (2016) Nanobioremediation: integration of nanoparticles and bioremediation for sustainable remediation of chlorinated organic contaminants in soils. Int Biodeterior Biodegrad 119:419–428. https://doi.org/10.1016/j.ibiod.2016.09.027

Chauhan N, Narang J, Jain U (2016) Amperometric acetylcholinesterase biosensor for pesticides monitoring utilising iron oxide nanoparticles and poly(indole-5-carboxylic acid). J Exp Nanosci 11:111–122. https://doi.org/10.1080/17458080.2015.1030712

Chen G, Guan S, Zeng G, Li X, Chen A, Shang C, Zhou Y, Li H, He J (2013) Cadmium removal and 2,4-dichlorophenol degradation by immobilized *Phanerochaete chrysosporium* loaded with nitrogen-doped TiO2 nanoparticles. Appl Microbiol Biotechnol 97:3149–3157. https://doi.org/10.1007/s00253-012-4121-1

Crist RH, Karl O, Jane M, Cirst DR, Jhonson JK, Brittsan JM (1992) Interaction of metals and protons with algae. 3. Marine algae, with emphasis on lead and aluminum. Environ Sci Technol 26:496–502. https://doi.org/10.1021/es00027a007

Dávila Costa JS, Romero CM, Rasuk MC (2020) Nanoparticles for new pharmaceuticals: metabolites from Actinobacteria. In: Environmental nanotechnology, vol 4. Springer, Cham, pp 195–213

Duan H, Wang D, Li Y (2015) Green chemistry for nanoparticle synthesis. Chem Soc Rev 44:5778–5792. https://doi.org/10.1039/c4cs00363b

Ealias AM, Saravanakumar MP (2017) A review on the classification, characterisation, synthesis of nanoparticles and their application. IOP Conf Ser Mater Sci Eng 263:032019. https://doi.org/10.1088/1757-899X/263/3/032019

El-deeb B, Mostafa N, Altalhi A, Gherbawy Y (2013) Extracellular biosynthesis of silver nanoparticles by bacteria *Alcaligenes faecalis* with highly efficient anti-microbial property. Int J Chem Eng 30:1137–1144

El-Kassas HY, Aly-Eldeen MA, Gharib SM (2016) Green synthesis of iron oxide (Fe_3O_4) nanoparticles using two selected brown seaweeds: characterization and application for lead bioremediation. Acta Oceanol Sin 35:89–98. https://doi.org/10.1007/s13131-016-0880-3

Erasmus M, Cason ED, Van Marwijk J, Botes E, Gericke M, van Heerden E (2014) Gold nanoparticle synthesis using the thermophilic bacterium *Thermus scotoductus* SA-01 and the purification and characterization of its unusual gold reducing protein. Gold Bull 47:245–253. https://doi.org/10.1007/s13404-014-0147-8

Esmaeilzadeh M, Jaafari J, Mohammadi AA, Panahandeh M, Javid P, Javan S (2019) Investigation of the extent of contamination of heavy metals in agricultural soil using statistical analyses and contamination indices. Hum Ecol Risk Assess 25:1125–1136. https://doi.org/10.1080/10807039.2018.1460798

Fawcett D, Verduin JJ, Shah M, Sharma SB, Poinern GEJ (2017) A review of current research into the biogenic synthesis of metal and metal oxide nanoparticles via marine algae and seagrasses. J Nanosci 2017:1–15. https://doi.org/10.1155/2017/8013850

González-Ballesteros N, González-Rodríguez JB, Rodríguez-Argüelles MC, Lastra M (2018) New application of two Antarctic macroalgae *Palmaria decipiens* and *Desmarestia menziesii* in the synthesis of gold and silver nanoparticles. Pol Sci 15:49–54. https://doi.org/10.1016/j.polar.2017.10.004

Gour A, Jain NK (2019) Advances in green synthesis of nanoparticles. Artif Cells Nanomed Biotechnol 47:844–851. https://doi.org/10.1080/21691401.2019.1577878

Hakim LF, Portman JL, Casper MD, Weimer AW (2005) Aggregation behavior of nanoparticles in fluidized beds. Powder Technol 160:149–160. https://doi.org/10.1016/j.powtec.2005.08.019

Hansda A, Kumar V, Usmani Z (2014) Phytoremediation of heavy metals contaminated soil using plant growth promoting rhizobacteria (PGPR): a current perspective. Recent Res Sci Technol 6:131–134

Hu EL, Shaw DT (1999) Chapter 2 synthesis and assembly. In: Nanostructure science and technology. Springer, Dordrecht, pp 15–34. https://doi.org/10.1007/978-94-015-9185-0_2

Hu L, Zeng G, Chen G et al (2016) Treatment of landfill leachate using immobilized Phanerochaete chrysosporium loaded with nitrogen-doped TiO_2 nanoparticles. J Hazard Mater 301:106–118. https://doi.org/10.1016/j.jhazmat.2015.08.060

Huang J, Lin L, Sun D, Chen H, Yang D, Li Q (2015) Bio-inspired synthesis of metal nanomaterials and applications. Chem Soc Rev 44:6330–6374. https://doi.org/10.1039/c5cs00133a

Jain N, Bhargava A, Rathi M, Dilip RV, Panwar J (2015) Removal of protein capping enhances the antibacterial efficiency of biosynthesized silver nanoparticles. PLoS One 10:1–19. https://doi.org/10.1371/journal.pone.0134337

Kanel SR, Greneche JM, Choi H (2006) Arsenic (V) removal from groundwater using nano scale zero-valent iron as a colloidal reactive barrier material. Environ Sci Technol 40:2045–2050. https://doi.org/10.1021/es0520924

Kanel SR, Manning B, Charlet L, Choi H (2005) Removal of arsenic (III) from groundwater by nanoscale zero-valent iron. Environ Sci Technol 39:1291–1298. https://doi.org/10.1021/es048991u

Karn B, Kuiken T, Otto M (2009) Nanotechnology and in situ remediation: a review of the benefits and potential risks. Environ Health Perspect 117:1823–1831. https://doi.org/10.1289/ehp.0900793

Khan I, Saeed K, Khan I (2019) Nanoparticles: properties, applications and toxicities. Arab J Chem 12:908–931. https://doi.org/10.1016/j.arabjc.2017.05.011

Koren K, Brodersen KE, Jakobsen SL, Kühl M (2015) Optical sensor nanoparticles in artificial sediments-a new tool to visualize O_2 dynamics around the rhizome and roots of seagrasses. Environ Sci Technol 49:2286–2292. https://doi.org/10.1021/es505734b

Liu W (2006) Nanoparticles and their biological and environmental applications. J Biosci Bioeng 102:1–7. https://doi.org/10.1263/JBB.102.1

López-Miranda JL, Esparza R, Rosas G, Perez R, Estévez-González M (2019) Catalytic and antibacterial properties of gold nanoparticles synthesized by a green approach for bioremediation applications. 3 Biotech 9:135. https://doi.org/10.1007/s13205-019-1666-z

Mahmoudi M, Simchi A, Imani M, Hafeli UO (2009) Superparamagnetic iron oxide nanoparticles with rigid cross-linked polyethylene glycol fumarate coating for application in imaging and drug delivery. J Phys Chem C 113:8124–8131. https://doi.org/10.1021/jp900798r

Makarov VV, Love AJ, Sinitsyna OV, Makarova SS, Yaminsky IV, Taliansky ME, Kalinina NO (2014) Green nanotechnologies: synthesis of metal nanoparticles using plants. Acta Nat 6:40–61. https://doi.org/10.4135/9781452231631.n3

Mishra A, Tripathy SK, Yun SI (2012) Fungus mediated synthesis of gold nanoparticles and their conjugation with genomic DNA isolated from *Escherichia coli* and *Staphylococcus aureus*. Process Biochem 47:701–711. https://doi.org/10.1016/j.procbio.2012.01.017

Moeinzadeh S, Esmaiel J (2017) Nanoparticles and their applications. In: Bhushan B (ed) Springer handbook of nanotechnology. Springer, Berlin, pp 85–147

Momeni S, Nabipour I (2015) A simple green synthesis of palladium nanoparticles with sargassum alga and their electrocatalytic activities towards hydrogen peroxide. Appl Biochem Biotechnol 176:1937–1949. https://doi.org/10.1007/s12010-015-1690-3

Monopoli MP, Åberg C, Salvati A, Dawson KA (2012) Biomolecular coronas provide the biological identity of nanosized materials. Nat Nanotechnol 7:779–786. https://doi.org/10.1038/nnano.2012.207

Mukherjee P, Ahmad A, Mandal D, Senapati S, Sainkar Sudhakar R, Khan MI, Renu P, Ajaykumar PV, Alam M, Kumar R, Sastry M (2001) Fungus mediated synthesis of silver nanoparticles and their immobilization in the mycelial matrix: a novel biological approach to nanoparticle synthesis. Nano Lett 1:515–519. https://doi.org/10.1021/nl0155274

Mukherjee S, Sushma V, Patra S, Barui AK, Bhadra MP, Shredhar B, Patra CR (2012) Green chemistry approach for the synthesis and stabilization of biocompatible gold nanoparticles and their potential applications in cancer therapy. Nanotechnol 23:455103. https://doi.org/10.1088/0957-4484/23/45/455103

Murugan K, Benelli G, Panneerselvam C, Subramaniam J, Jeyalalitha T, Dinesh D, Nicoletti M, Hwang JS, Suresh U, Madhiyazhagan P (2015) *Cymbopogon citratus*-synthesized gold nanoparticles boost the predation efficiency of copepod *Mesocyclops aspericornis* against malaria and dengue mosquitoes. Exp Parasitol 153:129–138. https://doi.org/10.1016/j.exppara.2015.03.017

Namdari P, Negahdari B, Eatemadi A (2017) Synthesis, properties and biomedical applications of carbon-based quantum dots: an updated review. Biomed Pharmacother 87:209–222. https://doi.org/10.1016/j.biopha.2016.12.108

Naseem T, Farrukh MA (2015) Antibacterial activity of green synthesis of iron nanoparticles using *Lawsonia inermis* and *Gardenia jasminoides* leaves extract. J Chem 2015:912342. https://doi.org/10.1155/2015/912342

Patel V, Berthold D, Puranik P, Gantar M (2015) Screening of cyanobacteria and microalgae for their ability to synthesize silver nanoparticles with antibacterial activity. Biotechnol Rep 5:112–119. https://doi.org/10.1016/j.btre.2014.12.001

Peng HI, Miller BL (2011) Recent advancements in optical DNA biosensors: exploiting the plasmonic effects of metal nanoparticles. Analyst 136:436–447. https://doi.org/10.1039/c0an00636j

Pereira L, Mehboob F, Stams AJM, Mota MM, Rijnaarts HHM, Alves MM (2015) Metallic nanoparticles: microbial synthesis and unique properties for biotechnological applications, bioavailability and biotransformation. Crit Rev Biotechnol 35:114–128. https://doi.org/10.3109/07388551.2013.819484

Philp JC, Atlas RM (2005) Bioremediation of contaminated soils and aquifers. In: Atlas RM, Philp JC (eds) Bioremediation: applied microbial solutions for real-world environmental cleanup. American Society for Microbiology (ASM) Press, Washington, DC, pp 139–236. https://doi.org/10.1128/9781555817596.ch5

Rajan CS (2011) Nanotechnology in groundwater remediation. Int J Environ Sci Dev 2:182–187. https://doi.org/10.7763/IJESD.2011.V2.121

Raliya R, Tarafdar JC (2013) ZnO nanoparticle biosynthesis and its effect on phosphorous-mobilizing enzyme secretion and gum contents in Clusterbean (*Cyamopsis tetragonoloba* L.). Agric Res 2:48–57. https://doi.org/10.1007/s40003-012-0049-z

Raliya R, Tarafdar JC, Mahawar H, Kumar R, Gupta P, Mathur T, Kaul RK, Kumar P, Kalia A, Gautam R, Singh SK, Gehlot HS (2014) ZnO nanoparticles induced exopolysaccharide production by *B. subtilis* strain JCT1 for arid soil applications. Int J Biol Macromol 65:362–368. https://doi.org/10.1016/j.ijbiomac.2014.01.060

Ribeiro RFL, Magalhães SMS, Barbosa FAR, Nascentes CC, Campos IC, Moraes DC (2010) Evaluation of the potential of microalgae *Microcystis novacekii* in the removal of Pb^{2+} from an aqueous medium. J Hazard Mater 179:947–953. https://doi.org/10.1016/j.jhazmat.2010.03.097

Riddin T, Gericke M, Whiteley CG (2010) Biological synthesis of platinum nanoparticles: effect of initial metal concentration. Enzym Microb Technol 46:501–505. https://doi.org/10.1016/j.enzmictec.2010.02.006

Salvadori S, Ando RA, Nascimento Oller CA, Corrêa B (2018) Biosynthesis of metal nanoparticles via fungal dead biomass in industrial bioremediation process. In: Prasad R, Kumar V, Kumar M, Wang S (eds) Fungal Nanobionics: principles and applications. Springer, Singapore, pp 165–199. https://doi.org/10.1007/978-981-10-8666-3_7

Saratale RG, Saratale GD, Shin HS, Jacob JM, Pugazhendhi A, Bhaisare M, Kumar G (2018) New insights on the green synthesis of metallic nanoparticles using plant and waste biomaterials: current knowledge, their agricultural and environmental applications. Environ Sci Pollut Res 25:10164–10183. https://doi.org/10.1007/s11356-017-9912-6

Schröfel A, Kratošová G, Šafařík I, Šafaříková M, Raška I, Shor LM (2014) Applications of biosynthesized metallic nanoparticles-a review. Acta Biomater 10:4023–4042. https://doi.org/10.1016/j.actbio.2014.05.022

Selid PD, Xu H, Collins EM, Face-Collins MS, Zhao JX (2009) Sensing mercury for biomedical and environmental monitoring. Sensors 9:5446–5459. https://doi.org/10.3390/s90705446

Sharma D, Kanchi S, Bisetty K (2019) Biogenic synthesis of nanoparticles: a review. Arab J Chem 12:3576–3600. https://doi.org/10.1016/j.arabjc.2015.11.002

Shi C, Zhu N, Cao Y, Wu P (2015) Biosynthesis of gold nanoparticles assisted by the intracellular protein extract of *Pycnoporus sanguineus* and its catalysis in degradation of 4-nitroaniline. Nanoscale Res Lett 10:147. https://doi.org/10.1186/s11671-015-0856-9

Singh P, Kim YJ, Wang C, Mathiyalagan R, El-Agamy Farh M, Yang DC (2016a) Biogenic silver and gold nanoparticles synthesized using red ginseng root extract, and their applications. Artif Cells Nanomed Biotechnol 44:811–816. https://doi.org/10.3109/21691401.2015.1008514

Singh P, Kim YJ, Yang DC (2016b) A strategic approach for rapid synthesis of gold and silver nanoparticles by *Panax ginseng* leaves. Artif Cells Nanomed Biotechnol 44:1949–1957. https://doi.org/10.3109/21691401.2015.1115410

Singh P, Kim YJ, Zhang D, Yang DC (2016c) Biological synthesis of nanoparticles from plants and microorganisms. Trends Biotechnol 34:588–599. https://doi.org/10.1016/j.tibtech.2016.02.006

Slavin YN, Asnis J, Häfeli UO, Bach H (2017) Metal nanoparticles: understanding the mechanisms behind antibacterial activity. J Nanobiotechnol 15:1–20. https://doi.org/10.1186/s12951-017-0308-z

Stark WJ, Stoessel PR, Wohlleben W, Hafner AJCSR (2013) Industrial applications of nanoparticles. Chem Soc Rev 16:5793–5805. https://doi.org/10.1039/x0xx00000x

Sudha PN, Sangeetha K, Vijayalakshmi K, Barhoum A (2018) Chapter 12-nanomaterials history, classification, unique properties, production and market. In: Emerging applications of nanoparticles and architecture nanostructures. Elsevier, Amsterdam

Tagad CK, Dugasani SR, Aiyer R, Park S, Kulkarni A, Sbharwal S (2013) Green synthesis of silver nanoparticles and their application for the development of optical fiber based hydrogen peroxide sensor. Sensors Actuators B Chem 183:144–149. https://doi.org/10.1016/j.snb.2013.03.106

Tripp SL, Pusztay SV, Ribbe AE, Wei A (2002) Self-assembly of cobalt nanoparticle rings: supporting information. J Am Chem Soc 124:7914–7915. https://doi.org/10.1021/ja0263285

Uqab B, Mudasir S, Nazir R (2016) Review on bioremediation of pesticides. J Bioremed Biodegr 7:2. https://doi.org/10.4172/2155-6199.1000343

Vaghari H, Jafarizadeh-Malmiri H, Mohammadlou M, Berenjian A, Anarjan N, Jafari N, Nasiri S (2016) Application of magnetic nanoparticles in smart enzyme immobilization. Biotechnol Lett 38:223–233. https://doi.org/10.1007/s10529-015-1977-z

Wen L, Zeng P, Zhang L, Huang W, Wang H, Chen G (2016) Symbiosis theory-directed green synthesis of silver nanoparticles and their application in infected wound healing. Int J Nanomedicine 11:2757–2767. https://doi.org/10.2147/IJN.S106662

Wypij M, Golinska P, Dahm H, Rai M (2017) Actinobacterial-mediated synthesis of silver nanoparticles and their activity against pathogenic bacteria. IET Nanobiotechnol 11:336–342. https://doi.org/10.1049/iet-nbt.2016.0112

Xu C, Sun S (2013) New forms of superparamagnetic nanoparticles for biomedical applications. Adv Drug Deliv Rev 65:732–743. https://doi.org/10.1016/j.addr.2012.10.008

Xu J, Sun J, Wang Y, Sheng J, Wang F, Sun M (2014) Application of iron magnetic nanoparticles in protein immobilization. Molecules 19:11465–11486. https://doi.org/10.3390/molecules190811465

Xu P, Zeng G, Huang D, Hu S, Feng C, Lai C, Zhao M, Huang C, Li N, Wei ZZ, Xie G (2013) Synthesis of iron oxide nanoparticles and their application in *Phanerochaete chrysosporium* immobilization for Pb (II) removal. Colloids Surf A 419:147–155. https://doi.org/10.1016/j.colsurfa.2012.10.061

Xu R, Chen M, Fang T, Chen J (2017) A new method for extraction and heavy metals removal of abalone visceral polysaccharide. J Food Process Preserv 41:1–9. https://doi.org/10.1111/jfpp.13023

Xue B, He D, Gao S, Wang D, Yokoyama K, Wang L (2016) Biosynthesis of silver nanoparticles by the fungus *Arthroderma fulvum* and its antifungal activity against genera of *Candida, Aspergillus* and *Fusarium*. Int J Nanomedicine 11:1899–1906. https://doi.org/10.2147/IJN.S98339

Zhang X, Qu Y, Shen W, Wang J, Li H, Zhang J, Li S, Zhou J (2016) Biogenic synthesis of gold nanoparticles by yeast *Magnusiomyces ingens* LH-F1 for catalytic reduction of nitrophenols. Colloids Surf A 497:280–285. https://doi.org/10.1016/j.colsurfa.2016.02.033

Plant–Microbe Interactions in Attenuation of Toxic Waste in Ecosystem

7

Monday Ubogu and Ejiro Akponah

Abstract

As a result of rapid human population growth and increased industrial activities, the world ecosystems more than ever before are perpetually inundated with anthropogenic toxic waste releases at levels and frequencies higher than natural recovery rates. To achieve sustainable development, timely, efficient, environmentally friendly, and cost-effective approaches are required for environmental pollution abatement. Phytoremediation technique involving plant–microbe synergy provides a simple plausible remediation alternative to existing intrusive and costly physicochemical and engineering-based decontamination techniques. Although plant and microorganisms can independently attenuate some toxic wastes, without microbial collaboration, this technique will not be a viable option for the remediation of most pollutants. This review examines the mutual relationship between microorganisms and plant within rhizosphere and phyllosphere and exploitation of their synergy for toxic organic and inorganic wastes attenuation in the ecosystem. Possible mechanisms and reasons for accelerated removal of pollutants within the vicinity of plants (rhizosphere and phyllosphere) are presented. The prominent role played by root-endophytes in toxic waste attenuation in soil ecosystem is highlighted.

Keywords

Bioremediation · Microbes · Plant · Phytoremediation · Toxic compounds

M. Ubogu (✉)
Department of Microbiology, Federal University of Agriculture Makurdi, Makurdi, Nigeria

E. Akponah
Department of Microbiology, Delta State University, Abraka, Nigeria

© The Author(s), under exclusive licence to Springer Nature Singapore Pte Ltd. 2021

V. Kumar et al. (eds.), *Rhizobiont in Bioremediation of Hazardous Waste*,
https://doi.org/10.1007/978-981-16-0602-1_7

7.1 Introduction

The world ecosystems have intrinsic ability to recover from toxic waste contamination. However, this remarkable recovery ability has been overstretched in the last few decades as a result of accelerated industrialization in order to keep gait with demands of ever-increasing human population. Consequently, world ecosystems are inundated perpetually with anthropogenic toxic waste releases at levels and frequencies higher than natural recovery rates. Globally, from moderate levels of 1.7×10^6 tons in the 1950s, plastic production rose astronomically to 3.22×10^8 tons in 2016 (Revel et al. 2018). Annually, over 4.0×10^9 tons of plastics are generated globally, most of which remain unaltered for a long period in refuse dump, landfills, and as litter in the environment (Madigan et al. 2012). Across the world, an estimated 5.6 billion pounds of pesticides are discharged yearly in the environment (Donaldson et al. 1999). In the past 50 years, approximately 1.3×10^7 barrels of crude oil have been discharged into Niger Delta environment (Federal Ministry of Environment (FME) 2006). India and China have witnessed astronomical rise in air pollution in the last three decades due to speedy economic growth accompanying rise in energy consumption (Wei et al. 2017a, 2017b).

Globally, air, soil, surface, and groundwater contamination has remained a serious issue due to its adverse health and environmental effects (Kuiper et al. 2004). Noxious environmental contaminants include various classes of inorganic and organic compounds including petroleum hydrocarbons, pesticides, chlorinated hydrocarbons, dyes, heavy metals, radionuclides, and gases (e.g. NO_x, CO_2, SO_2). Remediation of these contaminants using physicochemical and engineering-based decontamination techniques is usually inadequate (Dixon 1996). Besides, they are environmentally intrusive, complex, prohibitively costly, and lacking in public approbation (Niti et al. 2013). These obvious shortcomings have spurred up the involvement of bioremediation approaches. The trending plausible bioremediation strategy for toxic environmental waste attenuation is that which encompasses plant and microbial synergy, particularly at the rhizosphere (rhizoremediation) and phyllosphere (phylloremediation) (Bisht et al. 2014a, 2014b). Although delay in requisite critical biomass attainment, adverse climatic changes, and low tolerance of interacting plants and microorganisms to designated pollutants at certain threshold of concentrations may impede the effectiveness of this strategy; selection of well-adapted plants and microorganisms can help to address these challenges. Nonetheless, the preferential shift to plant-microbe synergy is anchored on several reasons: (1) sustainability, (2) viability, (3) cost-effectiveness, and (4) environmentally friendliness of this strategy. In this chapter, the relationship between plants and microbes in rhizosphere and phyllosphere for remediation of organic and inorganic toxic wastes in air and soil ecosystems is presented. The critical functions of root-endophytes in remediation of soil pollutants are also highlighted.

7.2 Microbe–Plant Relationship in Rhizosphere

Soil is a repository of intricate community of microorganisms where all the intrigues and battle for existence are brought to bear. The contention for survival among the constituent populations of microorganisms is invigorated within the rhizosphere (Parkinson and Waid 1960). The rhizosphere is the most influential ecosystem on our planet with immense energy flow rate (Barriuso et al. 2008), is defined as entire sphere of soil influenced by root and its exudations. Although this very crucial microbial hotspot in soil (Kuzayakov and Blagodatskaya 2015) stretches few millimeters to centimeters from the root (Pivetz 2001; Singleton and Sainsbury 2006; Prashar et al. 2013), its shape and size have no precise delimitation, rather encompasses a territorial gradient in physical, chemical, and biological properties that undergo radial and longitudinal change along the root (McNear 2013). The rhizosphere consists of three separately distinct but interacting components: ectorhizosphere (comprises soil immediately adjoining root); rhizoplane (actual root surface, along with tightly bound particles of soil and microbes), and endorhizosphere (the root tissue including cortex and endodermis) (Barea et al. 2005; Prashar et al. 2013; Brahmaprakash et al. 2017). Rhizosphere size is dependent on the specific plant root structural makeup in relation to its entire biomass. Although grasses offer enormous root surface area due to their fibrous nature in comparison to plants with tap root system (Atlas and Bartha 1987; Marshchner et al. 2002); trees generally have larger root biomass and penetrate deeper into soil than grasses, thus occupying larger volume of soil than grasses (Cook and Hesterberg 2013). Microbial assemblage and functions within rhizosphere are comparatively huge than unvegetated bulk soil. Beyond anchorage, plant roots depositions and exudates benefit root-associated-microorganisms enormously. Root exudations within rhizosphere which varies among species, genus, age, and cultivars of plant and other biotic and abiotic factors (Patkowska 2002) generally include organic materials such as dead fine roots and cell shelling, lysates, CO_2, O_2, ethylene, simple carbohydrates, plant hormones, organic acids, amino acids, sugar phosphate esters, phenolics, vitamins, proteins, enzymes, and mucilage (polysaccharides) (Bais et al. 2006; Prashar et al. 2013). These substances are utilized in the rhizosphere for growth and metabolism and it is utterly responsible for the elevated microbial populations and activities over regions devoid of root influence in the soil. Hence the rhizosphere effects (R/S) on microbial populations, particularly bacteria and fungi could be as high as 2 to 100-fold order of magnitude (Kołwzan et al. 2006; Jussila 2006; Ubogu et al. 2017; Ubogu et al. 2019). Mucilaginous substances and carbohydrate exudations aid huge microbial population growth during early stage of development. During maturity autolysis of some root substances occurs as part of the usual root development process with amino acids and simple sugar exudation (Atlas and Bartha 1987). Microorganisms gravitate toward the root zone in soil by chemotaxis induced by root exudations. Attachment of microorganisms to root surfaces (rhizoplane) is facilitated by agglutinin one of the plant root exudations (Kumar et al. 2007). Root exudation in rhizosphere also benefits plant itself. It promotes reduction of friction between soil and root tips, prevents root desiccation, and maintains soil

structural stability (Rougier and Chaboud 1989). Conversely, microbial activities (which are also influenced by root exudation) alter the operation and pattern of root exudation (Prashar et al. 2013). Root exudate chemical makeup can be modified by soil microorganisms (e.g. rhizobia, fungi, and plant growth promoting bacteria (PGPB)) and hence plant physiology through liberation of different signaling molecules like exopolysaccharides, nod factors, microbe-associated molecular patterns (MAMPs), and volatile organic compound (VOC) (Goh et al. 2013). Many rhizosphere organisms benefit their associated plants in several ways. Some of these organisms which are dinitrogen fixers, legume nodulators, mycorrhizae, nutrient solubilizers, etc. are involved in the synthesis of antibiotics, vitamins, phytohormones, transmission molecules, etc. that either promote growth, suppress pathogens, or cushion abiotic stress in plants (Brahmaprakash et al. 2017). Microbial interactions in rhizosphere enhanced plant nutrients and water uptake by mycorrhizal fungi (e.g. *Acaulospora*, *Archaeospora*, *Entrophospora*, *Gigaspora*, *Glomus*, *Paraglomus*, *Scutellospora*, *Sclerocysts*, etc.), mobilize and solubilize phosphorus (e.g. by *Pseudomonas*, *Bacillus*, *Acinetobacter*, *Rhizobium*, *Penicillium*, *Aspergillus*, etc.), fix nitrogen symbiotically (e.g. *Frankia*, *Rhizobium*, etc.) and non-symbiotically (e.g. *Azotobacter*, *Beijerinckia*, *Derxia*, etc.) produce phytohormones (e.g. auxin, gibberellins, cytokinins, ethylene, abscisic acids) that regulate plant growth, promote plant immunity against pathogens and responses to abiotic stress (which includes drought, salinity, and low temperature), antagonize plant pathogens through antibiosis (e.g. *Pseudomonas fluorescence*) and mycoparasitism (e.g. *Trichoderma harzianum*), degrade soil toxicants, etc. (Spaepen et al. 2007; Krishnaveni 2010; Barat et al. 2016; Brahmaprakash et al. 2017).

7.3 Attenuation of Toxic Waste in the Rhizosphere

7.3.1 Rhizoremediation

Toxic wastes attenuation may occur naturally in the rhizosphere or may be facilitated through human mediation. The attenuation of toxic waste in the rhizosphere ecosystem which is termed rhizoremediation is a sort of phytoremediation that involves pollutants elimination or abatement through reciprocal interactions of root (exudates) and its accompanying microbes. The term rhizoremediation emphasizes the relevant functions of rhizosphere-competent microbes and root exudates in the waste attenuation process (Shukla et al. 2010). Irrespective of the fact that plants and microorganisms can on their own degrade a number of toxic wastes (Frick et al. 1999), rhizoremediation without microbial participation may not be a viable technique for the remediation of a vast array of organic contaminants that are naturally hydrophobic (Chaudhry et al. 2005). Rhizoremediation offers an attractive means of cleaning up polluted soils. Unlike other forms of phytoremediation, pollutant degradation is in situ with high possibility of mineralization. Translocation of toxic waste in plant or atmosphere is also a rarity. However, attenuation of toxic waste in the rhizosphere may have some setbacks as degradation may be hampered by rivalry for

soil nutrient among plants and microorganisms. Plant exudations can also be a major source of carbon substitute for pollutants which can substantially limit the amount of pollutant degraded (Molina et al. 1995). Many plants also have short root systems, thus restricting the remediation process to depth of root area which is a major shortcoming (Pivetz 2001). These shortcomings notwithstanding rhizoremediation still remain one of the most effective, environmentally friendly, and economically viable means of pollutants attenuation in the ecosystem.

7.3.1.1 Rhizoremediation of Toxic Organic Wastes in Soil

Deliberate and accidental small chronic and huge sporadic releases of natural and synthetic toxic organic compounds into the environment particularly soil are regular occurrences across the world. These include petroleum hydrocarbons such as aliphatics, alicyclics, aromatics (e.g. toluene, benzene, ethylene, and xylene), polyaromatics (e.g. benzo(a)pyrene, pyrene, phenanthrene, naphthalene, etc.), chlorinated aliphatics, nitroaromatics, polychlorinated biphenyls, pesticides, herbicides, etc. Significant number of studies revealed elevated rates of attenuation of these organic pollutants occurring in rhizosphere of plants as compared to unvegetated soils. There are many reasons for the speedy breakdown of these organic toxicants in rhizosphere. First, nutrient-rich exudations promote astronomical rise in microbial populations in rhizosphere (Madigan et al. 2012). This swell in microbial populations provides the critical mass required to initiate and accelerate the degradation process. High microbial populations are needed to reduce the lag phase and accelerate bioremediation (Forczek et al. 2001). Second, some of the physicochemical factors limiting effective biodegradation of organic pollutants in soil are optimized within the rhizosphere. Microorganisms particularly mycorrhizae increase nutrients and water absorption in the rhizosphere proving the required moisture content for effective bioremediation. Furthermore, it has been revealed that environmental toxic wastes degradation drops off with soil depth (Olson et al. 2001). Required O_2 dispersion for efficient biodegradation takes place in the range of 30.0 cm soil vertical profile (Vidali 2001). Plant roots growth beyond this range of depth provide adequate aeration through their tilling actions as well as the direct release of O_2 into soil by particularized vas in root called aerenchyma (Muratova et al. 2003; Kuiper et al. 2004; Zalesny et al. 2005). Furthermore, O_2 released is also used for detoxification of some phytotoxic compounds generated under anoxic condition. For instance, *Beggiatoa* including other sulfur bacteria in rhizosphere of most swamp plant employ the released O_2 for the oxidation and detoxification of phytotoxic H_2S (Madigan et al. 2012). Besides N_2 fixation by rhizosphere microorganisms, exudates from roots harbor vast array of organic compounds that may function as reservoir of nitrogen and carbon for microbial growth and sustenance for organisms possessing the ability to degraded organic contaminants (Anderson et al. 1993; Pilon-Smits 2005). Third, exudate or lysates from roots may harbor lipophilic compounds that could improve water solubility of pollutants or stimulate growth of biosurfactant producing microbes (Read et al. 2003; Pilon-Smits 2005). Bioavailability through solubilization of organic pollutants can result from alteration of side groups mediated by plant and microbial produced enzymes

(Chaudhry et al. 2005). Fourth, microorganisms in the rhizosphere can secure accelerated remediation of organic contaminants via organic volatilization (e.g. PAH) or by facilitating organic pollutants humification (Salt et al. 1998), particularly the liberation of oxidoreductase such as peroxidase by microorganisms, similar to plant roots and catalyze contaminants polymerization into soil humic portion and root surfaces (Jussila 2006). Fifth, the liberation of degradative enzymes such as dehalogenase, peroxidase, laccase, nitroreductase, and nitrilase by plant which remains active over a period of time in the rhizosphere also contributes to the accelerated breakdown of organic pollutants in rhizosphere (Schnoor et al. 1995). Sixth, sizable number of organic constituents of root exudates can serve as co-metabolites in organic pollutants breakdown. Seventh, structurally some organic pollutants are related to some of the root exudates which are naturally utilized for growth and metabolism by rhizosphere microorganisms. Thus, microorganisms do not find it difficult to produce enzymes for the breakdown of such structural analogue (Hashmi et al. 2017). For example, organic pollutants having phenolic structure are easily degraded by rhizosphere microorganisms that readily utilize root exudates containing phenolic compounds. Eighth, there is a higher level of horizontal transfer of degradative genes in the rhizosphere. Conjugative plasmids that transfer genes responsible for bacterial adaption in the rhizosphere of polluted soils are stimulated by root exudations (Rohrbacher and St-Arnaud 2016).

There are current and overwhelming body of reports that lend credence to effective and accelerated diminution of petroleum hydrocarbons in root zones of plants over unvegetated contaminated soils (Euliss et al. 2008; Gaskin 2008; Phillips et al. 2009; Ezzatian et al. 2009; Tang et al. 2010a, 2010b; Soleimani et al. 2010; Zand et al. 2011; Ubogu et al. 2019). Ubogu et al. (2019) reported accelerated depletion of total petroleum hydrocarbon (TPH) in the rhizosphere of two wetland plants, *Phragmites australis* and *Eichhnornia crassipes* over unplanted mangrove swamp soil in Niger Delta. They reported a TPH loss of 74.7 and 82.3% in the rhizosphere of *P. australis* and *E. crassipes*, respectively, as against 67.5% loss in unplanted mangrove swamp soil receiving equivalent amount of NPK fertilization and inoculation of hydrocarbon utilizing bacteria and fungi within 120 days period; at a daily degradation rate of 44.64, 49.20, and 40.32 mg/kg/day, respectively. The higher degradative rate witnessed in the rhizosphere of *E. crassipes* was ascribed to increased populations of appropriate hydrocarbon utilizing fungi and bacteria stimulated by NPK fecundation (besides possible effects of root exudations) and ability of *E. crassipes* to absorb and metabolize some components of petroleum hydrocarbons (Nesterenko et al. 2012; Saleh 2016; Mishra and Maiti 2017; Gupta and Balomajumder 2018). Similarly, Gaskin (2008) reported elevated rate of TPH loss in contaminated soil cultivated with three Australian grasses, *Microlaena stipoides*, *Brachiaria decumbens*, and *Cymbopogon ambiguus* than uncultivated contaminated control. Tang et al. (2010a, 2010b) examined influence of fertilizer application together with inoculation of efficient microbial degrading agents along with plant growth-enhancing rhizobacteria in petroleum hydrocarbon contaminated soil planted with fescue, ryegrass, alfalfa, and cotton and reported higher TPH removal rate in planted soil than control. In this study, the rate of attenuation also

varied among species of plant tested and this variation was attributed to the differences in root physiological functions. This further emphasizes the importance of selecting appropriate plants–microbe interactions for maximum attenuation of petroleum hydrocarbon in the rhizosphere ecosystem.

Around the world, past industrial production and use of polychlorinated biphenyls (PCBs) still constitute serious environmental challenges (Passatore et al. 2014). PCBs are persistent toxic xenobiotics that get easily adsorbed onto organic matter in soil rendering its remediation by traditional techniques inefficient or difficult (Willey et al. 2017). However, in addition to being economical and environmentally friendly, rhizoremediation promises to be an easier and efficient clean-up of PCBs in the environment. There are reports of successful attenuation of PCBs in sugar beet rhizosphere (Brazil et al. 1995), reed canary grass, alfalfa, switchgrass, flatpea, deertongue, sericea lespedeza, and tall fescue (Chekol et al. 2004). Chekol et al. (2004) reported increased PCB attenuation in rhizosphere of all the plants investigated. Attenuation rate of 62% was recorded in the rhizosphere against 18% in unplanted soil after 4 months of remediation studies. In this study higher degradation rate of PCB also correlated positively with increased population of microorganisms and enzyme actions in rhizosphere as compared to unplanted soil. Plant root exudations obviously played pivotal part in accelerated attenuation of PCB in rhizosphere ecosystem through induction of PCB-degradative genes among rhizobacteria. Bacterial populations capable of degrading PCB in the rhizosphere are stimulated by root exudations such as coumarins, flavonoids (Donnelly et al. 1994; Gilbert and Crowley 1997), phenolics (Fletcher and Hegde 1995), and *L*-carvone (Gilbert and Crowley 1997).

Pesticides is a generic name for a variety of chemicals used for the eradication or control of pests which include herbicides, fungicides, insecticides, etc. More than 1000 different pesticides are marketed worldwide (Madigan et al. 2012) and these group of chemicals appear to be the most widely spread environmental contaminants in the past century (Schwitzguebel et al. 2006). Persistent pesticides in soil are of great concern because of the dangers they pose to human and environmental health. Undegraded pesticides in soil may be washed into surface water or leashed into groundwater with a high tendency of bioaccumulation into living tissues, some of these pesticides have been linked to cancer, organ failure, and other health issues. These underscore the importance of their accelerated removal from the environment. Like most other organic contaminants, rhizoremediation of pesticides provides a more promising and acceptable offer for their elimination from the environment. Significant number of studies reported enhanced degradation of pesticides in contaminated rhizosphere compared to unvegetated soil. Rainbird et al. (2018) examined degradation of the herbicide sulfonylurea in contaminated agricultural soil planted with Lentils (*Len culinaris*) and unplanted soil and reported an enhanced rate of degradation in planted soil with the presence of higher population of chlorsulfuron-degrading bacteria (*Pseudomonas fluorescens*). Similarly, Bibi et al. (2019) reported enhanced attenuation of the pesticide hexachlorocyclohexane in soil planted with *Solanum nigrum* along with inoculation of effective rhizobacteria code strain ST47, over unplanted inoculated soil. In earlier studies, elevated

pesticide-degrading populations and/or degradation of various pesticides were reported among different plants species over unplanted soil: atrazine in the rhizosphere of corn (Seibert et al. 1981); parathion in rhizosphere of rice (Reddy and Sethunathan 1983); 2.4-D (Sandmann and Loos 1984) and 2,4,5-T in rhizosphere of sugarcane (Boyle and Shann 1995); benthiocarb in rhizosphere of rice (Sato 1989); 1,4-dioxane in the rhizosphere of poplar (Schnoor et al. 1998; Kelley et al. 2001); and Chlorpyrifos in rhizosphere of ryegrass (Korade and Fulekar 2009).

7.3.1.2 Rhizoremediation of Heavy Metals and Radionuclides

Heavy metal is a poorly defined term consisting of transitional metals, metalloids, actinides, and lanthanides (Appenroth 2010), having specific density greater than 5.0 g/cm^3 (Ganesan 2012). These class of metals may also be grouped into three categories: the toxic metals which include Zn, Pb, As, Cu, Cd, Cr, Ni, Sn, Hg, etc.; the precious metals, Ag, Pd, Ru, Au, Pt, etc., and radionuclides, Am, Ra, Th, Cs, U, etc. (Nies 1999; Bishop 2002). Detrimental effects of heavy metal pollution on human health and ecosystems are well documented. Heavy metal tainting the environment is of much concern because of their remarkable toxicity at very minute concentrations (1.0–10.0 mg/L) (Ahemad 2014). Anthropogenic releases and mineral rock weathering are the main source of heavy metal pollution (Kumar et al. 2017). These releases may come from metalliferous mining and refining, atmospheric deposition, waste disposal, agricultural and industrial activities (Ross 1994). Soil is principally the sink for heavy metal releases in the environment (Kirpichtchikova et al. 2006). Unlike organic pollutants, heavy metals are non-biodegradable, therefor have to be taken out or contained within the contaminated site (Andreoni and Zaccheo 2010). Microorganisms have the capacity to remediate heavy metal pollution through a combine array of mechanisms such as metabolic uptake, precipitation, biosurfactant complexation, sorption, biofilm entrapment, and transformation (Parmar and Singh 2014). Siderophore production by rhizosphere microorganisms is known to chelate Fe^{3+}, this same mechanism may be applicable to other trivalent metals such as Cr, Ga, and Al (Schalk et al. 2011) and altering their bioavailability and reduction of toxicity (Mosa et al. 2016). Notwithstanding the fact that some species of plants have capacity to hyperaccumulate heavy metals, their application without microbial symbiotic involvement may not be effective in cleaning up sites with multiple contaminants hence, synergistic approach involving microbe–plant interaction in rhizosphere offers more effective remediation strategy (Wu et al. 2005). Karthika et al. (2017) reported improved root growth and reduction of toxicity in *Vigna mungo*, *Zea mays*, *Sesbania aculeata*, *Phaseolus vulgaris*, and *Vigna radiata* with the co-inoculation of Cr (IV) and resistant strains ARS6 of *Cellulosimicrobium funke* (PGPB). Bolan et al. (2016) evaluated rhizosphere-induced reduction of Cr (VI) among indigenous Australian plants: *Dichantheum sericeum*, *Acacia pubescens*, Enchylaena tomentosa, *Eucalyptus camaldulensis*, *Austrodanthonia richardsonii*, and *Templetonia retusa* and reported rhizosphere effect reduction of Cr (IV) in the range of 2.45–5.07 order of magnitude than unvegetated soil among tested plants. Significantly, increase in microbial activities correlated with Cr (VI) reduction in the rhizosphere. Wu et al. (2006)

reported 40 % improved cadmium accumulation in the root of sunflower and significant reduction of its phytotoxicity with the inoculation of genetically engineered rhizobacteria, *Pseudomonas putida* 06909. Similarly, increased uptake of nickel reportedly occurred in the shoot and leaves of *Alyssum murale* due to rhizospheric activities of three rhizobacteria: *Microbacterium arabinogalactanolyticum*, *Microbacterium liquefaciens*, and *Sphingomonas macrogoltabidus* in comparison with uninoculated control in a study by Abou-Shanab et al. (2006). Radioactive wastes are of great public concern. These types of waste are usually discharged into the environment as a result of nuclear weapon processing and testing, nuclear energy generation, and unintentional releases (Lloyd and Renshaw 2005). Radionuclides are elements that lack physical stability undergoing self-generated decay to emit energy either as electromagnetic waves, particles, or both (NABIR 2003). Many of the mechanisms for microbial remediation of heavy metals apply to radionuclides in soil environment. For instance, the bacterium *Microbacterium flavescens* has been shown to accumulate plutonium by the same mechanism used by microorganisms for iron uptake (siderophore-mediated accumulation) (NABIR 2003). Several bacterial such as *Kineococcus radiotolerans* sp. nov, *Deinococcus*, *Serratia*, *Geobacter*, and *Hymenobacter metalli* sp. nov. have been reported to act on radionuclides in radioactive wastes in the process altering solubility, bioavailability, and mobility of radionuclides (Lloyd 2003; Lloyd and Renshaw 2005; Lloyd and Gadd 2011a, 2011b; Dakora and Phillips 2002; Chung et al. 2010). Similarly, some plants have been recognized as proficient in remediating radionuclides (e.g. *Azolla imbricata*, *M. cordata*, and *P. australis* for phytoremediation of uranium-contaminated soil, *P. multifida* for ^{226}Ra-contaminated soil, and *P. australis* for thorium contaminated soil) based on their phytoremediation factor (PF) (Yadav and Kumar 2019). Although there is paucity of information on microbe–plant interactions in rhizosphere for radioactive wastes attenuation, metal resistant plant growth promoting rhizobacteria (PGPB) are known to enhance plant growth in heavy metal contaminated soils (Ahemad 2014). Therefore, synergistic effects of deliberate inoculation of wild or genetically modified rhizosphere-competent microbes able to remediate radionuclides into the rhizosphere of plants with high radionuclide-tolerance and phytoremediation factor could accelerate radioactive waste attenuation in the rhizosphere.

7.3.1.3 Root-Endophytic Attenuation of Toxic Wastes

One area that has attracted attention in recent years in toxic wastes attenuation in microbe–plant interactions in rhizosphere is the endorhizosphere. This microcosmic region is colonized by a set of soil microbes conjointly known as root-endophytes. Root-endophytes are non-pathogenic microorganisms (bacteria, fungi, and actinomycetes) which inhabit internal root tissue including cortex and endodermis (Schulz and Boyle 2006; Stepniewska and Kuzniar 2013; Kumar et al. 2018). These group of microorganisms are ubiquitous and nearly every species of plant on earth has one species of endophyte (Sessitsch et al. 2004; Germaine et al. 2006; Anyasi and Atagana 2016) and they are probably more abundant in tropical host plants due to their enormous biodiversity (Azevedo et al. 2000). Unlike ectorhizosphere

(Sessitsch et al. 2004; Germaine et al. 2006; Afzal et al. 2014) and rhizoplane microorganisms, they have profound intimate connection and enormous influence on the biochemical and genetic interactions with their host plants (Verma and Gange 2014; Kumar et al. 2018). Although endophytes are generally found in stem, leaves, seeds, and roots of plants, it has been incontrovertibly established that endophytes originate from soil environment (Compant et al. 2012). Except for seed endophytes, the primary point of entry into plant is the root and subsequently domicile in the root cortex or xylem or systematically colonize plant through movement via the vascular system or apoplast (Mahaffee et al. 1997; Quadt-Hallman et al. 1997).

Substantial part of the successes reported in toxic waste attenuation in the rhizosphere is attributable to root-endophytes. Bacteria degradation of recalcitrant pollutants occurs more with endophytes within the rhizosphere in contaminated soil (Siciliano et al. 2001). The increased removal of toxic waste is ascribed to the remarkable capacity of root-endophytes to generate plant growth promoting hormones, antagonize plant pathogens, increased plant nutrients uptake, fix nitrogen, assimilate, transform, and degrade environmental toxicants. These activities contribute to phytotoxicity reduction, improved plant health, growth, and adaptation to designated contaminants which is critical for effective and accelerated attenuation of toxic waste in the rhizosphere. Many endophytes in polluted sites have been reported to exhibit dual roles of pollutant degradation and plant growth promotion (Sheng et al. 2008; Dashti et al. 2009; Becerra-Castro et al. 2011). The involvement of large array of metabolic pathways by microbial endophytes makes them worthful tool in the bioremediation of environmental contaminants (Gai et al. 2009; Kim et al. 2012; Verma and Gange 2014). Numerous studies lend credence to the integral roles played by root-endophytes in the accelerated attenuation of soil pollutants in the rhizosphere. Soleimani et al. (2010) reported 72.0% total petroleum hydrocarbon (TPH) loss from contaminated soil cultivated with *Festuca* spp. infected with endophytic fungi as against 64.0 and 31.0% removal rate in uninfected *Festuca* spp. and uncultivated soil, respectively, from initial TPH amount of 47,400.0 mg/kg, and ascribed these differences to the rise in biomass of plant roots which consequently expanded root surface area and elicitation of microbial ameliorating metabolites like phenols that induced microbial activities in soil. Other reported cases of root-endophyte degradation of organic pollutants include BTEX and TCE degradation by *Acinetobacter lwoffi*, *A. nicotianae*, *Pseudomonas tolaasii*, *P. plecoglossicida*, *P. rhodesiae*, *P. fulva*, *P. jessenii*, *P. veronii*, *P. oryzihabitan*, *Paenibacillus amylolyticus*, and *Bacillus megaterium* in the root of *Populus* cv. Hazadens (Moore et al. 2006). Heavy metal bioremediation by root-endophytic microbes have also been reported. Karnwal (2018) investigated bioremediation of Cd, Cr, Ni, and Zn by biosurfactant producing *Pseudomonas fluorescence* RE1 and RE17 from the root of rice and reported reduced heavy metal concentration in medium by biosorption up to 90 % and above for all metal tested by both stains of *Pseudomonas fluorescence*. Similarly, Govarthanan et al. (2016) reported 59.4 and 51.4% removal rate of Cu and Zn, respectively, from medium by root-endophytic bacterium, *Paenibacillus* sp. RM isolated from *Tridax procumbens* root.

7.4 Microbe–Plant Interactions in Phyllosphere

Similar to rhizosphere, phyllosphere which is the aerial part of plants consists of four main distinct parts: the caulosphere (stem), phylloplane (leaf surface), anthrosphere (flower), and carposphere (fruit) (Bringel and Couee 2015). The phyllosphere microbiomes include bacteria, actinomycetes, molds, yeasts, and algae (Lindow and Brandl 2003; Willey et al. 2017). Bacteria are most dominants of these group of microorganisms. Bacterial population density on leaf surface is estimated to be as high as 10^6 to 10^8 cells per cm^2 (Leveau 2006; Willey et al. 2017). Among the fungi, ascomycetes are the most dominant prior to senescence (Abdelfattah et al. 2015). The orientation and cumulative large surface area offered by the phylloplane makes it the most significant zone for microbial activities and air-borne pollutants entrapment. The size of the phyllosphere varies among plant species. Generally, plants with broad leaves have the capacity to carry higher microbial populations than those with narrow leaves like grasses (Lindow and Brandl 2003). It has been estimated that overall planetary terrestrial leaf phyllosphere colonized by microorganisms could reach 6. 4×10^8 km^2 (Morris and Kinkel 2002). Thus, the phyllosphere and its microbiome interactions exert significant influence on individual plant behavior and many important global processes (Lindow and Brandl 2003). The extent and pattern of microbial interactions in phyllosphere are critically determined by vicissitudes of environmental conditions. These include the level of humidity, ultraviolet radiation, temperature, and nutrients (Lindow and Brandl 2003; Vorholt 2012) which are extremely variable in time and space (Leveau and Lindow 2001; Monier and Lindow 2003). Leaves play crucial roles in aiding phyllosphere microorganisms (Bringel and Couee 2015) by providing anchorage and required nutrients, hence the phyllosphere microbial community structure is influenced by the leaf morphology, chemistry, and growth condition (Kembel and Mueller 2014). Phyllosphere microbiomes also benefit the plant. Substantial number of microbial interactions in the phyllosphere enhances plant health and improves growth via: fixation of nitrogen (Furnkranz et al. 2008), cytokinins (CKs) production which stimulate nitrogen conveyance to plant shoot tissues, indole acetic acid (IAA) production (Romero et al. 2016), protection against desiccation and UV radiation damage through extracellular polymeric substances (EPS) production (Bram et al. 2018), disease prevention through antagonism and competitive exclusion (Innerebner et al. 2011), and remediation of environmental pollutants (Bram et al. 2018).

7.5 Attenuation of Toxic Waste in the Phyllosphere

7.5.1 Phylloremediation

Air pollution is of serious global concern because of its probable trans boundary spread and its link to major health issues (e.g. respiratory and cardiovascular diseases) and environmental hazards. Significant reduction of air pollution can be achieved by cutting down anthropogenic releases of toxic emissions. However,

released emissions may be substantially contained and degraded through phylloremediation process. Phylloremediation involves the trapping and attenuation/degradation of atmospheric pollutants by plants and its phyllosphere microbiomes. Anthropogenic releases of atmospheric pollutants include particulate matter (PM), organic compounds such as polyaromatic hydrocarbons (PAHs), volatile organic compounds (VOCs), formaldehyde and inorganic compounds (e.g. NO_x, CO_2, SO_2, $O_{3)}$ (Weyens et al. 2015). Huge amount of air pollutants is known to be scavenged by above-ground plants parts (Beckett et al. 1998; Popek et al. 2012; Weyens et al. 2015). Annually, approximately 772 tons of PM_{10} is reported to be taken off from the city of Beijing in China by trees (Yang et al. 2005). The long duration of leaves and its microbiomes exposure to atmospheric pollutants have been conjectured as a possible way of developing mechanisms for the adaptation of plant and microorganisms to air pollutants (Wei et al. 2017a, 2017b). Air pollution attenuation mechanisms in the phyllosphere include pollutant adsorption, absorption, sequestration, metabolic assimilation, transformation, and biodegradation by plant leaves and its associated phyllospheric and endophytic microorganisms (Weyens et al. 2015; Wei et al. 2017a, 2017b). For effective and successful remediation of atmospheric pollutants to occur, phyllosphere and rhizosphere synergy is required. Some of the scavenged, undegraded atmospheric pollutants in the phyllosphere are presented for rhizosphere degradation in soil via leaf falls and rain washout. Significant quantum of empirical evidences exists for the bioremediation of atmospheric pollutants in the phyllosphere. Forczek et al. (2001) reported trichloroacetic acid reduction in air sample was due to microorganisms inhabiting phyllosphere of spruce needles. Similarly, Charoenchang et al. (2003), reported pyrene, fluoranthene, and phenanthrene degradation by a consortium of microorganisms isolated from leaves of dried rain tress. Sandhu et al. (2007, 2009) also reported phenol degradation by *Alcaligenes*, *Acinetobacter*, and *Rhodococcus* isolated from bean and maize phyllosphere. Toluene degradation by *Pseudomonas putida* TVA8 from the phyllosphere of *Azalea indica* has also been reported (De Kempeneer et al. 2004).

7.6 Conclusion

Knowledge of the plethora of mutualistic interactions between microorganisms and plant in rhizosphere and phyllosphere and its exploitation provides a robust ground work for the effective attenuation of myriad of toxic organic and inorganic wastes in the ecosystem. While plant and microorganisms can independently remove pollutants from the environment, bioremediation involving the combined action of plants and colligate microbes proffers more viable mode of pollutant attenuation. The accelerated pollutant attenuation occurring within the vicinity of plant (rhizosphere and phyllosphere) is attributable to plant–microbial synergy as they interact with themselves and the pollutants in the ecosystem. Rhizoremediation and phylloremediation offer a viable, sustainable, cost-effective, and environmentally friendly means of attenuating toxic anthropogenic waste releases in the ecosystem.

References

Abdelfattah A, Li Destri Nicosia MG, Cacciola SO et al (2015) Metabarcoding analysis of fungal diversity in the phyllosphere and carposphere of olive (Olea europaea). PLoS One 10:e0131069

Abou-Shanab RAI, Angle JS, Chaney RL (2006) Bacterial inoculants affecting nickel up take by Alyssum murale from low, moderate and high Ni soils. Soil Biol Biochem 38:2882–2889. https://doi.org/10.1016/j.soilbio.2006.04.045

Afzal M, Khan QM, Sessitsch A (2014) Endophytic bacteria: prospects and applications for the phytoremediation of organic pollutants. Chemosphere 117:232–242

Ahemad M (2014) Remediation of metalliferous soils through the heavy metal resistant plant growth promoting bacteria: paradigms and prospects. Arab J Chem 12:1365–1377. https://doi.org/10.1016/j.arabjc.2014.11.020

Anderson TA, Guthrie EA, Walton BT (1993) Bioremediation in the rhizosphere: plant roots and associated microbes clean contaminated soil. Environ Sci Technol 27:2630–2636

Andreoni V, Zaccheo P (2010) Potential for the use rhizobacteria in the sustainable management of contaminated soil. In: Ashraf M, Ozturk M, Ahmad M (eds) Plant adaptation and phytoremediation. Springer, Dordrecht, pp 313–334. https://doi.org/10.1007/978-90-481-9370-7-14

Anyasi RO, Atagana HI (2016) Endophytes: an indicator for improved phytoremediation of industrial waste. In: *Proceedings of the 23rd WasteCon conference* 17–21 October 2016, Emperors Palace, Johannesburg, South Africa

Appenroth K (2010) Definition of "heavy metals" and their role in biological systems. In: Sherameti I, Varma A (eds) Soil heavy metals, Soil biology, vol 19. Springer, Cham, pp 19–29

Atlas RM, Bartha R (1987) Interaction between microorganisms and plants, 2nd edn. The Benjamin/Cummings Publishing Comp. Inc., San Francisco

Azevedo JL, JJr M, Pereira O, Ara WL (2000) Endophytic microorganisms: a review on insect control and recent advances on tropical plants. Electron J Biotechnol 3:40–65

Bais HP, Weir TL, Perry LG, Gilroy S, Vivanco JM (2006) The role of root exudates in rhizosphere interactions with plants and other organisms. Annu Rev Plant Biol 57:233–266

Barat SP, Gupta A, Singh D, Srivastav A (2016) Production of liquid biofertilizer by using *Azotobacter* species and their effect on plant growth. Int J Curr Microbiol App Sci 5(7):654–659

Barea JM, Pozo MJ, Azcon R, Azcon-Aguilar C (2005) Microbial co-operation in the rhizosphere. J Exp Bot 56:1761–1778

Barriuso J, Ramos Solano B, Gutiérrez Mañero FJ (2008) Protection against pathogen and salt stress by four plant growth-promoting rhizobacteria isolated from *Pinus* sp. on Arabidopsis thaliana. Phytopathology 98:666–672

Becerra-Castro C, Kidd P, Prieto-Fernández A, Weyens N, Acea MJ, Vangronsveld J (2011) Endophytic and rhizoplane bacteria associated with Cytisus striatus growing on hexachlorocyclohexane-contaminated soil: isolation and characterisation. Plant Soil 340:413–433

Beckett KP, Freer-Smith P, Taylor G (1998) Urban woodlands: their role in reducing the effects of particulate pollution. Environ Pollut 99:347–360

Bibi A, Un-Nisa W, Qasim A, Malik TH (2019) Rhizoremediation of hexachlorocyclohexane through pesticide contaminated soil by *Solanum nigrum*. J Bioremed Biodegr 10:457. https://doi.org/10.4172/2155-6199.1000457

Bishop PL (2002) Pollution prevention: fundamentals and practice. Tsinghua University Press, Beijing, China

Bisht S, Pandey P, Kaur G, Aggarwal H, Sood A, Sharma S, Kumar V, Bisht NS (2014a) Utilization of endophytic strain *Bacillus* sp. SBER3 for biodegradation of polyaromatic hydrocarbons (PAH) in soil model system. European J Soil. Biology 60:67–76

Bisht S, Kumar V, Kumar M, Sharma S (2014b) Inoculant technology in *Populus deltoides* rhizosphere for effective bioremediation of Polyaromatic hydrocarbons (PAHs) in contaminated

soil, Northern India. Emirates J Food Agric 26(9):458–470. https://doi.org/10.9755/ejfa.v26i9.18436

Bolan N, Kunhikrishnan A, Seshadri B, Naidu R (2016) Rhizoremediation of co-contaminants using Australian native vegetation. In: 18th international conference on heavy metals in the environment 12 to 15 September 2016, Ghent, Belgium

Boyle JJ, Shann JR (1995) Biodegradation of phenol, 2,4-DCP, 2,4-D, and 2,4,5-T in field-collected rhizosphere and nonrhizosphere soils. J Environ Qual 24:782–785

Brahmaprakash GP, Sahu PK, Lavanya G, Nair SS, Gangaraddi VK, Gupta A (2017) Microbial functions of the rhizosphere. In: Singh DP et al (eds) Plant-microbe interactions in agro-ecological perspectives. Springer, Singapore. https://doi.org/10.1007/978-981-10-5813-4_10

Bram WG, Stone EAW, Jackson CR (2018) The role of the phyllosphere microbiome in plant health and function. Annu Plant Rev 1:1–24. https://doi.org/10.1002/9781119312994.apr0614

Brazil GM, Kenefick L, Callanan M, Haro A, de Lorenzo V, Dowling DN, O'Gara F (1995) Construction of a rhizosphere pseudomonad with potential to degrade polychlorinated biphenyls and detection of bph gene expression in the rhizosphere. Appl Environ Microbiol 61:1946–1952

Bringel F, Couee I (2015) Pivotal roles of phyllosphere microorganisms at the interface between plant functioning and atmospheric trace gas dynamics. Front Microbiol 6:486. https://doi.org/10.3389/fmicb.2015.00486

Charoenchang N, Pinphanichakarn P, Pattaragulwanit K, Thaniyavarn S, Juntongjin K (2003) Utilization of agricultural materials to enhance microbial degradation of polycyclic aromatic hydrocarbons in soil. J Sci Res 28:1–3

Chaudhry Q, Bloom-Zandstra M, Gupta S, Joner EJ (2005) Utilizing the synergy between plants and microorganisms to enhance breakdown of organic pollutants in the environment. Environ Sci Pollut Res 12:34–48

Chekol T, Vough LR, Chaney RL (2004) Phytoremediation of polychlorinated biphenyl-contaminated soils: the rhizosphere effect. Environ Int 30:799–804

Chung AP, Lopes A, Nobre MF, Morais PV (2010) *Hymenobacter perfusus* sp. nov., *Hymenobacter flocculans* sp. nov. and *Hymenobacter metallic* sp. nov. three new species isolated from uranium mine waste water treatment system. Syst Appl Microbiol 33:436–443

Compant S, Sessitsch A, Mathieu F (2012) The 125th anniversary of the first postulation of the soil origin of endophytic bacteria – a tribute to M.L.V. Galippe. Plant Soil 356:299–301

Cook RL, Hesterberg D (2013) Comparison of trees and grasses for rhizoremediation of petroleum hydrocarbons. Int J Phytoremediation 15(9):844–860

Dakora FD, Phillips DA (2002) Root exudates as mediators of mineral acquisition in low-nutrient environments. Plant Soil 13:35–47

Dashti N, Khanafer M, El-Nemr I, Sorkhoh N, Ali N, Radwan S (2009) The potential of oil-utilizing bacterial consortia associated with legume root nodules for cleaning oily soils. Chemosphere 74:1354–1359

De Kempeneer L, Sercu B, Vanbrabant W, van Langenhove H, Verstraete W (2004) Bioaugmentation of the phyllosphere for the removal of toluene from indoor air. Appl Microbiol Technol 64:284–288

Dixon B (1996) Bioremediation is here to stay. ASM New 62:527–528

Donaldson D, Kiely T, Grube A (1999) Pesticide's industry sales and usage 1998-1999 market estimates. US Environmental Protection Agency; Washington (DC): Report No. EPA-733-R-02-OOI. Available from: http://www.epa.gov/oppbead/pesticides/99pestsales/market-estimates.pdf

Donnelly PK, Hegde RS, Fletcher JS (1994) Growth of PCB-degrading bacteria on compounds from photosynthetic plants. Chemosphere 28:981–988

Euliss K, Ho CH, Schwab AP, Rock S, Banks AK (2008) Greenhouse and field assessment of phytoremediation for petroleum contaminants in a riparian zone. Bioresour Technol 99:1961–1971

Ezzatian R, Voussoughi M, Yaghmaei S, Abedi-Koupai J, Borghei M, Ghafoori S (2009) Effects of *Puccinellia distans* and Tall Fescue on modification of C/N ratios and microbial activities in crude oil-contaminated soils. Pet Sci Technol 27:452–463

Federal Ministry of Environment (FME) (2006) Niger delta resource damage assessment and restoration project. Conservation Foundation Lagos, WWF UK and CEESP-IUCN Commission on Environmental, Economic, and Social Policy

Fletcher JS, Hegde RS (1995) Release of phenols by perennial plant roots and their potential importance in bioremediation. Chemosphere 31:3009–3016

Forczek ST, Matucha M, Uhlirova H, Albrechtova J, Fuksova K et al (2001) Biodegradation of trichloroacetic acid in Norway spruce/soil system. Biol Plant 44:317–320

Frick CM, Farrell RE, Germida JJ (1999) Assessment of phytoremediation as an in-situ technique for cleaning oil contaminated sites. Petroleum Technology Alliance Canada, Calgary, pp 1–88

Furnkranz M, Wanek W, Richter A, Abell G, Rasche F, Sessitsch A (2008) Nitrogen fixation by phyllosphere bacteria associated with higher plants and their colonizing epiphytes of a tropical lowland rainforest of Costa Rica. ISME J 2:561–570. https://doi.org/10.1038/ismej.2008.14

Gai CS, Lacava PT, Quecine MC, Auriac MC, Lopes JRS, Araujo WL, Miller TA, Azevedo JL (2009) Transmission of *Methylobacterium mesophilicum* by *Bucephalogonia xanthophis* for paratransgenic control strategy of citrus variegated chlorosis. J Microbiol 47:448–454. https://doi.org/10.1007/s12275-008-0303-z

Ganesan V (2012) Rhizoremediation: a pragmatic approach for remediation of heavy metal-contaminated soil. In: Zaidi A et al (eds) Toxicity of heavy metals to legumes and bioremediation. Springer, Wien

Gaskin BSE (2008) Rhizoremediation of hydrocarbon contaminated soil using Australian native grasses. Ph.D Thesis, Flinders University of South Australia

Germaine K, Liu X, Cabellos G, Hogan J, Ryan D, Dowling DN (2006) Bacterial endophyte-enhanced phyto-remediation of the organochlorine herbicide 2,4-dichlorophenoxyacetic acid. FEMS Microbiol Ecol 57:302–310

Gilbert ES, Crowley DE (1997) Plant compounds that induce polychlorinated biphenyl biodegradation by Arthrobacter sp. strain B1B. Appl Environ Microbiol 63(5):1933–1938

Goh HH, Sloan J, Malinowski R, Fleming A (2013) Variable expansion expression in *Arabidopsis* leads to different growth responses. J Plant Physiol 171:329–339. https://doi.org/10.1016/j.jplph.2013.09.009

Govarthanan M, Mythili R, Selvankumar T, Kamala-Kannan S, Rajasekar A, Chang YC (2016) Bioremediation of heavy metals using an endophytic bacterium *Paenibacillus* sp. RM isolated from the roots of tridax procumbens. Biotech 6(2):242

Gupta A, Balomajumder C (2018) Simultaneous phytoremediation of Cr (VI) and phenol using aquatic macrophyte water hyacinth: effect of pH and concentration. Int J Sci Res Chem 3 (2):60–69

Hashmi MZ, Kumar V, Verma A (2017) Xenobiotics in the soil environment: monitoring, toxicity and management. Springer, New York. https://doi.org/10.1007/978-3-319-47744-2

Innerebner G, Knief C, Vorholt JA (2011) Protection of Arabidopsis thaliana against leaf-pathogenic *Pseudomonas syringae* by *Sphingomonas* strains in a controlled model system. Appl Environ Microbiol 77:3202–3210

Jussila MM (2006) Molecular biomonitoring during rhizoremediation of oil-contaminated soil. Ph. D Dissertation, University of Helsinki, Finland

Karnwal A (2018) Use of bio-chemical surfactant producing endophytic bacteria isolated from rice root for heavy metal bioremediation. Pertanika J Trop Agric Sci 41(2):699–714

Karthika C, Elangovana N, Kumara TS, Govindharajua S, Barathia S, Ovesc M, Padikasan Indra Arulselvia PI (2017) Characterization of multifarious plant growth promoting traits of rhizobacterial strain AR6 under Chromium (VI) stress. Microbiol Res 204:65–71. https://doi.org/10.1016/j.micres.2017.07.008

Kelley SL, Aitchison EW, Deshpande M, Schnoor JL, Alvarez PJ (2001) Biodegradation of 1,4-dioxane in planted and unplanted soil: effect of bioaugmentation with Amycolata sp. CB1190. Water Res 35:3791–3800

Kembel SW, Mueller RC (2014) Plant traits and taxonomy drive host associations in tropical phyllosphere fungal communities. Botany 92:303–311. https://doi.org/10.1139/cjb-2013-0194

Kim TU, Cho SH, Han JH, Shin YM, Lee HB, Kim SB (2012) Diversity and physiological properties of root endophytic Actinobacteria in native herbaceous plants of Korea. J Microbiol 50:50–57. https://doi.org/10.1007/s12275-012-1417-x

Kirpichtchikova TA, Manceau A, Spadini L, Panfili F, Marcus MA, Jacquet T (2006) Speciation and solubility of heavy metals in contaminated soil using X-ray microfluorescence, EXAFS spectroscopy, chemical extraction, and thermodynamic modeling. Geochim Cosmochim Acta 70:2163–2190

Kołwzan B, Adamiak W, Grabas K, Pawełczyk A (2006) Introduction to environmental microbiology. Oficyna Wydawnicza Politechniki Wrocławskiej, Wrocław

Korade DL, Fulekar MH (2009) Rhizoremediation of Chlorpyrifos in mycorrhizospheric soil using rye grass. J Hazard Mater 30:1344–1350

Krishnaveni MS (2010) Studies on phosphate solubilizing bacteria (PSB) in rhizosphere and non-rhizosphere soils in different varieties of foxtail millet (Setaria italica). Int J Agric Food Sci Techol 1(1):23–39

Kuiper I, Lagendijk EL, Bloemberg GV, Lugtenberg JJ (2004) Rhizoremediation: a beneficial plant-microbe interaction. Mol Plant-Microbe Interact 17(1):6–15

Kumar R, Bhatia R, Kukreja K, Behl RK, Dudeja SS, Narula N (2007) Establishment of *Azotobacter* on plant roots: chemotactic response, development and analysis of root exudates of cotton (*G. hirusitum* L.) and wheat (*T. aestivum* L). J Basic Microbiol 47:436–439

Kumar SS, Kadier A, Malyan SK, Ahmad A, Bishnoi NR (2017) Phytoremediation and rhizoremediation: uptake, mobilization and sequestration of heavy metals by plants. In: Singh DP et al (eds) Plant-microbe interactions in agro-ecological perspectives. Springer, New York. https://doi.org/10.1007/978-981-10-6593-4_15

Kumar M, Sharma S, Gupta S, Kumar V (2018) Mitigation of abiotic stresses in *Lycopersicon esculentum* by endophytic bacteria. Environ Sustain 1(1):71–80

Kuzayakov Y, Blagodatskaya E (2015) Microbial hotspots and hot moments in soil: concept and review. Soil Biol Chem 83:25. https://doi.org/10.1016/j.soilboio.2015.01.025

Leveau JHJ (2006) Microbial communities in the phyllosphere. In: Riederer M, Muller C (eds) Biology of the plant cuticle. Blackwell, Oxford, pp 334–367

Leveau JHJ, Lindow SE (2001) Appetite of an epiphyte: quantitative monitoring of bacterial sugar consumption in the phyllosphere. Proc Natl Acad Sci U S A 98:3446–3453

Lindow SE, Brandl MT (2003) Microbiology of the phyllosphere. Appl Environ Microbiol 69 (4):1875–1883

Lloyd JR (2003) Microbial reduction of metals and radionuclides. FEMS Microbiol Rev 27:411–425

Lloyd JR, Gadd GM (2011a) The geomicrobiology of radionuclides. Geomicrobiol J 28 (5-6):383–386

Lloyd JR, Gadd GM (2011b) The geomicrobiology of radionuclides. Geomicrobiol J 28:383. https://doi.org/10.1080/01490451.2010.547551

Lloyd JR, Renshaw JC (2005) Bioremediation of radioactive waste: radionuclide–microbe interactions in laboratory and field-scale studies. Curr Opin Biotechnol 16:254–260. https://doi.org/10.1016/j.copbio.2005.04.012

Madigan MT, Martinko JM, Stahl DA, Clark DP (2012) Brock biology of microorganisms, 19th edn. Benjamin Cumming Publishing, San Francisco

Mahaffee WF, Kloepper JW, Van Vuurde JWL, Van der Wolf JM, Van den Brink M (1997) Endophytic colonization of *Phaseolus vulgaris* by *Pseudomonas fluorescens* strain 89B-27 and Enterobacter asburiae strain JM22. In: Ryder MHR, Stevens PM, Bowen GD (eds) Improving plant productivity in rhizosphere bacteria, vol 180. CSIRO, Melbourne

Marshchner P, Mario W, Lieberei R (2002) Seasonal effects on microorganisms in the rhizosphere of two tropical plants in a polyculture agroforestry system in Central Amazonia. Braz Biol Fert Soils 35:68–71

McNear DH (2013) The rhizosphere - roots, soil and everything in between. Nat Educ Knowl 4(3):1

Mishra S, Maiti A (2017) The efficiency of *Eichhornia crassipes* in the removal of organic and inorganic pollutants from wastewater: a review. Environ Sci Pollut Res 24:7921–7937

Molina M, Araujo R, Bond JR (1995) Abstract: Dynamics of oil degradation in coastal environments: effects of bioremediation products and some environmental parameters. Symposium on Bioremediation of Hazardous Wastes: Research, Development, and Field Evaluations, August 10-12, 1995, Rye Brook, NY. EPA/600?r-95/076

Monier JM, Lindow SE (2003) Differential survival of solitary and aggregated bacterial cells promotes aggregate formation on leaf surfaces. Proc Natl Acad Sci U S A 100:15977–15982. https://doi.org/10.1073/pnas.2436560100

Moore F, Barac T, Borremans B, Oeyen L, Vangronsveld J, Der LD, Campbell CD, Moore ER (2006) Endophytic bacterial diversity in poplar trees growing on a BTEX-contaminated site: the characterisation of isolates with potential to enhance phytoremediation. Syst Appl Microbiol 179(2):318–329

Morris CE, Kinkel LL (2002) Fifty years of phyllosphere microbiology: significant contributions to research in related fields. In: Lindow SE, Hecht-Poinar EI, Elliott V (eds) Phyllosphere microbiology. APS Press, St. Paul, pp 365–375

Mosa KA, Saadoun I, Kumar K, Helmy M, Dhankher OP (2016) Potential biotechnological strategies for the cleanup of heavy metals and metalloids. Front Plant Sci 7:303. https://doi.org/10.3389/fpls.2016.00303

Muratova A, Hubner T, Narula N, Wand H, Turkovskaya O, Kuschk P, Jahn R, Merbach W (2003) Rhizosphere microflora of plants used for the phytoremediation of bitumen-contaminated soil. Microbiol Res 158:151–161

NABIR (2003) Bioremediation of metals and radionuclides. 2nd ed. http://www.lbl.gov/NABIR/generalinfo/primersguides.html

Nesterenko MA, Kirzhner F, Zimmels Y, Armon R (2012) Eichhornia crassipes ability to remove naphthalene from waste water in the absence of bacteria. Chemosphere 87:1186–1191

Nies DH (1999) Microbial heavy-metal resistance. Appl Microbiol Biotechnol 51:730–750

Niti C, Sunita S, Kamlesh K, Rakesh K (2013) Bioremediation: an emerging technology for remediation of pesticides. Res J Chem Environ 17(4):88–105

Olson PE, Flechter JS, Philp PR (2001) Natural attenuation/phytoremediation in the vadose zone of a former industrial sludge basin. Environ Sci Pollut Res Int 8:243–249

Parkinson D, Waid JS (1960) The ecology of soil fungi. Liverpool University Press, Liverpool

Parmar N, Singh A (2014) Geomicrobiology and biogeochemistry. Springer, Dordrecht. https://doi.org/10.1007/978-3-642-41837-2

Passatore L, Rossetti S, Juwarkar AA, Massacci A (2014) Phytoremediation and bioremediation of polychlorinated biphenyls (PCBs): state of knowledge and research perspectives. J Hazard Mater 278:189–202

Patkowska E (2002) The role of rhizosphere antagonistic microorganisms in limiting the infection of underground parts of spring wheat. Electron J Pol Agric Univ 5:1–10

Phillips LA, Greer CW, Farrell RE, Germida JJ (2009) Field-scale assessment of weathered hydrocarbon degradation by mixed and single plant treatments. Appl Soil Ecol 42:9–17

Pilon-Smits E (2005) Phytoremediation. Annu Rev Plant Biol 56:15–39

Pivetz BE (2001) Phytoremediation of contaminated ground water at hazardous waste sites. In: Ground water issue. EPA/540/S-01/500

Popek R, Gawronska H, Wrochna M, Gawronski SW, Saebo A (2012) Particulate matter on foliage of 13 woody species: deposition on surfaces and phytostabilization in waxes - a 3-year study. Int J Phytoremediation 15:245–256

Prashar P, Kapoor N, Sachdeva S (2013) Rhizosphere: its structure, bacterial diversity and significance. Rev Environ Sci Biotechnol. https://doi.org/10.1007/s11157-013-9317-z

Quadt-Hallman A, Hallman J, Kloepper JW (1997) Bacterial endophytes in cotton: location and interaction with other plant associated bacteria. Can J Microbiol 43:254–259. https://doi.org/10.1139/m97-035

Rainbird B, Bentham RH, Soole KL (2018) Rhizoremediation of residual sulfonylurea herbicides in agricultural soils using *Lens culinaris* and a commercial supplement. Int J Phytoremediation 20 (2):104–113

Read DB, Bengough AG, Gregory PJ, Crawford JW, Robison D, Scrimgeour CM, Young IM, Zhang K, Zhang X (2003) Plant roots release phospholipid surfactants that modify the physical and chemical properties of soil. New Phytol 157:315–326

Reddy BR, Sethunathan N (1983) Mineralization of parathion in the rice rhizosphere. Appl Environ Microbiol 45(3):826–829

Revel M, Chatel A, Mouneyrac C (2018) Micro(nano)plastics: a threat to human health? Curr Opin Environ Sci Health 1:17–23

Rohrbacher F, St-Arnaud M (2016) Root exudation: the ecological driver of hydrocarbon rhizoremediation. Agronomy 6:19. https://doi.org/10.3390/agronomy6010019

Romero FM, Marina M, Pieckenstain FL (2016) Novel components of leaf bacterial communities of field-grown tomato plants and their potential for plant growth promotion and biocontrol of tomato diseases. Res Microbiol 167:222–233

Ross S (1994) Toxic metals in soil-plant systems. Wiley, Chichester

Rougier M, Chaboud A (1989) Biological functions of mucilages secreted by roots. Symp Soc Exp Biol 43:449–454

Saleh HM (2016) Biological remediation of hazardous pollutants using water hyacinth: a review. J Biotechnol Res 2(11):80–91

Salt DE, Smith RD, Raskin I (1998) Phytoremediation. Annu Rev Plant Physiol 49:643–668

Sandhu A, Halverson LJ, Beattie GA (2007) Bacterial degradation of airborne phenol in the phyllosphere. Environ Microbiol 2:383–392

Sandhu A, Halverson LJ, Beattie GA (2009) Identification and genetic characterization of phenol-degrading bacteria from leaf microbial communities. Microb Ecol 57:276–285

Sandmann ERIC, Loos MSA (1984) Enumeration of 2,4- D degrading microorganisms in soils and crop plant rhizospheres using indicator media: high populations associated with sugarcane (*Saccharum officinarum*). Chemosphere 13:1073–1084

Sato K (1989) Interrelationships between microorganisms and plants in soil. Elsevier, New York, pp 335–342

Schalk IJ, Hannauer M, Braud A (2011) New roles for bacterial siderophores in metal transport and tolerance. Environ Microbiol 13:2844–2854. https://doi.org/10.1111/j.1462-2920.2011.02556.x

Schnoor JL, Licht LA, McCutcheon SC, Wolfe NL, Carreira LH (1995) Phytoremediation of organic and contaminants. Environ Sci Technol 29:318–323

Schnoor JL, Aitchison EW, Kelley SL, Alvarez PJJ (1998) Phytoremediation and bioaugmentation of 1,4-dioxane. Abstr Adv Biol Syst Rem Conf March 1998:87–91

Schulz B, Boyle C (2006) What are endophytes? In: Schulz BJE, Boyle CJC, Sieber TN (eds) Microbial root endophytes. Springer, Berlin, pp 1–13

Schwitzguebel JP, Meyer J, Kidd P (2006) Pesticides removal using plants: phytodegradation versus phytostimulation. In: Mackova M et al (eds) Phytoremediation rhizoremediation. Springer, Cham, pp 179–198

Seibert K, Fuehr F, Cheng HH (1981) In theory and practical use of soil-applied herbicides symposium. European Weed Resource Society, Paris, pp 137–146

Sessitsch A, Reiter B, Berg G (2004) Endophytic bacterial communities of field grown potato plants and their plant-growth-promoting and antagonistic abilities. Can J Microbiol 50:239–249

Sheng X-F, Xia J-J, Jiang C-Y, He L-Y, Qian M (2008) Characterization of heavy metal-resistant endophytic bacteria from rape (*Brassica napus*) roots and their potential in promoting the growth and lead accumulation of rape. Environ Pollut 156:1164–1170

Shukla KP, Singh NK, Sharma S (2010) Bioremediation: development, current practices and perspectives. Genet Eng Biotechnol J 3:1–20

Siciliano SD, Fortin N, Mihoc A, Wisse G, Labelle S, Beaumier D, Ouellette D, Roy R, Whyte LG, Banks MK, Schwab P, Lee K, Greer CW (2001) Selection of specific endophytic bacterial genotypes by plants in response to soil contamination. Appl Environ Microbiol 67:2469–2475. https://doi.org/10.1128/AEM.67.6.2469-2475.2001

Singleton P, Sainsbury D (2006) Dictionary of microbiology and molecular biology, 3rd edn. John Wiley and Sons Ltd., London

Soleimani M, Afyuni M, Hajabbasi MA, Nourbaksh F, Sabzalian MR, Christensen JH (2010) Phytoremediation of an aged petroleum contaminated soil using endophyte infected and non-infected grasses. Chemosphere 81:1084–1090

Spaepen S, Vanderleyden J, Remans R (2007) Indole-3-acetic acid in microbial and microorganism-plant signalling. FEMS Microbiol Rev 31(4):425–448

Stepniewska Z, Kuzniar A (2013) Endophytic microorganisms-promising applications in bioremediation of greenhouse gases. Appl Microbiol Biotechnol 97:9589–9596

Tang JC, Wang RG, Niu XW, Wang M, Chu HR, Zhou QX (2010a) Characterization of petroleum-contaminated soil: effect of different influencing factors. Biogeosciences 7:3961–3969

Tang JC, Wang RG, Niu XW, Wang M, Chu HR, Zhou QX (2010b) Characterization of petroleum-contaminated soil: effect of different influencing factors. Biogeosciences 7:3961–73969

Ubogu M, Akponah E, Vinking GE, Loho NG (2017) Assessment of the hydrocarbon utilizing mycoflora of the root zones of saccharum officinarum. SF J Mycol 2:1

Ubogu M, Odokuma LO, Akponah A (2019) Enhanced rhizoremediation of crude oil contaminated mangrove swamp soil using two wetland plants (*Phragmites australis* and *Eichhornia crassipes*). Braz J Microbiol. https://doi.org/10.1007/s42770-019-00077-3

Verma VC, Gange AC (2014) Advances in endophytic research. Springer, Delhi. https://doi.org/10.1007/978-81-322-1575-2_7,

Vidali M (2001) Bioremediation: an overview. Pure Appl Chem 73:1163–1172

Vorholt JA (2012) Microbial life in the phyllosphere. Nat Rev Microbiol 10:828–840

Wei X, Lyu S, Yu Y, Wang Z, Liu H, Pan D, Chen J (2017a) Phylloremediation of air pollutants: exploiting the potential of plant leaves and leaf-associated microbes. Front Plant Sci 8:1318. https://doi.org/10.3389/fpls.2017.01318

Wei X, Lyu S, Yu Y, Wang Z, Liu H, Pan D, Chen J (2017b) Phylloremediation of air pollutants: exploiting the potential of plant leaves and leaf-associated microbes. Front Plant Sci 8:1318. https://doi.org/10.3389/fpls.2017.01318

Weyens N, Thijs S, Popek R, Witters N, Przybysz A, Espenshade J, Gawronska H, Vangronsveld J, Gawronski SW (2015) The role of plant–microbe interactions and their exploitation for phytoremediation of air pollutants. Int J Mol Sci 16:25576–25604. https://doi.org/10.3390/ijms161025576

Willey JM, Sherwood LM, Woolverton CJ (2017) Prescott's microbiology, 10th edn. McGraw-Hill Education, New York, p 10121

Wu SC, Cao ZH, Li ZG, Cheung KC, Wong MH (2005) Effects of biofertilizer containing N-fixer, P and K solubilizers and AM fungi on maize growth: a greenhouse trial. Geoderma 125:155–166

Wu CH, Wood TK, Mulchandani A, Chen W (2006) Engineering plant-microbe symbiosis for rhizoremediation of heavy metals. Appl Environ Microbiol 72(2):1129–1134

Yadav D, Kumar P (2019) Phytoremediation of hazardous radioactive wastes. IntechOpen, London. https://doi.org/10.5772/intechopen.88055

Yang J, McBride J, Zhou J, Sun Z (2005) The urban forest in Beijing and its role in air pollution reduction. Urban For Urban Green 3:65–68

Zalesny JRS, Bauer EO, Hall RB, Zalesny JA, Kunzman J, Rog CJ, Riemenschhneinder DE (2005) Clonal variation in survival and growth of hybrid poplar and willow in an in-situ trial on soils heavily contaminated with petroleum hydrocarbons. Int J Phytoremediation 7:177–197

Zand AD, Khodaei HR, Nabibidhendi GR, Mehrdadi N (2011) Rhizoremediation of total petroleum hydrocarbons (TPHS) under the effect of plant species in Iran. In: Proceedings of the 12th International Conference of Environmental Science and Technology. Rhodes, Greece, 8-10 September, 2011

Biotransformation of Pollutants: A Microbiological Perspective

8

Jupinder Kaur and S. K. Gosal

Abstract

Microorganisms perform an important function in many of the biological processes that sustain ecosystem. Degradation or detoxification of toxic contaminants is one of such process which contributes towards sustainability of environment. Microorganisms such as bacteria, fungi, and actinomycetes can utilize wide range of substrates as their energy and carbon source. This attribute of microbes makes them suitable candidate in the remediation process of pollutants. The research interest in biotransformation of pollutants has been intensified recently, as mankind is looking for the sustainable ways to clean up the hazardous pollutants. The process of biotransformation harnesses the potential of diverse microbes to decompose, transform, or assimilate the broad spectrum of toxic materials like stiff alloys, hydrocarbons, pharmaceutical content, polychlorinated biphenyls, pesticides, etc. Natural transformation processes are non specific, time consuming and less productive. So, microbial transformations are very beneficial in bioremediation as they are more specific and productive.

Keywords

Bioremediation · Environmental pollutants · Microorganisms · Microbial transformation · Toxic contaminants

J. Kaur (✉) · S. K. Gosal
Department of Microbiology, Punjab Agricultural University, Ludhiana, India
e-mail: jupinderkaur@pau.edu

© The Author(s), under exclusive licence to Springer Nature Singapore Pte Ltd. 2021

V. Kumar et al. (eds.), *Rhizobiont in Bioremediation of Hazardous Waste*,
https://doi.org/10.1007/978-981-16-0602-1_8

8.1 Introduction

Presence of contaminants in soil, air, or water is one of the major problems of every country. Heavy metals, pesticides, and hydrocarbons are among the examples of commonly encountered pollutants. These harmful pollutants are not only a serious threat to our environment but these toxic contaminants will interfere in the functioning of natural processes also. The presence and persistence of these pollutants in natural system like soil or air cause extensive harm as these pollutants accumulate in the tissues of plants and animals leading to mutations and sometimes even death. So, management of these toxic contaminants is the major focus of researchers in these days. There are many methods like incineration, pump and treat systems, etc. which aim to reduce, remove, or mitigate the effects of toxic contaminants. But each of these conventional methods has risk associated with them apart from their drawbacks (cost and effectiveness).

The prominent organizations like USEPA "(United States Environmental Protection Agency)" prefer the process of biotransformation to control pollutants (US EPA 2006). The process of biotransformation uses microbes like bacteria, fungi, and actinomycetes for detoxification and degradation of pollutants. There are many studies which highlight the potential of microbes in treatment of contaminants in effective and economical way. Microbes with their activities lead to complete mineralization of toxic compounds to the end products which are not harmful to health and environment. There are many microbes which are able to degrade, assimilate, or consume hydrocarbons, heavy metals, pesticides, etc. resulting in non-toxic end products. So, this ability of microbes to manage toxic pollutants helps in cleanup of many contaminated sites. So, microbes are not only boon for the process of biotransformation of pollutants but also for the various other remediation techniques also. In this chapter, we will emphasize on the contribution of biotransformations in remediation of pollutants with microbes as our center of attraction.

8.2 Pollutants/Toxic Contaminants

Pollutants or contaminants are the substances which may be naturally present in the nature but they are serious hazard for the health of human and their surrounding if present in concentration greater than the permissible threshold limit. These contaminants when present in higher concentration pose a risk of toxicity and they even affect various non-target organisms also. The presence of these toxicants can lead to undesirable changes in physico-chemical and biological characteristics of air, water, and soil. So, elimination of the hazardous waste or toxic pollutants from the environment is very essential for sustainable functioning of environment and ecosystem.

Vast arrays of microorganisms are inhabitant of soil or other natural resources (Gosal and Kaur 2017). These microbes possess many functional activities like nitrogen fixation, phosphate solubilization, production of plant growth promoting

hormones, etc. (Gosal et al. 2017). Apart from these activities, the diverse catabolic abilities of microbes (like their efficiency to harness xenobiotic composites as their carbon or energy source) act as boon in the bioremediation field as microbes can utilize diverse range of compounds as substrates leading to their decomposition or transformation to non-toxic end products.

8.3 Prominent Source of Toxic Compounds

There are number of ways by which environment can be polluted. The source of these contaminants can be natural as well as anthropogenic. The natural source of waste like remains of animals, dead plants, rotten fruits, and vegetables very rarely affects the environment in negative way. But, the waste produced from human activities or anthropogenic sources is full of harmful contaminants. Sometimes, the release of toxicants into environment can be the intentional human activity also for monetary benefits. The presence of pollutants in environment interferes with the many natural occurring processes. Industrial effluents are source of many pollutants like heavy metals, radionuclides, etc. Due to lack of municipal services dealing with waste management, inadequate ways of waste disposal are adopted, which also contribute toward accumulation of toxic contaminants. Another prominent source of pollutants is excessive use of agrochemicals (fertilizers, manures as well as pesticides) and use of untreated sewage, saline, or waste water for irrigation. Apart from this, atmosphere also contributes toward accumulation of pollutants. Gaseous pollutants from industries mix up with air leading to origination of pollution source. Acid rain and contaminated dust are examples. The various prominent sources of pollutants are explained in Fig. 8.1.

8.4 Bioremediation: Biotransformations, Biodegradation, and Biocatalysis

The contaminants present in the soil or water can undergo many fates. These toxicants can have many negative impacts on the human heath as well as environment. The bioremediation of these toxic pollutants is very essential as these contaminants pose a serious threat to mankind and ecosystem. There are many remediation technologies prevailing nowadays. Each remediation technology has its own advantages as well as drawbacks.

Bioremediation is the most promising approach for the elimination of contaminants or pollutants from natural environment like air, water, or soil. This technology of waste remediation exploits microbes with diverse functional abilities. However, the remediation technology exploiting plants (phytoremediation) is also the hot topic of talk for environmentalists. Keeping in view the sustainability and safety of environment, B3 technology is gaining interest of researchers. B3 refers to biodegradation, biotransformation, and biocatalysis. Sometimes these terms can be

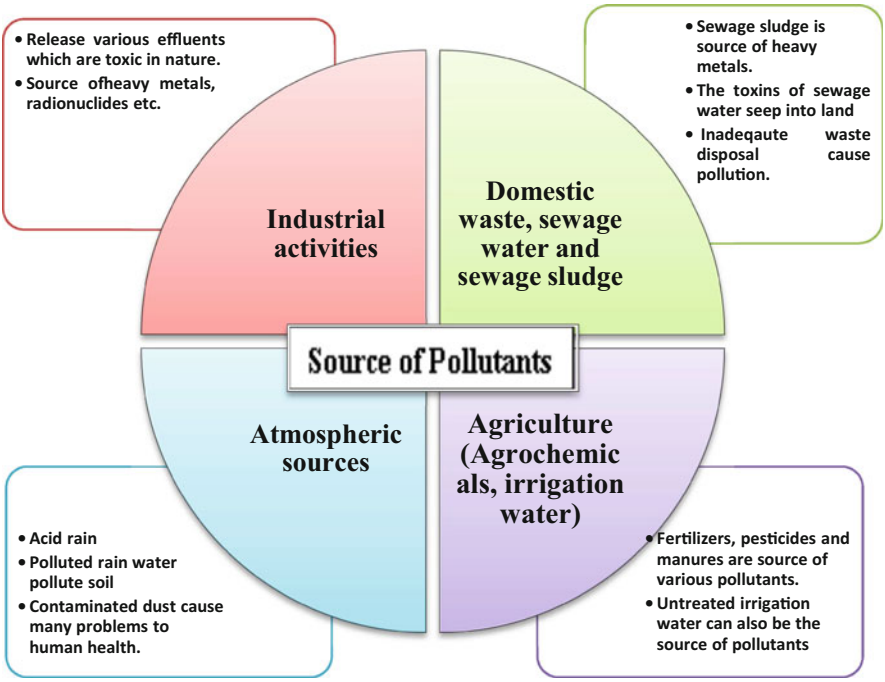


Fig. 8.1 The various causes of pollutants

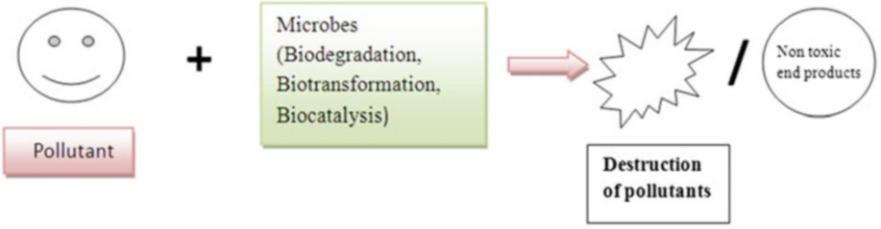


Fig. 8.2 Role of Microbes in remediation of pollutants

overlapping also. These three mechanisms work synergistically for the complete remediation of any toxicant.

Biodegradation refers to breakdown of pollutants by microbes into environmental safe end products in single step or sequence of stages. Biotransformation refers to transformation of pollutants into non-toxic form by alteration or modification in their structure. Biocatalysis refers to use of microbes or enzymes to speed up the transformation or degradation reactions (Fig. 8.2). So, biocatalysis can work synergistically with biodegradation or biotransformation to enhance the effectiveness of these processes.

8.5 Biotransformations and Microbes

Biotransformation refers to the degradation or decomposition of pollutants using microbes or any other biological method. The process of biotransformation uses the mitigation processes like natural attenuation, biostimulation, and bioaugmentation (Fig. 8.3).

In natural attenuation, the soil indigenous microflora is used and the process of decomposition or degradation is totally dependent on natural conditions. The process of biostimulation is also dependent on native microflora of soil but in this process nutrients or other substances are added which speed up the process of decomposition. Bioaugmentation process utilizes non-native microflora also, for the process of contaminant decomposition. Sometimes, genetically modified organisms, capable of degrading specific pollutant, are also used in this process. So, biotransformation process is a vital process for the cleanup of hazardous pollutants.

The process of biotransformation is also used in combination with the other traditional or conventional methods of pollutant remediation to increase the effectiveness of those processes (Vidali 2001). The various other methods of pollutant management usually involve removal of contaminants from the site and their disposal by incineration or by land filling (Speight and Lee 2000). But, with the ever increasing human population, the land area for the remediation technologies like land filling or incineration is decreasing. Moreover, the toxins from landfills seep down into the ground resulting in pollution of groundwater and soil. The gaseous pollutants produced from the process of incineration lead to pollution of air and environment. So, the traditional methods like landfilling, incineration, composting, bioslurry reactor, land farming, and biopiling do not ensure the complete cleanup of toxic pollutants. Additionally, the cost of these techniques is quite high relative to their effectiveness. The use of microbes for the management of

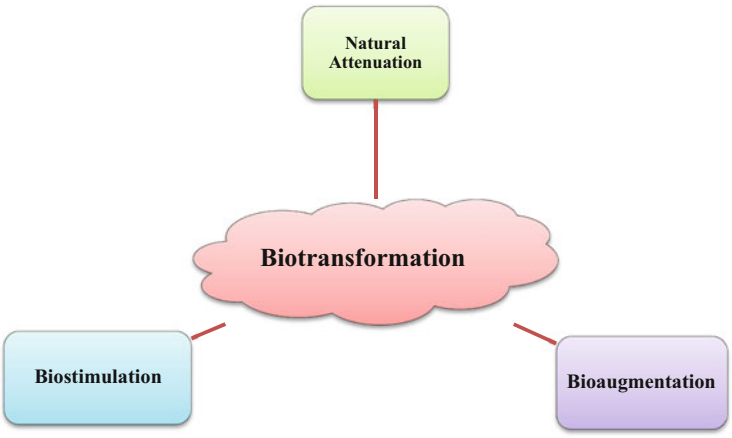


Fig. 8.3 Mitigation processes used in biotransformation

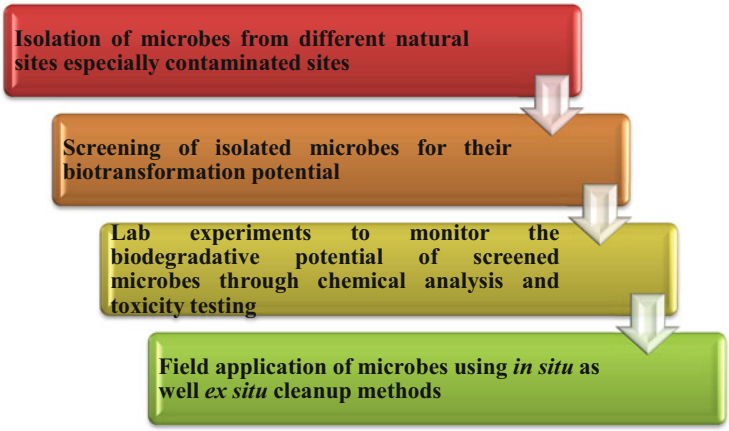


Fig. 8.4 Biotransformation using microbes: the basic procedure

contaminants has full potential. There are some basic steps employed for the use of any microbe in the biotransformation process which are described in Fig. 8.4.

Biotransformation using microbes is employed as purification process for polluted soil. Microbial biotransformation is of two types: in situ or ex situ. In situ biotransformation does not need excavation. In these, contaminants are treated in the place in which they are identified whereas ex situ biotransformation method involves excavation of polluted soil prior to treatment. In situ biotransformation has many advantages over ex situ biotransformation processes as it is not expensive and large amount of soil can be processed. However, in situ biotransformation takes more time than ex situ and is complicated to administer sometimes.

8.6 Mechanism of Biotransformation

The basic underlying principle behind the microbial transformation or biotransformation is mineralization and cometabolism. Mineralization refers to the process of converting organic substances to inorganic end products. The end products formed usually are either non-toxic or less toxic than the parent substrate. The process of mineralization is carried out by consortium microbes. The word consortium here refers to combination of two or more than two beneficial bacteria that with their biodegradative potential carry out the biotransformation process better than single microbe (Shelton and Tiedje 1984).

In the process of cometabolism, partial transformation occurs, leading to the formation of an intermediate product. This intermediate product can serve as energy or carbon source to microbes and thus can be utilized by them. However, sometimes this intermediate can be toxic to the microbial cells. The biotransformation process using microbes can be aerobic or anaerobic depending upon the type of pollutant to be degraded and the type of microbes to be employed in degradation process. In

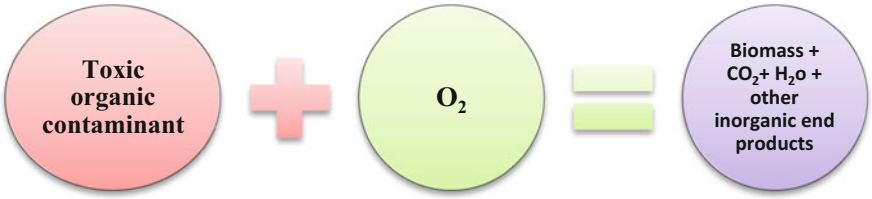


Fig. 8.5 Aerobic biotransformation mechanism

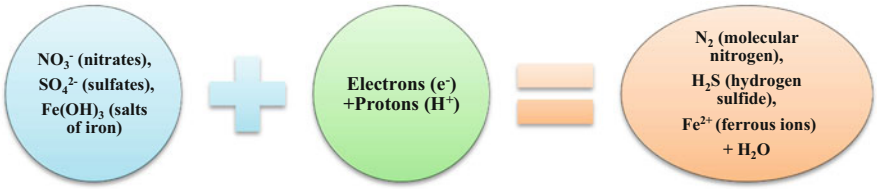


Fig. 8.6 Anaerobic biotransformation mechanism

aerobic biotransformation process, O_2 (molecular oxygen) receives electrons from organic pollutants and acts as terminal electron acceptor (Fig. 8.5). So, by addition of oxygen, oxidation of organic pollutant occurs with simultaneous reduction of oxygen to water. Some microorganisms like chemoautotrophic or lithotrophic bacteria, in order to gain energy, oxidize the inorganic contaminant (reduced) instead of using organic substrate.

Sometimes, with the activities of aerobic bacteria, the level of oxygen starts depleting. This leads to build up of anerobic conditions. In such conditions, terminal electron acceptor other than oxygen is required to carry out the process of transformation, mineralization, and cometabolism. There are many anerobic bacteria that use nitrate, sulfate, or iron salts as terminal electron acceptor as alternative to oxygen and can continue the process of biotransformation. Such transformation is called anerobic biotransformation (Fig. 8.6).

Anaerobic biotransformation is a many step process. Firstly, polymeric contaminants are broken down into monomeric by the process of hydrolysis. Then the final step is usually carried out by methanogens, denitrifying bacteria, or sulfate reducing bacteria to carry out the further decomposition to monomeric substances to alcohol, acids (soluble), hydrogen, and carbon dioxide.

8.7 Examples of Microbial Transformations

There are many remediation technologies available. But the selection of appropriate technology depends on many factors like type of pollutant, time allotted for cleanup, budget for cleanup, etc. Microbial biotransformation is employed mainly for the conversion of several toxic impurities or other wide range of contaminants like heavy metals, pesticides, pharmaceuticals, and hydrocarbons (Karigar and Rao

2011). The basic chemical reactions like isomerization, condensation, oxidation, reduction, functional groups introduction, hydrolysis, and formation of new carbon bond form the basis of microbial transformations. Microbial biotransformation has emerged as an imperative tool in bioremediation field. The characteristics of microbes like high surface to volume ratio, high expansion rate, and high rate of metabolism make them ideal choice for biotransformation of toxic pollutants. These processes are carried under sterile conditions as presence of contaminants can lead to the formation of faulty end products. Some common examples of microbial transformations are as under:

8.7.1 Transformation of Pollutants

Cleanup of polluted sites using microbes has gained momentum due to awareness regarding environment sustainability and human health issues. Microbes are used for the bioremediation of wide range of pollutants like hydrocarbons, radionuclides, polyaromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and pharmaceuticals.

Xenobiotic pollutants have been biotransformed using both aerobic and anaerobic bacteria. The examples of aerobic genera include *Bacillus*, *Escherichia*, *Pseudomonas*, *Gordonia*, *Moraxella*, *Rhodococcus*, *Micrococcus* etc., whereas the anaerobic types include *Desulfotomaculum*, *Desulfovibrio, Pelatomaculum*, *Syntrophobacter*, *Syntrophus*, and methanogens spp. (Chowdhury et al. 2008). PCB (Polychlorinated Biphenyls) has been degraded very effectively by *Pseudomonas* and *Bacillus.* The biotransformation of carcinogenic azo compounds has also been observed by the action of bacteria like *Pseudomonas*, *Acetobacter*, and *Klebsiella.* The non-chlorinated compounds like compounds like acetone, benzene, cyclohexane, styrene, dioxane, etc. can be catabolized by *Mycobacterium vaccae* (DiGioia et al. 2008). Anaerobic methanogens are also able to degrade many recalcitrant pollutants.

8.7.2 Biotransformation of Petroleum

The contamination from petrochemical industries is the topic of major concern. Accidental leakage is the principal basis of soil and water pollution by hydrocarbons. The remediation of hydrocarbon impurity from soil and water is very important as some petrochemicals are carcinogenic in nature (Das and Chandran 2010). There are several microbes which play role in the biodegradation of oil contaminants by conversion of them into non-toxic form. There are many genera of bacteria, fungi as well as yeast which have been reported to be efficient degraders of petroleum hydrocarbons. Bacterial genera, such as *Actinocorallia*, *Bacillus*, *Brevibacterium*, *Corynebacterium* sp., *Flavobacterium* sp., *Klebsiella*, *Pseudomonas fluorescens*, *P. aeruginosa*, *Rhizobium,* etc. and fungal genera such as *Amorphoteca*, *Aspergillus*, *Cephalosporium*, *Neosartorya*, *Penicillium*, *Talaromyces* have been isolated from petroleum sites. These bacterial and fungal genera were found to perform an important function in bioremediation of oil spills (Koul and Fulekar 2013).

8.7.3 Transformation of Pesticides

Pesticides are the formulations used in cultivation of agricultural crops for the control of unwanted pests. But, the presence of these pesticides in soil or environment is of great risk as these residues undergo biomagnification via food chain thus act as threat to human and animal health. Keeping this in view, many pesticides have been banned also. So, microbial biotransformations are of great interest in this field for the detoxification of pesticides.

a. The herbicide dalapon which is a chlorinated fatty acid is transformed into pyruvate by *Arthrobacter species* (Fig. 8.7). This herbicide is used as source of energy and carbon by bacteria so this conversion is the result of microbial metabolism.
b. Conversion of DDT to DDE by bacteria is example of microbial catabolism. The reaction mechanism is dehalogenation (Fig. 8.8). Such type of reactions fall under the category of cometabolism as microbes do not obtain energy from these molecules. They just modify the pollutants. However, the toxicity of modified product can be more or less than the parent product.

Apart from hydrocarbons, pesticides, etc., there are various other examples of microbial transformation like biotransformation of steroids and sterols, biotransformation of antibiotics. Such transformations have significant contribution in research and welfare of mankind.

8.8 Factors Affecting Microbial Transformation

The concentration of contaminants, their toxicity level, the biodegradation potential of microbes, the environmental conditions are among the major factors affecting the process of microbial biotransformation. The detailed explanation of various factors affecting microbial transformation is given in Fig. 8.9.



Fig. 8.7 Biotransformation of herbicide dalapon to pyruvic acid by bacteria (metabolism)



Fig. 8.8 Biotransformation of DDT pesticide to DDE by dechlorination (Cometabolism)

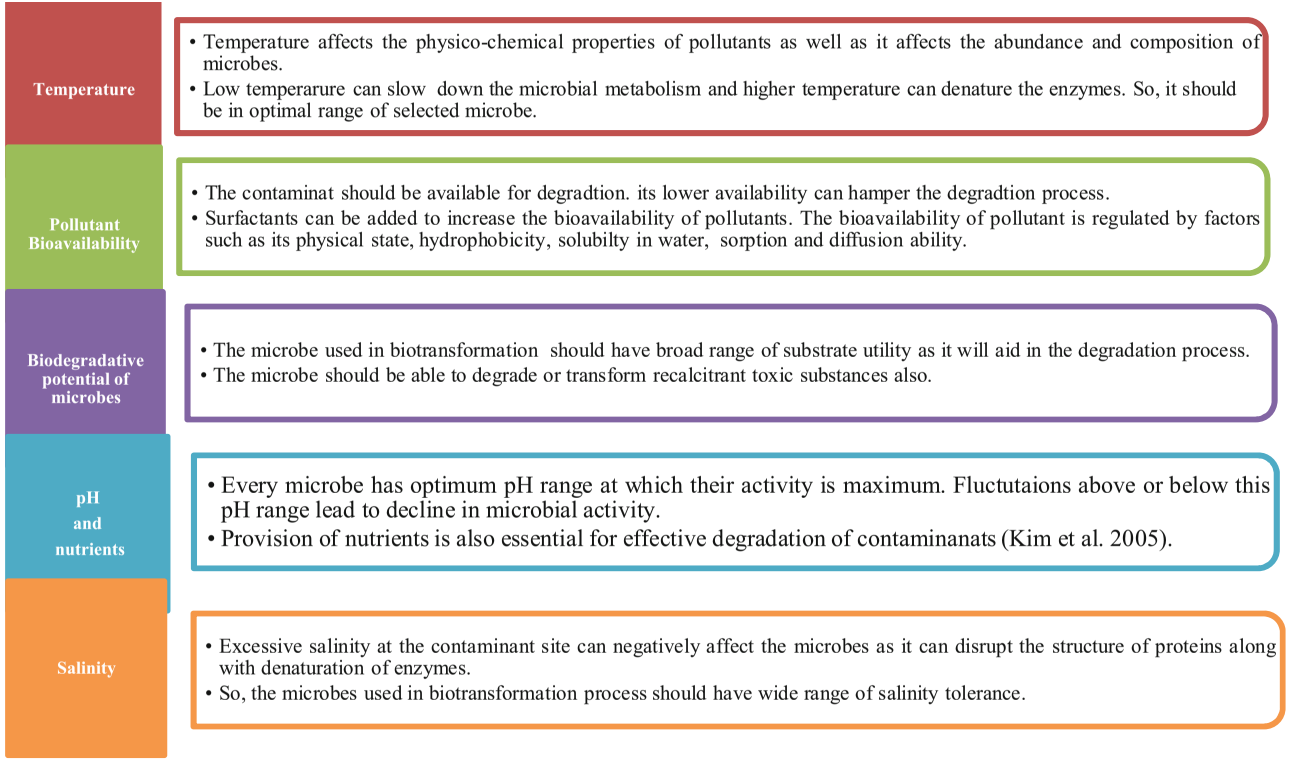


Fig. 8.9 Various factors affecting the process of microbial transformations

8.9 Future Prospects

Biotransformation of toxic contaminants using microbes is a promising remediation technology for cleanup of polluted sites. But, use of molecular approaches like genomics, proteomics, metagenomics, and other advanced molecular tools in this field can provide a good insight into the main pathways used by microbes for the degradation or transformation of toxic pollutants. The information from these studies can be major breakthroughs in bioremediation technologies as these tools can also widen the capability of organisms to accommodate to variable environmental conditions for better degradation or transformation of toxic pollutants.

8.10 Conclusion

Nowadays, biotransformation is the preferred remediation technology used for the cleanup of various contaminates sites. However, the success of this remediation technique relies on the use of adequate microbes capable of effective biodegradation. Sometimes, the prevailing environmental conditions are not optimal for biotransformation of pollutants. Therefore, biotransformation will be the effective remediation technology for reduction and elimination of harmful impurities provided that the microbes used are effective degraders and conditions are favorable for decomposition.

References

Chowdhury A, Pradhan S, Saha M (2008) Impact of pesticides on soil microbiological parameters and possible bioremediation strategies. J Ind Microbiol 48(1):114–127

Das N, Chandran P (2010) Microbial degradation of petroleum hydrocarbon contaminants: an overview. Biotechnol Res Int 2011:941810

DiGioia D, Michelles A, Pierini M (2008) Selection and characterization of aerobic bacteria capable of degrading commercial mixtures of low– ethoxylated nonyl phenols. J Appl Microbiol 104 (1):231–242

Gosal SK, Kaur J (2017) Microbial inoculants: a novel approach for better plant microbiome interactions. In: Kumar V, Kumar M, Sharma S, Prasad R (eds) Probiotics in agroecosystem. Springer, Singapore, pp 269–289

Gosal SK, Kaur J, Kaur J (2017) Plant growth-promoting rhizobacteria: a probiotic for plant health and productivity. In: Kumar V, Kumar M, Sharma S, Prasad R (eds) Probiotics and plant health. Springer, Singapore, pp 589–600

Karigar CS, Rao SS (2011) Role of microbial enzymes in the bioremediation of pollutants: a review. Enzyme Res 2011:11

Kim SJ, Choi DH, Sim DS, Oh YS (2005) Evaluation of bioremediation effectiveness on crude oil-contaminated sand. Chemosphere 59(6):845–852

Koul S, Fulekar MH (2013) Petrochemical industrial waste: bioremediation techniques an overview. Int Adv Res Technol 2(7):1–47

Shelton DR, Tiedje JM (1984) Isolation and partial characterization of bacteria in an anaerobic consortium that mineralizes 3-chlorobenzoic acid. Appl Environ Microbiol 48:840–848
Speight JG, Lee S (2000) Environmental technology handbook, 2nd edn. Taylor & Francis, New York
US EPA (2006) In situ and ex situ biodegradation technologies for remediation of contaminated sites report No. EPA/625/R-06/015. Office of Research and Development National Risk Management Research Laboratory, United States Environmental Protection Agency, Cincinnati
Vidali M (2001) Bioremediation. An overview. Pure Appl Chem 73:1163–1172

9 Plant–Microbe Interactions in Bioremediation of Toxic Wastes in Tropical Environment

Angela Chika Udebuani, Chidinma Ogochukwu Ukachukwu, Emmanuel Uzoma Onweremadu, and Ifeanyi Charles Okoli

Abstract

Pollution occurs through natural and anthropogenic activities. Toxic substances generated from different sources may accumulate in the soil and water bodies and potentially alter their physicochemical properties and ecosystem function. Although several environmental remediation methods have traditionally been tried with some success, bioremediation processes have been found eco-friendlier and cost-effective. Plant-assisted bioremediation, a remediation method that utilizes green plants and their associated microflora to eliminate contaminants from the soil or environment has been found commercially applicable because of its cost-effectiveness among other benefits. Phytoextraction, rhizofiltration, phytostabilization, and phytovolatilization among others are techniques commonly used to remove heavy metals and inorganic contaminants from polluted environments. Endophytes such as bacterial or fungal organisms that live within or between healthy plant tissues are known to portray either obligate or facultative association along with complex interaction with their host plant, which may be mutualistic and antagonistic in nature. Plant root exudates also contribute to plant–microbe interaction due to the fact that these exudates provide important nutrients and energy for associated soil microorganisms.

A. C. Udebuani (✉) · C. O. Ukachukwu
Department of Biotechnology, Federal University of Technology Owerri, Owerri, Nigeria
e-mail: angela.udebuani@futo.edu.ng

E. U. Onweremadu
Department of Soil Science, Federal University of Technology Owerri, Owerri, Nigeria

I. C. Okoli
Department of Animal Science and Technology, Federal University of Technology Owerri, Owerri, Nigeria
e-mail: ifeanyi.okoli@futo.edu.ng

© The Author(s), under exclusive licence to Springer Nature Singapore Pte Ltd. 2021

V. Kumar et al. (eds.), *Rhizobiont in Bioremediation of Hazardous Waste*,
https://doi.org/10.1007/978-981-16-0602-1_9

Chemotaxis influences the movement of bacteria to plant root by the attraction of root exudates that exist between the soil and the rhizosphere. Specifically, the natural ability of most rhizospheric bacteria to tolerate environmental contaminants has lent them to phytoremediation use, especially in removing organic pollutants from food crops. Similarly, the ability of some plant species to be tolerant to specific stress in a time-dependent manner is being exploited in phytoremediation processes. For example, maintenance of high antioxidant levels that are capable of detoxifying toxic reactive oxygen species is associated with a plant's ability to tolerate environmental stress. Therefore, information on rhizospheric microorganisms and their benefits in phytoremediation processes should continually be updated, especially in tropical environments where cost is a critical factor. Furthermore, screening of plants to identify those with phytoremediation potentials, especially in tropical regions of the world that harbor rich plant biodiversity is imperative for cost-effective bioremediation of polluted environments.

Keywords

Toxic waste · Pollution · Detoxification · Phytoremediation · Rhizosphere · Endophytes

9.1 Introduction

Environmental pollution has continued to increase globally due to anthropogenic activities of man linked to urbanization, industrialization, mineral exploitation, and modern agricultural practices. Pollutants released into the environment may persist and pose threats to the biosphere. Environmental degradation issues have therefore become important concerns of governments and environmental organizations all over the world. It is now broadly accepted that polluted environments are a threat to human health, and this realization in recent times has steered global efforts at pollution control sites, in order to either mitigate the adverse health risks or to enable ecosystems recovery. Although several environmental remediation methods have traditionally been tried with some success, researchers continue to explore better and environmentally friendlier treatment methods, such as bioremediation processes.

Bioremediation is the use of microorganisms and plants in the conversion of pollutants into less harmful materials by natural biological processes (ELC 2008). As a pollution treatment option, bioremediation offers the possibility of degrading various contaminants by natural biological activities. It is therefore increasingly being employed in solid waste cleanup operations, due to its comparatively low cost and environmental impact than the more conventional clean-up technologies (Ojumu et al. 2005). Earlier reports by Blaylock et al. (1997) showed that a 50–65% reduction in remediation costs was made possible through bioremediation approaches instead of conventional methods like excavation and landfilling (Chibuike and Obiora 2014).

In bioremediation processes, naturally occurring microorganisms (bacteria and fungi) or plants use their enzymes and other metabolites to convert pollutants into less harmful compounds. Bioremediation is essentially controlled by several microbial factors and environmental factors like soil physical and nutrient characteristics (Agwu and Kalu 2012). Two basic approaches (in situ and ex situ techniques) have been applied to the bioremediation processes, depending on the nature of pollution at a site. According to Naik and Duraphe (2012), while in situ techniques are applied at the site with nominal disruption, ex situ techniques are applied to materials that have been removed from the site through excavation or pumping.

Contaminants like petroleum hydrocarbons, alcohols, solvents, industrial chemicals, pesticides, coal tars, chlorinated solvents, and poly-nuclear aromatic hydrocarbons have been shown to be biodegradable (Naik and Duraphe 2012), although some may take longer time and may require some form of augmentation (Udebuani et al. 2012). Furthermore, the success of bioremediation predicated on the appropriateness of the selected candidate organisms used in the process. For example, microorganisms isolated from the polluted site have been shown to possess inherent mechanisms that they utilize in converting pollutants into less harmful substances (Ojuederie and Babalola 2017). Similarly, microorganisms could be genetically engineered to convert pollutants to non-hazardous substances (Gupta et al. 2016). Specifically, numerous research efforts have exploited the capacity of indigenous microorganisms to sequester, precipitate, or change the oxidation status of different pollutants in the bioremediation processes (Gupta et al. 2016; Kang et al. 2016). In some cases, the application of a group of bacterial organisms may be preferred to using one strain (Ojuederie and Babalola 2017). For example, biofilm which is groups of microorganisms growing in an exudate made up of polysaccharides (Balcázar et al. 2015; Teschler et al. 2015) are being exploited for more efficient bio-sorption and bio-mineralization of metal ions based on their exopolysaccharide production associated with their processes (François et al. 2012).

The rhizosphere is the narrow area of nutrient-enriched soil adjoining the plant roots, which is influenced by the root exudates and the activities of microbes known as rhizospheric microorganisms (Venturi and Keel 2016a, b). Rhizospheric microorganisms associated with plant roots aid bioremediation through a process termed phytoremediation. Phytoremediation processes have been reported to be a particularly inexpensive, environmentally friendly, and relatively effective technique for restoring polluted sites (Jan and Parray 2016; Ojuederie and Babalola 2017). Candidate plants selected for phytoremediation processes are usually hyper-accumulators of pollutants, which may be of low biomass efficiency (Choudhary et al. 2017) or non-hyper-accumulators that exhibit high biomass yield and rapid growth (Udebuani and Ozoh 2007; Choudhary et al. 2017). For example, the sunflower plant (*Helianthus annuus*) is employed in phytoremediation processes due to its capacity to hyper-bio-accumulate heavy metals, in addition to other characteristics such as enhanced translocation of mineral elements, efficient heavy metal detoxification, good rooting system, and rapid growth rate (Muszynska and Hanus-Fajerska 2015).

Indeed, phytoextraction is increasingly being preferred over other methods used for the remediation of polluted sites because of the added beneficial effects of rhizobacteria associated with plant roots (Ojuederie and Babalola 2017). Phytoextraction has also been shown to be commercially viable (Slatter 2013). The natural ability of most rhizospheric bacteria to tolerate environmental contaminants has lent them to phytoremediation use, especially for the removal of organic pollutants in food crops. These organisms thrive near the rhizosphere of the host plant and through direct or indirect mechanisms make soil nutrients available for plant growth, synthesize plant hormones, and also safeguard the plant against harmful organisms, while performing other soil amendment functions (Ahemad and Kibret 2014; Nehra and Choudhary 2015). These rhizobacteria may include *Erwinia*, *Flavobacterium*, *Micrococcus*, *Pseudomonas*, *Serratia*, *Chromobacterium*, *Caulobacter*, *Azospirillum*, *Azotobacter*, and *Agrobacterium* genera (Bhattacharyya and Jha 2012)

Thus, several tropical plants and their associated microorganisms may possess inherent mechanisms that would make them candidates for use in the phytoremediation of polluted environments. Such candidate plants should not only be able to provide a viable habitat for its associated microbes but also should be able to improve soil's physical and nutrient qualities. The rhizospheric microorganisms in return should be able to enhance the important physiological parameters responsible for optimal plant growth. The root-associated organisms should also be able to ensure soil nutrient cycling by fixing nitrogen and by sequestering soil nutrients (Gkorezis et al. 2016). These properties and their interactions in phytoremediation processes are important for effective bioremediation. Therefore, information on rhizospheric microorganisms and their benefits in phytoremediation processes should continually be updated, especially in tropical environments where cost is a critical factor. This chapter reviews the current knowledge on plant–microbe interactions in bioremediation of toxic wastes in tropical environments.

9.2 Physicochemical, Socioeconomic, and Health Impacts of Pollution

Chemical substances existing in nature exert deleterious effects on humans and their ecosystem. The existence of these substances has far-reaching consequences on several tropical ecosystems and the services derivable from them for the benefit of mankind. An environment is polluted when there is an unfavorable change in its physical, chemical, and biological characteristics, which can greatly affect environmental health. Pollution occurs through both natural and anthropogenic activities. Intensified urban and industrial activities, modernized agricultural practices, mining, and intensive exploitation of the natural environment (Brassington et al. 2007; Ontoyin and Agyemang 2014; Mbewe et al. 2016) among others are the major anthropogenic causes of environmental pollution. The toxic substances generated from these activities can spread to remote areas, far from the source of pollution through hydrological pathways (Blas et al. 2006). Studies have shown that several

toxic substances and their transformed products are persistent and bio-cumulative (Davies 1999; Adeola 2004; Theodorakis et al. 2012). Because of these qualities, they are regarded as the most dangerous group of chemicals in the natural ecosystem. For example, polycyclic aromatic hydrocarbons (PAHs), originating from crude oil may persist in the environment (Theodorakis et al. 2012). Of great concern is the soil environment which helps in sustaining ecosystem services, and whose physicochemical and biological properties may be compromised due to pollution (Pouyat et al. 2007). Since the soil serves as a general sink for many substances, toxicants emitted from different sources may accumulate in the soil and potentially alter its physicochemical properties (Hagan et al. 2012).

Soil physical characteristics include particle size distribution or soil textural class, soil structure (including micropore and macropore) constituting the total soil porosity and bulk density (in the range 1.1–1.5 g cm^{-3}). Soil physical properties are important in accessing soil productivity and potential plant root penetration in the soil (Pouyat et al. 2007; Steele et al. 2010). Soil chemical properties include pH, conductivity, and nutrient contents. Hagan et al. (2012) reported that in urban polluted soils, chemical properties showed greater changes than the physical ones. Pollutants generally reduce soil fertility, alter soil microbial distribution and abundance, and lower hydrological function (infiltration) and pH (Holman-Dodds et al. 2003; Cook and Ni 2007). Alterations in soil pH, cation exchange capacity, nutrient retention, especially storage of carbon and nitrogen, make the soil lose its ability to bind toxic substances such as heavy metals, thereby making metals more available (Farfel et al. 2005). Soil biota which contributes to ecosystem processing may also be affected. Important bacterial activities recorded in soils include decomposition of organic matter and nutrient transformation as exemplified by nitrogen fixation and denitrification (conversion of nitrate NO_3^- ion to N_2 gas). The sensitivity of soil invertebrates to chemical substances has also been reported (Reddy et al. 1996; Dureja and Rayendra 2012). Earthworms that contribute to the complex processing of the ecosystem through the decomposition of litter, cycling of nutrients, and formation of soils are susceptible to pesticides and even herbicides (Frampton et al. 2006; Dureja and Rayendra 2012).

In many tropical countries, toxic substances are indiscriminately discharged directly into the aquatic environment (rivers, lakes, streams, and ponds) from industrial activities and indirectly through runoffs from sources such automobile emissions, agrochemicals, and waste dump sites (Li et al. 2008; Zhaoyong et al. 2015). The occurrence, effects, and fate of these chemical substances in humans and aquatic organisms have been widely documented (Batayneh 2010; Zhang et al. 2011; Zhang et al. 2013). For example, high levels of these chemical substances alter the physicochemical properties of water bodies, with potential threats to the aquatic ecosystem. Some of the reported alternations include decreased pH, increased biochemical and chemical oxygen demands, increased turbidity, and reduction in light penetration in pollution, which may cause an impact in aquatic environment (Al-Taaniel et al. 2015; Zhaoyong et al. 2015). Heavy metals from industrial, agricultural, and mining processes also have some direct effect on the physicochemical properties of water, inhibiting microbial activity, and thus,



Fig. 9.1 Mangrove forest impacted by an oil spill in the Niger Delta, Nigeria

reducing nutrients supply to higher aquatic life (Davis et al. 2003; Zhaoyong et al. 2015), since the aquatic environment is diverse in nature, supporting different species of microorganisms, plants, and animals such as fish, amphibians, insects, crustaceans, snails, mussels, etc. Such negative impacts of pollution of water bodies usually start with its effects on its physical and chemical properties (Bassem 2020; Hassan 2008; Khan 2003), which are important in the functioning and maintenance of its ecological processes. Their inability to sustain ecosystem services due to pollution is, however, the driving force impacting human health.

Oil pollution in the aquatic environment, for example, may deposit thick oil films on water bodies, thereby preventing oxygen and light penetration into the water bodies. Inhibition of photosynthetic processes in primary producers such as algae, plants, cyanobacteria, etc. destroys the source of food for growth and reproduction of higher organisms. Oil pollution, therefore, leads to death and behavioral changes in animals such as birds that have physical contact with the oil through their feeding habits. Oil spillage also destroys the spawning, nursery, and feeding grounds of many aquatic organisms, for instance, the mangrove forest in Niger Delta area of Nigeria (Fig. 9.1) has devastated by crude oil pollution arising from incessant spillage (Duke 2016; Zhang et al. 2019; CEHRD 2019). Similarly, urban and agricultural runoffs have contributed to eutrophication in lakes and ponds which destroys fish and other relevant animals in the food chain.

Environmental pollution in tropical countries is caused by indiscriminate discharge of chemical substances that impact the ecosystem services of both aquatic and terrestrial habitats. The response of the terrestrial environment to such continuous pollution has been drastic because most terrestrial organisms are highly sensitive to toxic substances. Studies have shown that pollution of the terrestrial environment contributes to the direct or indirect response of soil organisms to the chemical

substances, resulting in their death, decrease in soil fertility, which manifests as poor productivity of important crops. Chemical substances such as heavy metals are particularly harmful to plants (Tripathy et al. 2007; Cherian et al. 2012), thus, a major physical impacts of crude oil pollution have a devastating effect on crop farming (Nwilo and Badejo 2008; Elum et al. 2016; Osuagwu and Olaifa 2018). This is the major factor impeding agricultural productivity food security in many crude oil bearing locations in Nigeria. Ogwu et al. (2015) reported that increasing frequency oil spillage in the mangrove forest zone of Nigeria has led to losses in vegetation, with major impact being low agricultural productivity in a region that serves as a food basket of country in the recent past. Ebegbulam et al. (2013) have analyzed the effect of oil pollution on poverty and hunger in oil-producing communities of Nigeria and found a strong correlation. Agricultural land and crops in acid mined areas have also been contaminated with heavy metal (Ojeh et al. 2010). A similar report from studies carried out at Manitoba, Canada showed that a high level of trace elements prevented plant growth in the Gunnar gold mine tailing pond (Renault et al. 2007).

In many developing tropical countries, rural dwellers depend on agricultural practices to produce their staple food and fiber on a subsistence level. Therefore, any loss of farmland due to mining activities as witnessed in many of these areas is a threat to food security. Farmers and farm laborers are thrown out of jobs, leading to food insecurity, with resultant starvation and nutrition imbalance in vulnerable groups. Lack of adequate nutrition leads to stunted growth, mental retardation, and developmental disorders in children. Again, majority of rural dwellers in many tropical developing countries depend on surface water such as rivers, streams, ponds, lakes, for drinking and other domestic purposes. The freshwater ecosystems also serve the water needs of livestock and wildlife, as well as being a fishery and aquaculture resource for human livelihood. Therefore, pollution of such aquatic environments affects both human and animal well-being in many ways. Susan et al. (2001) reported the extinction of lake trout in the great lake due to contamination with chlorinated pesticides and heavy metals.

Pollutants may also accumulate in fishes (Mbewe et al. 2016; Ekpenyong and Udeme 2015) resulting in potential health problems to humans who depend on them as food. Pesticide residues have been found to accumulate in the tissues of three species of fish that are a significant part of the diet of residents of Lagos, Nigeria, and Uganda (Kasozi et al. 2005; Adeyemi et al. 2008). The pollution of fishery resources also affects the resident fishermen, who depend on fishing as both employment and source of livelihood and the mainstay of their economy. Such freshwater pollution specifically deprives fishermen of their traditional livelihood activities and their immediate families of a major source of high protein food. In most cases, children are the worst hit, because low protein intake in children and the concomitant effects such as stunting, mental and developmental retardation may be lifelong.

Health effects of pollution on humans and animals are seen in two categories, may either be an acute poisoning effect due to short exposure to relatively high dose of the toxicant and thus result in an instant or significant cause of morbidity or mortality resulting (Mansour 2012). Generally, this effect is severe and may cause

the death of the organism. Ellenhorns et al. (1997) reported that 95 percent of the pesticide poisoning occurring in less developed countries is fatal. The body response to acute poisoning is usually inflammation, immunotoxicosis, myopathy, as well as reproductive effects (Ballantyne and Marrs 1992). The chronic poisoning is concerned with adverse health effects, or long-term effects, leading to chronic endpoints such as carcinogenesis, neurotoxicity, cytogenetic damage, teratogenesis, and immunological effects (Mendes 2002; Mino et al. 2002; Mansour 2012). Crude oil pollution, for example, has been shown to cause several health problems of far-reaching consequences in host communities. Studies at this location have shown that intake of water or oil contaminated food resulted in illnesses such as nausea, dizziness, neurological dysfunctions, reproductive and developmental disorders, and in extreme cases terminal illnesses such as cancer (Aguilera et al. 2010; Chang et al. 2014. Other diseases linked to exposure to toxic substances include pulmonary disease, heart failure, allergic reaction, many of these events lead to injuries or death. Organic pollutants implicated and recognized as carcinogens include polycyclic aromatic hydrocarbon (PAH), aromatic amines, benzene amino azo dyes, and vinyl chloride (Yu et al. 2011), while the inorganic substances include salts of arsenic, chromium, cadmium, nickel, lead, etc.

9.3 Phytoremediation Techniques in Removal of Toxic Waste

In phytoremediation, naturally associating plants and the microorganisms are able to sequester, detoxify, or neutralize the effects of toxic pollutants in soils, water, and air (Weyens et al. 2009; Cherian et al. 2012). Phytoremediation is an efficient, affordable, eco-friendly, aesthetically pleasing, and generally effective method of removing of toxic substances (Garbisu et al. 2002; Jing et al. 2007). The objective is usually to limit the biological availability of toxicants to other endpoints through the movement of toxicants. Higher plants are considered appropriate in this process because the contaminants are absorbed and sequestered in the roots and transported to the shoots and leaves (Reichenauer and Germida 2008). The nature and bioavailability of the contaminants, soil properties, and the type of plant amongst others are factors that can affect phytoremediation efficiency (Sreelal and Jayanthi 2017). Toxicants such as heavy metals (Jing et al. 2007; Cherian et al. 2012), petroleum hydrocarbons (Cartmill et al. 2014; Riberro et al. 2014), uranium (Malaviya and Singh 2012) can be successfully attenuated through phytoremediation processes. However, the phytoremediation is not without its own limitations. Studies have shown that phytoremediation potentials are influenced by plant growth rate, biomass generation rate, and availability of the toxicants in the root sphere (Chaney et al. 2005; Cherian et al. 2012). Major phytoremediation techniques include rhizofiltration, phytoextraction, phytostabilization, and phytovolatilization.

9.3.1 Rhizofiltration

In rhizofiltration aquatic plant roots are used to eliminate toxicants from aquatic environments. These aquatic plants are first grown and nursed in water, before being transferred into a toxicant contaminated water. Rhizofiltration can also be achieved by raising terrestrial plants in polluted water, in order to bioaccumulate the pollutants in different parts of the plant (Zhu et al. 1999; Malaviya and Singh 2012). It has been reported that rhizosphere and several microbes associated with hyper-accumulators, such as *Pseudomonas fluorescens* G10 (Sheng et al. 2008), *Pseudomonas putida* (Farwell et al. 2007, 2006), *Bacillus* sp. (Sheng and Xia 2006), *Enterobacter* sp., and *Pseudomonas* sp. (Mastretta et al. 2009) also participate in the remediation of heavy metals.

9.3.2 Phytoextraction

Plants can also extract some soil toxicants (heavy metals and organic content) by concentrating them in their biomass (Ali et al. 2013), so that the toxicants are eliminated when the biomass is harvested and discarded elsewhere. The toxicants are taken up from the soil and are transformed into another product or are accumulated in the tissue area of the plant and biomass (Table 9.1). Phytoextraction occurs in plants characterized by rapid growth and optimal biomass yield, which encourages substantial removal of contaminants from the soil. The biomass when harvested could be incinerated to completely eliminate the contaminants. The phytoextraction technique depends essentially on bioaccumulation factor or bioconcentration factor: C_{plant}/C_{soil}, which is the ratio of the concentration of toxicants in harvested plants to the concentration of the toxicant in the soil. Studies have described over 400 hyper-accumulators made up of annual and perennial shrubs and used in phytoextraction (Li et al. 2009a; Bissonnette et al. 2010). Uranium transfer factor (UTFs) for shoots range from 0.0002 to 0.34 kg^{-1}, while that of the roots range from 0.007 to 8.1 (Malaviya and Singh 2012). Molecular techniques have revealed that root UTFs could be raised to the range of

Table 9.1 Some tropical plant with hyper-accumulation capabilities

S/N	Plants	Source
1	*Solanum lycopersicum*	Hediji et al. (2015)
2	*Brassica napus*	Wu et al. (2015)
3	*Daucus carota*	Carvallo et al. (2015)
4	*Solanum aethiopicum*	Nabulo et al. (2012)
5	*Oryza sativa*	Khalid et al. (2017)
6	*Brassica juncea*	Khalid et al. (2017)
7	*Zea mays*	Avci and Deveci (2013)
8	*Allium cepa*	Chiroma et al. (2014)
9	*Spinacia oleracea*	Khan et al. (2013)
10	*Lactuca sativa*	Perveen et al. (2012)

76.69–123.52 (Eapen et al. 2003). Plants such as *Alyssum bertolonii*, *Pteris vittata*, and *Thlaspi caerulescens* have been used in the phytoextraction of contaminants from soil (Vander Ent et al. 2013).

9.3.3 Phytostabilization

Plant roots control the availability and mobility of toxicants, by preventing their movements to other receptors (Berti and Cunningham 2000; Cherian et al. 2012). They use biological amendments to immobilize toxic elements to prevent further spread or their entrance into the food chain. The aim is to prevent migration or mobilization of such contaminants, thus limiting their diffusion into the soil and other environmental components (Ali et al. 2013). This will stop the spread of such toxic elements toward underground waters or through runoffs, wind, and the food chain. Phytostabilizers are able to tolerate stress from soil conditions and must be able to grow rapidly, have a dense rooting system, and be able to self-propagate (Cherian et al. 2012). The biological amendment could be done by the use of fungi for the removal of such toxicants. Rufyikiri et al. (2004) highlighted the effectiveness of the soil fungus, *Arbuscular mycorrhizal* (AM), as the most widely distributed root symbiosis that forms an association with terrestrial flowering plants. Other studies (Rufyikiri et al. 2002; Chen et al. 2005; Roos and Jakobsen 2008) have also reported the effectiveness of *Arbuscular mycorrhiza* in the phytostabilization of uranium accumulation in various plants. Plants that act in phytostabilization processes are usually trace element extruders that exhibit sufficient root to shoot transfer coefficient (Kidd et al. 2009).

9.3.4 Phytovolatilization

Certain green plants can accumulate toxic substances in their tissues and then subsequently convert them into less toxic compounds, which they release into the atmosphere. The technique through which the toxicant is naturally released into the atmosphere is usually by harvesting the part of the plant involved and disposing of it, especially through incineration and the like. Through this method, heavy metals such as mercury, selenium, and arsenic-containing compounds have been removed from contaminated sites (Banuelos and Lin 2010; Lin et al. 2000). Some of the plants used in the phytovolatilization process are *Nicotiana tabacum* and *Brassica napus* (Ali et al. 2013). The method has also been applied to the removal of organic contaminants such as petroleum hydrocarbons (Ali et al. 2012) from polluted soils. Phytovolatilization therefore is a viable approach to the removal of toxic substances that may be harmful to the biota.

9.4 Uptake and Transportation of Toxic Substances in Plants

Terrestrial plants may be exposed to toxicants in two major ways: exposure of leaves to atmospheric pollutants and uptake or absorption of pollutants through plant roots growing in the contaminated site (Udebuani and Ozoh 2007; Uzu et al. 2010). The uptake and transportation mechanisms of heavy metals such as cadmium, mercury, lead and organic substances such as pesticides and petroleum hydrocarbons in candidate plants have been researched. The essential micronutrients such as iron, molybdenum, and manganese are important to plants for normal growth and functioning, while trace elements (Zn, Ni, Cu, Cr, Pb, Cd, Hg, etc.) are not important in plant biological functions (Schutzendubel and Polle 2002), although at high concentrations they may become toxic (Gamalero et al. 2009). The absorption of pollutants through the roots primarily depends on the availability of the toxicants in their ionic form. For example, Arsenic (As) is absorbed by plants mostly as As (III) or As(V) into the plant cell (Neidhardt et al. 2015), where As(V) is subsequently reduced to As(III) by the enzyme arsenic reductase (Ghosh et al. 2015). Similarly, Cd is passively absorbed in the form of Cd^{2+} (Cherian et al. 2012). The xylem and phloem are the tissues in both roots and shoots involved in the distribution of the toxic element to other parts of the plant (Mirza et al. 2014).

In rice (*Oryza sativa*), the accumulation of methylated arsenic species through the roots using the aquaporin nodulin-26-like intrinsic proteins (NIP2) has been observed (Li et al. 2009a). The methylated organic arsenic is generally less absorbable than inorganic form (Chandrakar et al. 2016). Raab et al. (2005) reported that the movement of methylated As in the xylem tissue is fastest from root to shoot. Several complex transport mechanisms have been implicated in the movement of arsenic from the soil into the plant xylem (Mitani-Ueno et al. 2011), with the Lsi1 and Lsi2 transporters being prominently involved in arsenic inclusion and exclusion movements, respectively (Khalid et al. 2017). Nodulin-26-like intrinsic proteins (NIP) transporters are equally part of the arsenic transport mechanism.

Lead absorption at plant roots is mostly achieved through Ca^{2+}-permeable routes and usually bound to compounds located on the rhizoderm cell surface Experiments conducted with *Funaria hygrometrica* have shown that lead can enter roots inactively and travel translocating water streams. Again, Pb absorption in plant roots depends on the concentration available at root tips; however, it should be noted that lead concentrations are usually high at the root tips. Low pH increases the solubility of lead in soil solution. Thus, lead absorption is essentially a non-selective energy-dependent process that sustains the appropriate lead concentrations in rhizoderm cells (Pourrut et al. 2008).

Cadmium (Cd) uptake and transport mechanism, by plants, depend on its concentration and bioavailability in soil, modulated by pH, organic matter, redox potentials, and concentration of other elements (Jingguang et al. 2019). Benavidez et al. (2005) reported that zinc and cadmium co-accumulate in aerial parts of *Arabidopsis halleri*, suggesting that their uptake is genetically correlated and that both metals are similarly transported and regulated. Studies carried out with rice have specifically highlighted similar uptake mechanisms for Cd, Mn, Zn, and Fe

(Nakanishi et al. 2006; Sasaki et al. 2012). Cadmium accumulates in the shoot after absorption from the soil, and this can be determined by xylem-mediated Cd translocation from the roots (Uraguchi and Fujiwara et al. 2012). The transporters playing this role include OsHMA2 and OsHMA3 (Satoh-Nagasawa et al. 2013). Transporter OsHMA2 translocates Cd through the roots to the shoots, while regulating its circulation via the phloem to other tissues. The level of OsHMA2 is however significantly low (Yamaji et al. 2013), while the contribution of OsHMA3 indicates functional deficiency resulting from high root to shoot cadmium translocation (Miyadate et al. 2011).

Toxicants like heavy metals and polyaromatic hydrocarbon are known to react with substances already in the soil to form new complexes, thereby ensuring that only a fraction of the toxicants are made available to plants. Toxicants absorbed by plants often enter the food chain. Although they may play significant roles in plant development, their presence constitutes a serious threat to higher animals. Absorption of heavy metals usually occurs through the Ca^{2+} permeable routes. Metals uptake by plants is however mediated by its form, soil physicochemical characteristics, speciation, and the amount of mycorrhizal transpiration (Cherian et al. 2012).

Caspian strips located in the endodermis of the root cells exhibit a blocking effect that ensures that some of the metal toxicants accumulate in root cells after uptake (Pourrut et al. 2011). Excessive accumulation of such toxic substances may however impair essential structural, functional, and chemical activities in the plant. The adverse toxic effects arising from metal accumulation in plants, especially on the leaves integrity, seed germination, and overall plant health have been documented (Perfus-Barbeoch et al. 2002; Rahman et al. 2005). For example, Tomulescu et al. (2004) and Islam et al. (2007) reported the inhibitory effects of lead on seed germination even at low concentrations, while other researchers (Islam et al. 2007; Sengar et al. 2009) specifically reported the inhibitory effects of lead on *Hordeum vulgare*, *Elsholtzia argyi*, *Spartina alterniflora*, *Pinus halepensis*, *Oryza sativa*, and *Z. mays* seeds germination. These inhibitory effects have been attributed to the disruption of the enzymes, protease and amylase, in particular by lead (Sengar et al. 2009). Pb accumulation also results in low biomass production linked adverse effects on leaf structure and functions (Islam et al. 2007, 2008; Piotrowska et al. 2009; Gupta et al. 2009; Singh et al. 2010). Zinc can form complexes with histidine in the root cells and organic acids in the shoot cells, which are ultimately accumulated in the plant cell vacuoles (McGrath and Zhao 2003; Cherian et al. 2012). This explains the physiology of zinc hyper-tolerance usually observed in plants. Again, metals can cause oxidative injury to plants by activating chemical processes that produce reactive oxygen species (ROS) or oxygen-free radical species. Flora (2009) reported that ROS disrupts essential chemical balance in cells, gene and protein structures, and membrane integrity in plant cells, thereby causing cell death.

9.5 Detoxification of Toxic Substances in Plant Species

Plants have well-developed defense mechanisms such as chelation, compartmentalization, biotransformation, and cellular repair that ensure tolerance of the negative effect of toxic metals or metalloids. These mechanisms include chelation, compartmentalization, biotransformation, and cellular repair. Under stress conditions, the defense systems mounted by plants become hyperactive in order to control the ROS facilitating cellular injury more efficiently (Armendariz et al. 2016). In addition, certain plants can block induced toxicity by producing and accumulating of osmolytes, which may include glycine, betaine, proline, and mannitol. Accumulation of osmolytes has specifically been shown to be an essential characteristic needed for plants survival during stress (Ghulam et al. 2019).

Mechanism of detoxification of toxic substances by plants includes the following: Phytochelatins (PC) formation, which occurs through binding of toxicants (heavy metal) to the cysteinyl sulfhydryl group and carboxyl groups binding site to form stable complexes. Such complex formation culminates in the degeneration of protein or enzyme structures, resulting in their inactivation (Dwivedi et al. 2012). Phytochelatins at toxic levels have been known to display high affinity for heavy metals (Shukla et al. 2013). They are also involved in the defense against metal-related stresses and excess heat, salt, UV-B, and herbicide induced stress, thereby serving as biomarkers of stress in plants exposed to such stressors (Saba et al. 2013). Cd^{2+} ions were reported to stimulate four to sixfold more PCs synthesis than Cu^{2+} and Zn^{2+} in cell cultures of *Rauwolfia serpentina* and *Picea rubens Sarg*, respectively, indicating that it is the most effective stimulator of PCs synthesis in plant cells (Thangavel et al. 2007).

Arsenic (As(III)) has a strong attraction to peptide groups such as the sulfhydryl found in PCs and GSH (Zhao et al. 2009). The As(III) binding site produced due to this strong affinity has been found to be more stable in acidic than basic environments (Raab et al. 2007; Zhao et al. 2009). Generally, the arsenic tolerance observed in non-As-hyper-accumulator plants occurs through this As(III) and PC complex formation (Kumar et al. 2015). Phytochelatin can also combine with anti-oxidative enzymes, to form a synergistic defensive system in some plants, and under heavy metal stress conditions can help to inhibit intoxication in such plants. Studies with *Brassica chinensis* have shown that cadmium detoxification was achieved through increased enzymatic biosynthesis of PCs and amplified anti-oxidative system activity in the plant.

Metallothioneins (MTs), ligands found in plants, help to nullify heavy metal toxicity via cellular confiscation, homeostasis of various metal ions, and metal passage modification (Guo et al. 2013). These ligands are acknowledged active mediators of a number of cellular events, such as ROS scavenging and redox levels maintenance (Macovei et al. 2010), plasma membrane repairs, cell multiplication, and growth and restoration of impaired DNA (Grennan 2011). Apart from toxic heavy metals, other factors such as water stress, poor nutrients availability, disease, and aging among others have been shown to induce metallothionein production. The types 1, 2, 3, and 4 MTs in roots, shoots, leaves/fruits, and seeds, respectively, are

the MTs identified in plants. These MT types have also been subdivided further into isoforms (Guo et al. 2013). The MT types include heavy metals, forming metal chelators. There is evidence, however, that these plant MTs exhibit distinct treatment characteristics for different metal types, while their functionality, metal-binding, affinity capacity, and tissue localization also vary within a plant species. Furthermore, MT types have shown dissimilar and sometimes corresponding functions during homeostasis and heavy metal decontamination (Du et al. 2012).

Proline is a major osmoprotectant, known to accumulate in plants in response to different stress conditions (Begum et al. 2016). Rejeb et al. (2014) reported that proline as an osmolyte exhibits a stabilizing effect on the plant cell wall while aiding the maintenance of the minimal hydration level required in cells and cell membranes (Rejeb et al. 2014). Again, proline has been implicated in the protection of plants against damages mediated by ROS (Ozturk et al. 2010), especially by acting as a singlet oxygen quencher and OH forager. Through these functions proline therefore aids in the stabilization of protein, DNA, and cell membrane structures (Chandrakar et al. 2016). As a proteinogenic five-carbon α-amino acid, proline has also been shown to function as temporary carbon and nitrogen source for developing embryos. Elevated proline level is equally known to activate a non-enzymatic reaction to a variety of tensions caused by biotic and abiotic stressors in plants (Szabados and Savour 2010). In summary, proline plays an important role in combating the roles of adaptation, recovery, and signaling in plants (Fidalgo et al. 2013).

Proline uses different mechanisms to enhance resistance to metal toxicity in plants. Clemens (2006) reports that accumulation of proline in plants is not actually induced by heavy metal stress but due to water balance disorder that occurs because of excess metal. Again, proline scavenges for ROS mostly by neutralizing hydroxyl radicals and reducing singlet oxygen associated with metal stress. According to Mourato et al. (2012) proline also enhances the antioxidant activities, guards, and conserves redox homeostasis, in addition to other functions like choline reconstruction and intracellular pH control (Rastgoo et al. 2011). Indeed, proline initiation into heavy metal stress depends on the concentration gradient, type of metal, and specific organ. Interestingly, a corresponding increase in endogenous proline concentration, linked to exogenous proline application has been reported to aid better mental stress response in plants (Shahid et al. 2014).

9.6 The Response of Plants to Stress from Toxic Substances

Stress in plants caused by external factors affects their growth, development, and productivity (Verma et al. 2013). Stress activates a different response in plants such as the alteration in gene expression and cellular metabolism, as well as alterations in plant growth and yield among others. Under stress, plants are usually able to mirror any sudden change in environmental conditions. Thus, plant species that are stress-tolerant on exposure to a particular stress are able to initiate physiological adaptations to the stress condition in a time-dependent manner. The sessile nature of plants, when exposed to various environmental stressors, often induces oxidative

and genotoxic stress resulting in various forms of lesion formation in the DNA double helix structure (Dutta et al. 2018). Plant stress has been divided into abiotic and biotic stress. Abiotic stress is caused by environmental factors, which have been categorized into physical (drought, flood, high soil salinity, etc.) and chemical (poor nutrients, high UV light, etc.) factors, while biotic stress is caused by biological factors (diseases, insects, etc.) affecting the plants (Verma et al. 2013). However, plants can recover from an injury caused by mild stress, while severe stress induces plant loss through flowering, seed formation, and induced senescence prevention. Most wild plant species are known to survive different forms of stress (Sewelam et al. 2014).

9.6.1 Plant Stress Response Induced by Environmental Pollutant

9.6.1.1 Reactive Oxygen Species Signaling

Reactive oxygen species (ROS) are formed due to unavoidable escape of electrons during electron transport in different cellular compartments or different metabolic pathways (Blokhina and Fagerstedt, 2010). Environmental stress induced ROS poses serious threats to cells and usually results in cell damage and death (Mishra et al. 2011). ROS though having destructive activity are known as secondary messengers in several of cellular functions that include stress tolerance (Yan et al. 2007). Plants are able to detect ROS signal and translate them into applicable cellular response through certain redox-sensitive proteins and other metabolic activities, including gene expression (Sharma et al. 2012). Excess ROS is eliminated through specific antioxidant activities comprising enzymatic and non-enzymatic antioxidants (Sharma 2012). Maintenance of high antioxidants capable of detoxifying toxic ROS is, therefore, connected to an increase in the tolerance of plant to environmental stress (He et al. 2012).

9.6.1.2 Abscisic Acid Signaling

Abscisic acid (ABA) is one of the stress induced signaling primary hormones (Cramer 2011) that moderates the abiotic stress. Biotic stress on the other hand is specifically facilitated by the antagonism amongst the other stress hormones such as acid JA/ET (Liu and Schnoor 2008). However, ABA has been shown to accumulate after certain infections (Ton et al. 2009), with resultant overriding of other defense reactions (De Torres-Zabala et al. 2007). ABA has been shown to initiate SnRK2s production, which phosphorylates the plasma membrane enzyme, NADPH oxidase RbohF to generate O_2^-, and subsequently forms hydrogen peroxide. The hydrogen peroxide in turn serves as a signaling chemical that regulates different types of ABA responses, like stomatal closure (Sirichandra et al. 2009).

9.6.1.3 Osmolytic Signaling

The large families of mitogen-activated protein kinase (MAP) pathway components in plants can combine in different ways to form MAP kinase modules, such as MAP3K, MAP2K, and MAPK (de Zelicourt et al. 2016). Activation og these

MAPKs has been described in plants during both biotic and abiotic stress (de Zelicourt et al. 2016), especially biotic stresses like osmotic and temperature stress that mediate the generation of various lipid signals (Hou et al. 2016). These lipid signal molecules have however been shown to bind to other signaling proteins, with resultant modulation of their activities and that of membrane associations.

9.6.1.4 Systemic Signaling

Pathogen infections trigger systemic responses in plants, although abiotic stressors also elicit systemic responses both at their point of application and in tissues distal. Such abiotic stressors are capable of initiating systemic acquired acclimation (SAA) in plants, involving long-distance signals (Choi et al. 2014). Stress triggered by such long-distance signals is known to move at substantial speed (>1000μm/s) in plants and can cause transcriptional reactions in distal tissues (Choi et al. 2014). Enzymes like NADPH oxidase, derived from plasma membrane, are particularly needed for ROS signal propagation, while the calcium signals rely on certain vacuolar ion channels (Choi et al. 2014). It is therefore postulated that the generation of ROS triggers the calcium signal which subsequently through other complex reactions also generates a self-propagating mutual activation circuit that links ROS and calcium signals (Dubiella et al. 2013). Similarly, H_2O_2 generated by NADPH oxidase also plays a role in the activation of plasma membrane calcium channel (Grondin et al. 2015), with the aid of certain receptor-like kinases (Hua et al. 2012).

9.7 Plant–Microbe Interactions in Attenuation of Toxic Substances

9.7.1 Plant–Microbial Interactions in Remediation of Polluted Aquatic and Terrestrial Ecosystems

Plant–microbe interactions are of great relevance in agronomy, not only in bio-fertilization as seen in various rhizobia-plant root relationships, but also in detoxification of contaminants. In bio-fertilization, a substance which contains living microbes is smeared on the plant material, or the soil, so that the microbes take over the immediate environment (rhizosphere) or the interior of the plant. Biofertilizers exert their effects by promoting the growth and development associated crops by enhancing the generation of primary nutrients for the host. Such biofertilizers include *Rhizobium*, *Azotobacter*, *Azospirillum*, phosphate-solubilizing bacteria, mycorrhiza, and blue-green algae (BGA). Generally, biofertilizers are classified as mycorrhizae, organic fertilizers, algal biofertilizers, symbiotic and non-symbiotic nitrogen fixers, and phosphate-solubilizing bacteria. Sometimes, bacteria are used as the major component of the product and have been referred to as bacterial fertilizer.

Soil microbes produce siderophores and protons when micronutrients such as iron are deficient in soils. Bacteria implicated in this process include *Psychrobacter* species etc, hence their application on iron-deficient and nickel-contaminated soils cultivated with sunflower (*Helianthus annuus*) as this association enhances iron

solubilization and uptake. Studies have shown that bacteria, such as *Janthinobacterium* species, *Arthrobacter* species, Leifsonia species, and *Polaromonas* species increase the speed of the mineral nutrients dissolution and deployment in soils (Uroz et al. 2009). Through this mechanism, biofertilizers trap atmospheric nitrogen to the soil where it is transformed to plant usable forms. Again, some biofertilizers able to make phosphates more available for plant use. Biofertilizers are therefore critical to the supply of nutrients by nitrogen fixation, stimulation of crop growth through the production of growth-stimulating compounds, and solubilization of phosphorus to make it more available to the crop. Bacteria are known to possess several traits that are beneficial or otherwise in the plant–microbe interactions, which has been categorized into symbiosis, antibiotic production, competence, conjugation, motility, sporulation, biofilm, and virulence.

9.7.2 Plant–Microbe Interaction by Mutualism

Microbes are in symbiotic relations with plant roots and this associative cooperation is vital in the root zone of the soil system. Some bacteria and arbuscular mycorrhizal fungi are used as bio-inoculants which positively influence metabolic activities of associated plants and membrane permeability of their root cells. These organisms enhance the formation, growth, and development of hyper-accumulators in polluted soils. Multi-beneficial effects of plant–microbe mutualistic interactions include phytostimulation, phytoavailability of nitrogen, calcium, phosphorus, potassium and iron, stress bioalleviation, biomodification of root biomass, and utilization of some as biopesticides (Song et al. 2004). Phytoavailability is the accessibility of toxic metals to plants for their uptake (Song et al. 2004). An example is the uptake of trace elements by the perennial ryegrass, *Lotium perenne* (Antonangelo and Zhang 2019). Gomez-Bernal et al. (2017) reported *B. rapens* and *T. domingnensis* as important plant species that can take up heavy metals and store them in various tissues. Phytoavailability makes nutrient elements in the soil available for plant growth and development in times of stress. In this way, plants have interacted with bacteria to achieve fixing and mobilizing nutrient elements such as nitrogen, phosphorus, and other mineral elements for plant development (Hardoin et al. 2008).

Under varying climatic conditions, fungi like arbuscular mycorrhizal have been shown to develop a symbiotic association with plant roots, especially vascular plant species. In such symbiotic association, these mycorrhizal fungi benefit through photosynthetic activities of the plants, while in return they help to enhance mineral utilization by the plants (Upadhyaya et al. 2010). This type of plant-fungi association has also been shown to aid better plant pollution tolerance. Rahmati and Khara (2011) in their study of chromium (Cr) stressed maize plants treated with the arbuscular mycorrhizal fungus, *Glomus intraradices*, suggested that such plant-fungi association can also produce early stress warning signals that help the plant initiate protective mechanisms early enough. Abdelmoneim et al. (2014) reported that no such benefit was observed with Cu and Cd stressed maize plants inoculated

with two species of mycorrhizal fungi (*Glomus mosseae* and *Acaulospora laevis*). These contradictory results may be due to differences in the type of metal stressors applied or maize variety used in the studies.

9.7.3 Plant–Microbe Interaction in Decontamination of Soils

Plant roots and soil microbes have long-standing relationships in the rhizosphere. Secretions or exudates and soil biota are therefore important components of the rhizosphere ecosystem as they perform important roles in transforming soil materials leading to the bioavailability of metals and nutrients. Root exudates, for example, supply soil microbiota abundant energy and nutrients while in return they stimulate the release of exudates from roots of plants. Some plants and their obligate or facultative microorganisms struggle for existence, and in their relationship, they coexist for mutualistic or beneficial purposes. Plant exudates promote phytoremediation by stimulating activities of soil microorganisms in the root zone (Sessitsch et al. 2013) and release of organic acid-metal complexes that acidify soils and speed up the mobility of nutrients and metallic ions. Plant root exudates are also capable of forming intracellular binding materials like amino acids, organic acids, and phytochelatins. Solanki and Dhankhar (2011) reported that phytochelatins and certain metal-binding peptides can be produced through several available chemical options like enzymatic reactions or even from tripeptide glutathione. It has been reported that the phytotoxic effects of metal ions can be through the effects of metal-binding peptides, thus, allowing for metal uptake and other physiologic processes within the plant. Hyper-accumulators exude various compounds that stimulate bacterial growth, solubilize mineral nutrients like phosphorus, iron, and zinc, and detoxify some metals such as arsenic, cadmium, and lead (Li et al. 2009b).

Hyper-accumulators are able to eliminate metal toxins through chelation at the plant root zone. Their ability to release exudates from the roots, also hence their high tolerance of elevated concentrations of contaminants. According to Magdziak et al. (2011), this prevents metal ions from entering the cell symplast. In agronomy, some crops are known to undergo root exudation of citric, oxalic, malic, and succinic acids when stressed by heavy metals and other contaminants thereby minimizing their proneness to phytotoxicity. Soil microbiota can withstand high concentrations of pollutant metals. Ma et al. (2015) reported that soil microbes evolve resistance strategies against soil contaminants. Soil microorganisms enhance phytoremediation by plant biomass by increasing phytoextraction or by reducing the available metals in the soil (phytostabilization), as well as enabling metal transport into the roots (bioaccumulation) and subsequently to the shoot (Rajkuma et al. 2012). Some microbes are used in cleaning contaminated soils or in reducing the level of contamination in soils through the biological degradation and transformation of toxicants into non-toxic substances.

Some plant roots release flavonoids, which play significant roles in plant-microbe collaborations in the soil system. Included in such interactions are legume-rhizobia symbiosis as well as mycorrhiza formation. The flavonoids play key roles in the

growth of hypha, its diversity, and root establishment in arbuscular mycorrhizal formation–plant interaction, as well as in spore formation. In addition to this, flavonoids act as chemo-attractants and inducers of the nodulation genes implicated in the production of lipochitin–oligosaccharide, and also promote the growth of host-specific rhizobia. There are other flavonoids related compounds like isoflavonoids and flavones, which are identified as inducers of rhizobial nodulation gene expression (Juan et al. 2007). In a mycorrhizal association, certain fungi symbiotically relate to the roots of some vascular plants. All these are necessary in the activities of soil biota and in the chemical reactions taking place in the soil sphere. Because of their capacities in recycling recalcitrant polymers like lignin and hazardous toxicants, and use in bioremediation, application of mycorrhizal formation in improving soil quality is often known as mycorrhizo remediation.

9.7.4 Plant–Microbe Interaction by Phytostabilization and Phytoextraction

Some microbes like *Funneliformis mosseae* have been linked with phytostabilization of toxic metals (Hassan et al. 2013), through metal mobilization or immobilization processes (Ma et al. 2011). Arbuscular mycorrhizal fungi establishment by *Rhizophagus irregularis* has been shown to aid phytoextraction of cadmium (Hassan et al. 2013). Again, organic acids enhance the heavy metal immobilization via the formation of stable metal complexes in soil milieu. However, rhizospheric bacterial interactions with plant roots can be beneficial, neutral, or harmful. Plant growth-promoting rhizobacteria (PGPR) produce a mixture of complex volatile substances that is different from other bacteria species (Groenhagen et al. 2013). These volatile substances can encourage plant growth (Penuelas et al. 2014), stimulate suppression of disease (Yi et al. 2013), and antagonize phytopathogens, insects, or nematodes. In addition, rhizospheric bacteria also ensure soil nutrients availability for optimal plant growth, while phytohormones elaborated also provide protection against important pathogens in addition to remediation of contaminated soils (Paul and Lade 2014).

PGPR are found in the surroundings of the rhizosphere where they boost performance by different mechanisms (Bhattacharyya and Jha 2012). Through a direct mechanism that includes solubilization of phosphate, and production of siderophore, among other processes, it enhances the plants' ability to withstand biotic stress. PGPR through an indirect mechanism can also act as a biocontrol agent that allows the decontamination of heavy metals and pesticides (Glick 2010). *Pseudomonas aeruginosa*, a growth-promoting rhizobacteria has been shown to tolerate heavy metals like cadmium and is used as bioremediation against Cd induced stress (Huang et al. 2016). Reports have established that rhizospheric bacteria not only mitigate damage arising from metal toxicity (Etesami and Maheshwari 2018), but also through several mechanisms help to reduce the access of plants to metallic pollutants (Etesami 2018).

9.8 Plant–Microbe Interaction in Biodegradation Processes

Microbes are excellent agents of biodegradation. They are able to break down many foreign and natural chemical substances found in animal and human wastes. Human and animal waste are bio-wastes made up of remains from food and feed digestion as well as the microorganisms resident in them. Bio-wastes also include agricultural residues, like wood, paper wastes, leaves, grass clippings, and several food processing wastes among many others. Bio-wastes are biodegradable and have recently been used to produce biodegradable plastics and packaging materials. The biodegradation process involves essentially the breakdown of these materials by microorganisms in nature, certain bacteria, and fungi. The metabolites released into the rhizosphere in situ by microbes are also biodegradable, thus, they do not constitute much danger when compared with inorganic compounds. The use of plant growth-promoting microorganisms in biodegradation processes, therefore, ensures biosafety, in addition to remediation of contaminated soils. This they do by immobilizing or mobilizing or transforming heavy metals in soil, thereby reducing metal toxicity. Scholars (Huang et al. 2016) reported reductions in metal-induced toxicity, alteration in soil reaction, thereby minimizing metal availability (Rajkuma et al. 2012).

Some bacteria are able to alleviate the effects of metal toxicity, while metal immobilizing or mobilizing bacteria reduce metal availability, while others known as solubilizing bacteria help to plant growth bacteria by solubilizing metallic elements like phosphate and potassium. Certain bacterial organisms with properties such as siderophores, biosurfactants, indole-3-acetic acid, organic acid, and nitrogen-fixing have also been found to play beneficial roles in their associations with plants. The effective microorganisms (EMs), on the other hand, are those organisms that have been shown to improve soil quality, and therefore crop production under different agro-ecological settings when applied to the soil as inoculants (Yamada and Xu 2000). Because soil physical properties play important roles in crop production and water efficiency, EMs are useful in conditioning important soil physical properties. Invariably, plants are inherently able to selectively promote the establishment of the root microbes in their surrounding soil, and this has been linked to the properties of rhizosphere soil and the nature of root exudates.

9.8.1 Plant–Endophytes Interaction

Endophytes are bacterial and fungal organisms living in normal plant tissues without being harmful to the host (Dhanya and Padmavanthy 2014). Endophytes are microbes that have an either obligate or facultative association or complex interaction with their host plant. Their relationship may be either mutualistic or antagonistic (Dhanya and Padmavanthy 2014). The obligate relationship shows the two living organisms relying on each other. Endophytes depend on plants for their metabolic activities and survival as the plants secrete substances used in this capacity, and the plant depends on the endophytes for nutrient element supply (Andreote and Durrer

2014). Plants are able to restrict the growth of endophytes, through the synthesis of several growth-promoting substances which also help to improve plant survival in the environment. These endophytes also assist in protecting the plant from bacterial and viral infections, colonization of plants by rhizobium-host, thereby improving the capacity of such plants to withstand stress condition (Hashem et al. 2016). The symbiotic association of the plant species and endophytes provides protection to organisms which in turn produce metabolites that enhance nutrient absorption, growth, and biomass production. Essentially, therefore, endophytes are useful to plants through nutrients and bioactive compounds supply, protection against biotic and abiotic stresses, and detoxification of pollutants (Brader et al. 2014).

Thus, the several beneficial properties of endophytic bacteria have been exploited in promoting the growth of important crops (Mitter et al. 2013). Importantly, endophytes have been employed in bioremediation of polluted soils because of their capacity to support plant life and development in such soils (Glick 2010). They are particularly able to aid their associated plants in breaking down organic pollutants already taken up by the plants (Bittsánszky et al. 2011; Van et al. 2011). During this process of phytoremediation of organic pollutants, endophytes secrete various enzymes for the mineralization of these pollutants. Endophytic bacteria are widespread in nature and have been isolated from plant species, including crops, aromatic and medicinal plants (Sharma et al. 2012). Examples of endophytes isolated from plant tissues include *Acetobacter*, *Anthrobater*, *Bacillus*, *Burkholderia*, *Enterobacter*, *Herbaspillum*, and *Pseudomonas* (McGuinness and Dowling 2009). Endophytic bacteria used in degrading pollutant can be isolated from plants internal tissues grown on soils contaminated with organic pollutants (Germaine et al. 2009), degradation of aromatic hydrocarbon (e.g., toluene, xylene, ethylbenzene, and benzene) as well as from different parts of poplar tree (Taghavi et al. 2011), oak tree, and common ash for the degradation of volatile organic pollutants (Kang et al. 2012).

9.9 Conclusion

This study has uncovered plants with phytoremediation, phytoavailability, phytostimulation, and biomodification qualities. Natural plants exist, which help in mobilizing, absorbing, accumulating, and detoxification of toxic substances, from activities of man, thereby sustaining our ecosystem. Many of these plants with phytoremediation qualities are yet to be covered and the fact that many of the plants are going into extinction because of the devastating effect of climate change. Identification of these plants will help boost the phytoremediation technique, which is an aesthetically accepted environmentally friendly method with the potentials of cleaning our polluted environment. In addition, microorganisms inhabiting the tissues of plants have been discovered as an important complementary tool in mitigating and total removal of toxic substances in the environment. This approach has helped to establish environmental quality standards that sustain the anthropogenic release of toxicants in impacted areas.

The presence or use of plant–microbe association in enhancing phytoremediation highlighted two important microbes; endophytes and rhizosphytes as important species in removing toxic substances. Endophytic species generally promote plant yield, nutrient uptake, and totally detoxify and render toxic substances in the environment harmless. In this mutual relationship, plant root provides root exudate which attracts chemoattractant bacteria that increases ion solubility thereby increasing the activities of microbes associated with plant root. Rhizospheric bacteria are also implicated in the bioaccumulation of toxic substances in the tissues of the shoot and roots of plants. And more still the toxic elements can be sequestered in the vacuoles of the plant cell. Plant–microbe interaction is an important method that appears with prominence in achieving sustainable clean-up at pollution sites without further damage to the ecosystem.

However, knowledge of the general mechanism involved in toxicant's accumulation, translocation, and detoxification is important in developing efficient and sustainable phytoremediation techniques. Many plants capable of secreting chelating substances that attract microbes utilizing them exist in nature. Knowledge of these chemical secreting plants is limited, therefore, screening of plants to identify those with this potential, especially in tropical regions of the world that harbor rich plant biodiversity is needed for cost-effective bioremediation of polluted environments.

References

Abdelmoneim TS, Moussa TAA, Almaghrabi OA, Abdelbagi I (2014) Investigation the effect of arbuscular mycorrhizal fungi on the tolerance of maize plant to heavy metals stress. Life Sci J 11 (4):255–263

Adeola FO (2004) Boon or bane? The environmental and health impacts of persistent organic pollutant (POPs). Hum Ecol Rev 11(1):27–35

Adeyemi D, Ukpo G, Anyakora C, Unyimadu JP (2008) Organochlorine pesticide residue in fish sample from Lagos Lagoon, Nigeria. Am J Environ Sci 4(6):649–653

Aguilera F, Mendez J, Pasaro E, Laffon B (2010) Review on the effects of exposure to spilled oils on human health. J Appl Toxicol 30:291–301

Agwu A, Kalu AU (2012) Bioremediation and environmental sustainability in Nigeria. Int J Acad Res Progr Educ Dev 1(3):26–31

Ahemad M, Kibret M (2014) Mechanisms and applications of plant growth promoting rhizobacteria: current perspective. J King Saud Univ Sci 26:1–20

Ali N, Sorkhoh N, Salamah S, Eliyas M, Radwan S (2012) The potential of epiphytic hydrocarbon-utilizing bacteria on legume leaves for attenuation of atmospheric hydrocarbon pollutants. J Environ Manag 93:113–120

Ali H, Khan E, Sajad MA (2013) Phytoremediation of heavy metals-concepts and applications. Chemosphere 91(7):869–881

Al-Taaniel AA, Batgyne TA, El-Radaideh EN, Ghrefat H, Zumlot T, Al-Rawabdeh MA, Al-Momani T, Taani A (2015) Spatial distribution and pollution assess of trace metals in surface sediments of Ziqlab Reservoir, Jordan. Environ Mount Assess 187:32

Andreote FD, Durrer A (2014) Exploring interaction of plant microbiomes. Sci Agric 71:528–539

Antonangelo AJ, Zhang H (2019) Heavy metal phytoavailability in a contaminated soil of north-eastern Oklahoma as affected by biochar amendment. Environ Sci Pollut Res 26(1):152–168

Armendariz AL, Talano MA, Travaglia C, Reinoso H, Oller ALW, Agostini E (2016) Arsenic toxicity in soybean seedlings and their attenuation mechanisms. Plant Physiol Biochem 98:119–127

Avci H, Deveci T (2013) Assessment of trace element concentrations in soil and plants from cropland irrigated with wastewater. Ecotoxicol Environ Saf 46:322–328

Balcázar JL, Subirats J, Borrego CM (2015) The role of biofilms as environmental reservoirs of antibiotic resistance. Front Microbiol 6:1216

Ballantyne B, Marrs TC (1992) Overview of ecological and clinical aspects of organophosphate and carbamate. In: Ballantyne B, Marrs TC (eds) clinical and experimental toxicology of organophosphate and carbamate. Butterworth-Heinemann, Oxford, pp 3–14

Banuelos GS, Lin ZQ (2010) Cultivation of the Indian Fig *Opuntia* in selenium-rich drainage sediments under field conditions. Soil use. Management 26:167–175

Bassem SM (2020) Water pollution and aquatic biodiversity. Biodiversity Int J 4(1):10–16

Batayneh AT (2010) Heavy metal in water springs of the Yarmouk Basin, North Jordan and their potentiality in health risk. Int J Phys Sci 5:997–1003

Begum MC, Islam MS, Islam M, Amin R, Parvez MS, Kabir AH (2016) Biochemical and molecular responses underlying differential arsenic tolerance in rice (*Oryza sativa* L.). Plant Physiol Biochem 104:266–277

Benavidez MP, Gallego MS, Tomaro LM (2005) Cadmium toxicity in plants. Braz J Plant Physiol 17(1):21–34

Berti WR, Cunningham SD (2000) Phytostabilization of metals. In: Raskin I, Ensley BD (eds) Phytoremediation of toxic metals: using plants to clean the environment. Wiley, New York, pp 71–78

Bhattacharyya PN, Jha DK (2012) Plant growth promoting rhizobacteria (PGPR): emergence in agriculture. World J Microbiol Biotechnol 28:1327–1350

Bissonnette L, St-Arnaud M, Labrecque M (2010) Phytoextraction of heavy metals by two Salicaceae clones in symbiosis with arbuscular mycorrhizal fungi during the second year of a field trial. Plant Soil 332:55–67

Bittsánszky A, Gullner G, Gyulai G (2011) A case study: uptake and accumulation of persistent organic pollutants in Cucurbitaceae species. In: Komives T (ed) Organic xenobiotics and plants. Springer, Dordrecht, pp 77–85

Blas JM, Charpentic S, Pick F, Kimpe LM, Amand AS, Regnault-Roger C (2006) Mercury polybrominated diphenyl either organochlorine pesticide and polychlorinated biphenyl concentration in Fish from lakes along an elevation transect in the French pyrenees. Ecoloxicol Environ Saf 63(1):91–99

Blaylock MJ, Salt DE, Dushenkov S, Zakharova O, Gussman C, Kapulnik Y, Ensley BD, Raskin I (1997) Enhanced accumulation of Pb in Indian mustard by soil-applied chelating agents. Environ Sci Technol 31:860–865

Blokhina O, Fagerstedt R (2010) Reactive oxygen species and nitric oxide in plant mitochondria: origin and redundant regulatory system. Physiol Plant 138(4):447–462

Brader G, Compant S, Mitter B, Trognitz F, Sessitsch A (2014) Metabolic potential of endophytic bacteria. Curr Opin Biotechnol 27:30–37

Brassington KI, Hough RL, Paton GI, Semple KT, Risdon GC, Gossley J (2007) Weathered hydrocarbon wastes: a risk management primer. Crit Rev Environ Sci Technol 37:199–232

Cartmill AD, Cartmill DL, Alarcon A (2014) Controlled release fertilizer increased phytoremediation of petroleum-contaminated sandy soil. Int J Phytoremediation 16:285–301

Carvallo DRM, dos Santos JA, Silva JAS, do Prado TG, de Fonseca AF, Chaves ES, Frescura VLA (2015) Determination of metals in Brazilian soils by inductively coupled plasma mass spectrometry. Environ Monit Assess 187:535–537

CEHRD (2019) Environmental health human rights and gender baseline for Ogoniland clean-up centre for environment. Human Right and Development, Port Harcourt

Chandrakar V, Dubey A, Keshavkant S (2016) Modulation of antioxidant enzymes by salicylic acid in arsenic exposed Glycine max L. J Soil Sci Plant Nutr 16:662–676

Chaney RL, Angle JS, McIntosh MS, Reeves RD, Li YM, Brewer EP, Chen KY, Roseberg RJ, Perner H, Synkowski EC, Broadhurst CL, Wang S, Baker AJM (2005) Using hyperaccumulator plants to phytoextract soil Ni and Cd. Z Naturforsch 60:190–198

Chang S, Stone J, Demes K, Piscitelli M (2014) Consequences of oil spills: a review and framework for informing planning. Ecol Soc 19(2):26–34

Chen SB, Zhu YG, Hu QH (2005) Soil to plant transfer of ^{238}U, ^{226}Ra and ^{232}Th on a uranium mining-impacted soil from southeastern China. J Environ Radioact 82:223–236

Cherian S, Weyen N, Lindberg S, Vangronsveld J (2012) Phytoremediation of trace element-contaminated environments and the potential of endophytic bacteria for improving this process. Crit Rev Environ Sci Technol 4:2215–2260

Chibuike G, Obiora S (2014) Heavy metal polluted soils: effect on plants and bioremediation methods. Appl Environ Soil Sci 2014:752708. https://doi.org/10.1155/2014/752708

Chiroma TM, Ebewele RD, Hymore FK (2014) Comparative assessment of heavy metal levels in soil, vegetables and urban grey waste water used for irrigation in Yola and Kano. Int Ref J Eng Sci 3:1–9

Choi WG, Toyota M, Kim SH, Hilleary R, Gilroy S (2014) Salt stress-induced Ca^{2+} waves are associated with rapid, long-distance root-to-shoot signaling in plants. Acad Sci 111:6497–6502

Choudhary DK, Varma A, Tuteja N (2017) Plant-microbe interaction: an approach to sustainable agriculture. Springer, New Delhi

Clemens S (2006) Toxic metal accumulation, responses to exposure and mechanisms of tolerance in plants. Biochemie 88(11):1707–1719

Cook RD, Ni LO (2007) Elevating soil lead: statistical modeling and apportionment of contribution from lead-based paint and leaded gasoline. Ann Appl Stat 1:130–151

Cramer GR (2011) Effects of abiotic stress on plants: a systems biology perspective. BMC Plant Biol 11(1):163–170

Davies M (1999) Compilation of EU Dioxin exposure and health data Take 7-Ecotoxicology, European commission D.G Environment, UK Department of Environment Transport and the Region (DETR) 97/322/3040/DEB/EI

Davis TA, Volesky B, Mucci A (2003) A review of the biochemistry of heavy metal bios oration by brown algae. Water Res 37(18):4311–4330

De Torres-Zabala M, Truman W, Bennett MH, Lafforgue G, Mansfield JW, Egea PR, Bogre L, Grant M (2007) *Pseudomonas syringae pv*. Tomato hijicks the Arabidopsis abscisic acid-signaling pathway to cause disease. EMBO J 26:1434–1443

de Zelicourt A, Colcombet J, Hirt H (2016) The role of MAPK modules and ABA during abiotic stress signaling. Trends Plant Sci 21:677–685

Dhanya NN, Padmavanthy S (2014) Impact of endophytic microorganism on plants, environment and humans. Sci World J 2:250–693

Du J, Yang JL, Li CH (2012) Advances in metallotionein studies in forest trees. Plant OMICS 5 (1):46–51

Dubiella U, Seybold H, Durian G, Komander E, Lassig R, Witte CP, Schulze WX, Romeis T (2013) Calcium-dependent protein kinase/NADPH oxidase activation circuit is required for rapid defense signal propagation. Proced Nat. Acad Sci 110:8744–8749

Duke NC (2016) Oil spill impacts on mangroves recommendations for operational planning and action based on global review. Mar Pollut Bull 190:700–715

Dureja P, Rayendra ST (2012) Pesticide residues in soil invertebrates. In: Hamir SR, Nollet LML (eds) Pesticide evaluation of environmental pollution. CRC Press, Boca Raton, pp 337–360

Dutta S, Mitra M, Agarwal P, Mahapatra K, De S, Sett U, Roy S (2018) Oxidative and genotoxic damages in plants response to heavy metal stress and maintenance of genome stability. Plant Signal Behav 13(8):1–17

Dwivedi S, Mishra A, Tripathi P, Dave R, Kumar A, Srivastava S, Chakrabarty D, Trivedi PK, Adhikari B, Norton GJ (2012) Arsenic affects essential and non-essential amino acids differentially in rice grains: inadequacy of amino acids in rice based diet. Environ Int 46:16–22

Eapen S, Suseelan KN, Tivarekar S, Kortwal SA, Mitra R (2003) Potential for rhizofilteration of uranium using hairy root cultures of *Brassica Juncea* and *Chenopodium amaranticolor*. Environ Res 91:127–133

Ebegbulam J, Ekperechi D, Adejumo TO (2013) Oil exploration and poverty in the Niger Delta region of Nigeria: a critical analysis. Int J Bus Soc Sci 4(3):279–287

Ekpenyong NS, Udeme US (2015) Crude oil spill and its consequences on sea food safety in coastal area of Ibeno: Akwa Ibom state: studies. Sociol Sci 6(1):1–6

ELC (2008) Bioremediation, environmental literacy council. http://www.enviroliteracy.org/625php. Accessed 20 June 2020

Ellenhorns MJ, Schonwald S, Ordog G, Wasserberger J (1997) Ellen's medical toxicology Diagnosis and treatment of human poisoning, 2nd edn. Baltimore, William and Wilkins

Elum ZA, Monini K, Henri-Ukoha A (2016) Oil exploitation and its socioeconomic effects on the Niger Delta region of Nigeria. Environ Sci Pollut Res 23(13):12880–12889

Etesami H (2018) Bacteria mediated alleviation of heavy metal stress and decreased accumulation of metals in plant tissues: mechanisms and future prospect. Ecotoxicol Environ Saf 148:159–191

Etesami H, Maheshwari DK (2018) Use of plant growth promoting traits in stress agriculture: action mechanisms and future prospects. Ecotoxicol Environ Saf 156:225–246

Farfel MR, Orlova AO, Chaney RL, Lees PS, Rohde C, Ashley PJ (2005) Biosolids compost amendment for reducing soil lead hazards: a pilot study of Orgro® amendment and grass seeding in urban yards. Sci Total Environ 340:81–95

Farwell AJ, Vesely S, Nero V, Rodriguez H, Shah S, Dixon DG, Glick BR (2006) The use of transgenic canola (*Brassica napus*) and plant growth-promoting bacteria to enhance plant biomass at a nickel contaminated field site. Plant Soil 288:309–318

Farwell AJ, Vesely S, Nero V, Rodriguez H, McCormack K, Shah S, Dixon DG, Glick BR (2007) Tolerance of transgenic canola plants (*Brassica napus*) amended with plant growth-promoting bacteria to flooding stress at a metal-contaminated field site. Environ Pollut 147:540–545

Fidalgo F, Azenha M, Silva AF (2013) Copper-induced stress in *Solanum nigrum* L. and antioxidant defense system response. Food Energy Secur 2(1):70–80

Flora SJS (2009) Structural, chemical and biological aspects of antioxidants for strategies against metal and metalloid exposure. Oxidat Med Cellular Long 2(4):191–206

Frampton GK, Jansch S, Scott-Fordsman JJ, Rombke J, vanDen BPJ (2006) Effects of pesticides on soil invertebrates in laboratory studies; a review and analysis using species sensitivity distribution. Envrion Toxicol Chem 25:2480–2489

François F, Lombard C, Guigner JM, Soreau P, Brian-Jaisson F, Martino G, Vandervennet M, Garcia D, Molinier AL, Pignol D (2012) Isolation and characterization of environmental bacteria capable of extracellular biosorption of mercury. Appl Environ Microbiol 78:1097–1106

Gamalero E, Lingua G, Berta G, Glick BR (2009) Beneficial role of plant growth promoting bacteria and arbuscular mycorrhizal fungi on plant responses to heavy metal stress. Can J Microbiol 55(5):501–514

Garbisu C, Hernandez-Allica J, Barrutia O, Alkorta I, Becerril JM (2002) Phytoremediation: a technology using green plants to remove contaminants from polluted areas. Rev Environ Health 17(3):173–188

Germaine KJ, Keogh E, Ryan D, Dowling DN (2009) Bacterial endophytemediated naphthalene phytoprotection and phytoremediation. FEMS Microbiol Lett 296:226–234

Ghosh P, Rathinasabapathi B, Ma LQ (2015) Phosphorus solubilization and plant growth enhancement by arsenic-resistant bacteria. Chemosphere 134:1–6

Ghulam A, Behzad M, Irshad B, Muhammad S, Nabeel KN, Muhammed IK, Mohammed A, Munawar N (2019) Arsenic uptake, toxicity, detoxification and speciation in plants; physiological, biochemical and molecular aspects. Int J Environ Res Public Health 15:59–77

Gkorezis P, Daghio M, Franzetti A, Hamme JD, Sillen W, Vangronsveld J (2016) The interaction between plants and bacteria in the remediation of petroleum hydrocarbons: an environmental perspective. Front Microbiol. https://doi.org/10.3389/fmicb.2016.01836

Glick BR (2010) Using soil bacteria to facilitate phytoremediation. Biotechnol Adv 28:367–374
Gomez-Bernal JM, Ruiz-Huerta EA, Hernande MAA (2017) Heavy metals and arsenic phytoavailability index in pioneer plants from a semi-permanent natural wetland. Environ Prog Sustain Energy 36(1):78–84
Grennan K (2011) Metallothioneins, a diverse protein family. Plant Physiol 155(4):1750–1751
Groenhagen U, Baumgartner R, Gardiner A, Eberl L, Schulz S (2013) Production of bioactive volatiles by different *Burkholderia ambifaria* strains. J Chem Ecol 39(7):892–906
Grondin A, Rodrigues O, Verdoucq L, Merlot S, Leonhardt N, Maurel C (2015) Aquaporins contribute to ABA-triggered stomatal closure through OST1-mediated phosphorylation. Plant Cell 27:1945–1954
Guo JL, Xu LP, Su YC (2013) ScMT2-1-3, a metallothionein ngene of sugarcane, plays an important role in the regulation of heavy metal tolerance/accumulation. Biomed Res Int 1:1–12
Gupta D, Nicoloso F, SchetingerM RL, Pereira L, Castro G, Srivastava S, Tripathi R (2009) Antioxidant defense mechanism in hydroponically grown *Zea mays* seedlings under moderate lead stress. J Hazard Mater 172(1):479–484
Gupta A, Joia J, Sood A, Sood R, Sidhu C, Kaur G (2016) Microbes as potential tool for remediation of heavy metals: a review. J Microb Biochem Technol 8:364–372
Hagan D, Dobbs C, Timilsina N, Escobedo F, Toor GS, Andreu M (2012) Anthropogenic effect on the physical and chemical properties of subtropical coastal urban soil. Soil Use Manag 28:78–88
Hardoin P, Overbeek LS, Elsas JD (2008) Properties of bacteria endophytes and their proposed role in plant growth. Trends Microbiol 16:463–471
Hashem A, Abd-Allah EF, Algarawi AA, Al-Hugail AA, Wirth S, Egamberdieva D (2016) The interaction between arbuscular mycorrhizal fungi and endophytic bacteria enhances plant growth of *Acaica gerrardii* under salt stress. Front Microbiol 7:1–15
Hassan M (2008) Ecological studies on Zooplankton and Macrobenthos of Lake Edku Egypt
Hassan TU, Bano A, Naz I (2013) Alleviation of heavy metal toxicity by the application of plant growth promoting rhizosphere and effect on wheat grown in saline sodic field. Int J Phytoremediation 19:522–529
He J, Duan Y, Hua D, Fan G, Wang L, Liu Y, Chen Z, Han L, Qu LJ, Gong Z (2012) DEXH box RNA helicase-mediated mitochondrial reactive oxygen species production in Arabidopsis mediates crosstalk between abscisic acid and auxin signaling. Plant Cell 24:1815–1833
Hediji H, Djebali W, Belkadhi A, Cabasson C, Moing A, Rolin D, Brouquisse R, Gallusci P, Chaebi W (2015) Impact of long term cadmium exposure on mineral content of *Solanium Lycopersicum* plants: consequences on fruit production. S Afr J Bot 7:176–181
Holman-Dodds JK, Bradley AA, Potter KW (2003) Evaluation of hydrologic benefits of infiltration based urban storm water management. J Am Water Resour Assoc 39:205–215
Hou Q, Ufer G, Bartels D (2016) Lipid signalling in plant responses to abiotic stress. Plant Cell Environ 39:1029–1048
Hua D, Wang C, He J, Liao H, Duan Y, Zhu Z, Guo Y, Chen Z, Gong Z (2012) A plasma membrane receptor kinase, GHR1, mediates abscisic acid- and hydrogen peroxide regulated stomatal movement in Arabidopsis. Plant Cell 24:2546–2561
Huang J, Liu Z, Li S, Xu B, Gong Y, Yang Y, Sun H (2016) Isolation and engineering of plant growth promoting rhizobacteria. *Pseudomonas aeruginosa* for enhanced Cadmium bioremediation. J Gen Appl Microbiol 6(5):258–265
Islam E, Yang X, Li T, Liu D, Jin X, Meng F (2007) Effect of Pb toxicity on root morphology, physiology and ultrastructure in the two ecotypes of *Elsholtzia argyi*. J Hazard Mater 147 (3):806–816
Islam E, Liu D, Li T, Yang X, Jin X, Mahmood Q, Tian S, Li J (2008) Effect of Pb toxicity on leaf growth, physiology and ultrastructure in the two ecotypes of *Elsholtzia argyi*. J Hazard Mater 154(1–3):914–926
Jan S, Parray JA (2016) Approaches to heavy metal tolerance in plants. Springer, New Delhi
Jing YD, He ZL, Yang XE (2007) Role of soil rhizobacteria in phytoremediation of heavy metal contaminated soils. J Zhejiang Univ Sci B 8:192–207

Jingguang C, Wenli Z, Lijun M, Xiaorong F, Guohua X, Guoyou Y (2019) Advances in the Uptake and Transport Mechanisms and QTLs Mapping of Cadmium in Rice. Int J Mol Sci 20 (3417):1–17

Juan Z, Subramanian S, Zhang Y, Yu O (2007) Flavone synthases from *Medicago truncatula* are flavanone-2-hydroxylases and are important for nodulation. Plant Physiol 144:741–751

Kang JW, Khan Z, Doty SL (2012) Biodegradation of trichloroethylene by an endophyte of hybrid poplar. Appl Environ Microbiol 78:3504–3507

Kang CH, Kwon YJ, So JS (2016) Bioremediation of heavy metals by using bacterial mixtures. Ecol Eng 89:64–69

Kasozi GN, Kiremire BT, Bugenyi FWB, Kirsch NH, Nkedi-Kizza P (2005) Organochlorine residues in fish and water sample from Lake Victoria, Uganda. J Environ Qual 35(2):584–589

Khalid S, Shahid M, Niazi NK, Rafiq M, Bakhat HF, Imran M, Abbas T, Bibi I, Dumat C (2017) 1132 Arsenic behavior in soil-plant system: Biogeochemical reactions and chemical speciation 1133 influences. In: Enhancing cleanup of environmental pollutants. Springer, Berlin, pp 97–140

Khan RA (2003) Faunal Diversity of Zooplankton in freshwater wetlands of southeastern West Bengal Zoological Survey

Khan MU, Malik RN, Muhammad S (2013) Human health risk from heavy metal via food crops consumption with waste water irrigation practices in Pakistan. Chemosphere 93:2230–2238

Kidd P, Barcelo J, Bernal MP, Izzo FN, Poschenrieder C, Shilev S, Clemente R, Monterosso C (2009) Trace element behavior at the root-soil interface: implications in phytoremediation. Environ Exp Bot 67:243–259

Kumar S, Dubey RS, Tripathi RD, Chakrabarty D, Trivedi PK (2015) Omics and biotechnology of arsenic stress and detoxification in plants: current updates and prospective. Environ Int 74:221–230

Li SY, Xu ZF, Cheng XL, Zhang QF (2008) Dissolved trace element and heavy metal in the Danjiangkou Reservoir, China. Environ Geol 55(5):977–983

Li RY, Ago Y, Liu WJ, Mitani N, Feldmann J, McGrath SP, Ma JF, Zhao FJ (2009a) The rice aquaporin Lsi1 mediates uptake of methylated arsenic species. Plant Physiol 150:2071–2080

Li TQ, Yang XE, Lu LL, Islam E, He ZL (2009b) Effect of Zn and Cd interactions on root morphology and metal translocation in a hyperaccumulating species under hydroponic conditions. J Hazard Mater 169:734–741

Lin Z, Schemenauer R, Cervinka V, Zayed A, Lee A, Terry N (2000) Selenium volatilization from a soil-plant system for the remediation of contaminated water and soil in the San Joaquim Valley. J Environ Qual 29:1048–1056

Liu J, Schnoor JL (2008) Uptake and translocation of lesser-chlorinated polychlorinated biphenyls (PCBs) in whole hybrid poplar plants after hydroponic exposure. Chemosphere 73:1608–1616

Ma Y, Prasad MNV, Rajkuma M, Freitas H (2011) Plant growth promoting rhizobacteria and endophytes accelerate phytoremediation of metalliferous soils. Biotechnol Adv 29:248–258

Ma Y, Rajkumar M, Rocha I, Oliveira RS, Freitas H (2015) Serpentine bacteria influence metal translocation and bioconcentration of *Brassica juncea* and *Ricinus communis* grown in multi-metal polluted soils. Front Plant Sci 5:757

Macovei JL, Ventura L, Dona M, Fae M, Balestrazzi A, Carbonera D (2010) Effects of heavy metal treatments onmetallothionein expression profiles in white poplar (*Populus albaL.*) cell suspension cultures. Anal Univ Oradea-Fascicula Biol 18(2):274–279

Magdziak Z, Gasecka M, Golinski P, Mleczek M, Chadzinikolau T, Drzewieeka K, Golinski P (2011) Influence of Ca/Mg ratio on phytoextraction properties of salix viminalis H, secretion of low molecular weight organic acid to the rhizosphere. Ecotox Environ Safety 74:33–40

Malaviya P, Singh A (2012) Phytoremediation strategies for remediation of uranium-contaminated environment. A review. Crit Rev Environ Sci Technol 42:2575–2617

Mansour SA (2012) Pesticide residues in man in pesticides evaluation of environmental pollution Rathore HS Nollet LML. CRC Press, New York, pp 467–514

Mastretta C, Taghavi S, van der Lelie D, Mengoni A, Galardi F, Gonnelli C, Barac T, Boulet J, Weyens N, Vangronsveld J (2009) Endophytic bacteria from seeds of Nicotiana tabacum can reduce cadmium phytotoxicity. Int J Phytoremediation 11:251–267

Mbewe G, Mutondo M, Maseka K, Sichilongo K (2016) Assessment of heavy metal pollution in sediments and tilapia fish species in Kafue River of Zambia. Arch Environ Contain Toxicol 71:383–393

McGrath SP, Zhao FJ (2003) Phytoremediation of metals and metalloids from contaminated soils. Curr Opin Biotechnol 14(3):277–282

McGuinness M, Dowling D (2009) Plant-associated bacterial degradation of toxic organic compounds in soil. Int J Environ Res Public Health 6:2226–2247

Mendes JJ (2002) The endocrine disrupters: a major medical challenge. Food Chem Toxicol 40:781–788

Mino CP, Bustamante G, Sanchez ME, Leone PE (2002) Cytogenetic monitoring in a population occupationally exposed to pesticide in Ecudor. Environ Health Perspect 110(11):1077–1080

Mirza N, Pervez A, Mahmood Q, Ahmad SS (2014) Plants as useful vectors to reduce environmental toxic arsenic content. Sci World J 9:1–11

Mishra S, Jha AB, Dubey RS (2011) Arsenite treatment induces oxidative stress, upregulates antioxidant system, and causes phytochelatin synthesis in rice seedling. Protoplasma 248 (3):565–577

Mitani-Ueno N, Yamaji N, Zhao FJ, Ma JF (2011) The aromatic/arginine selectivity filter of NIP aquaporins plays a critical role in substrate selectivity for silicon, boron, and arsenic. J Exp Bot 62:4391–4398

Mitter B, Brader G, Afzal M, Compant S, Naveed M, Trognitz F, Sessitsch A (2013) Advances in elucidating beneficial interactions between plants, soil, and bacteria. In: Donald LS (ed) Advances in agronomy. Academic, New York, pp 381–445

Miyadate H, Adachi S, Hiraizumi A, Tezuka K, Nakazawa N, Kawamoto T, Katou K, Kodama I, Sakurai K, Takahashi H (2011) OsHMA3, a P1B-type of ATPase aects root-to-shoot cadmium translocation in rice by mediating eux into vacuoles. New Phytol 189:190–199

Mourato M, Reis R, Martins L (2012) Characterization of plant antioxidative system in response to abiotic stresses: a focus on heavy metal toxicity. In: Montanaro G, Dichio B (eds) Advances in selected plant physiology aspects. In Tech, Vienna, pp 23–44

Muszynska E, Hanus-Fajerska E (2015) Why are heavy metal hyperaccumulating plants so amazing? Biotechnol J 96:265–271

Nabulo G, Black CR, Craigon J, Youngi SD (2012) Does consumption of leafy vegetables grown in peri-urban agriculture pose a risk to human health? Environ Pollut 162:389–398

Naik MG, Duraphe MD (2012) Review paper on-parameters affecting bioremediation. Int J Life Sci Pharma Res 2(3):77–80

Nakanishi H, Ogawa I, Ishimaru Y, Mori S, Nishizawa NK (2006) Iron deficiency enhances cadmium uptake and m trans location mediated by the Fe2+ transporters OsIRT1 and OsIRT2 in rice. Soil Sci Plant Nutr 52:464–469

Nehra V, Choudhary M (2015) A review on plant growth promoting rhizobacteria acting as bioinoculants and their biological approach towards the production of sustainable agriculture. J Appl Nat Sci 7:540–556

Neidhardt H, Kramar U, Tang X, Guo H, Norra S (2015) Arsenic accumulation in the roots of *Helianthus annuus* and *Zea mays* by irrigation with arsenic-rich groundwater: Insights from synchrotron X-ray fluorescence imaging. Chem Erde-Geochem 75:261–270

Nwilo PC Badejo OT (2008) Oil dispersion and trajectories on Nigerian open sea. In: The conference proceedings of the international conference on the Nigeria state, oil industry and the Niger Delta, pp 164–192

Ogwu FA, Salihat Badamasuiy S, Joseph C (2015) Environmental risk assessment of petroleum industry in Nigeria. Int J Sci Res Innovat Technol 2(4):60–71

Ojeh AO, Peter NU, Onwurah NEI, Nwodo UU (2010) Environmental pollution levels of lead and zinc in Ishiagu and Uburu communities of Ebonyi State, Nigeria. Bull Environ Contam Toxicol 85:313–317

Ojuederie OB, Babalola OO (2017) Microbial and plant-assisted bioremediation of heavy metal polluted environments: a review. Int J Environ Res Public Health 14:1504

Ojumu TV, Bello OO, Sonibare JA, Solomon BO (2005) Evaluation of microbial systems for bioremediation of petroleum refinery effluents in Nigeria. Afr J Biotechnol 4(1):31–35

Ontoyin J, Agyemang I (2014) Environmental and rural livelihood implication of small scale gold mining in Tolensi-Nabdam Districts in Northern Ghana. J Geog Reg Plan 7(8):150–159

Osuagwu ES, Olaifa E (2018) Effects of oil spill on fish production in the Niger Delta. PLoS ONE 13(10):1–14

Ozturk F, Duman F, Leblebici Z, Temizgul R (2010) Arsenic accumulation and biological responses of watercress (Nasturtium officinale R. Br.) exposed to arsenite. Environ Exp Bot 69:167–174

Paul D, lade H (2014) Plant growth promoting rhizobacteria to improve crop growth in saline waters; a review. Agron Sustain Dev 34:737–752

Penuelas J, Asensio D, Tholl D, Wenke K, Rosenkranz M, Piechulla B (2014) Biogenic volatile emissions from the soil. Plant Cell Environ 37(8):1866–1891

Perfus-Barbeoch L, Leonhardt N, Vavasseur A, Forestler C (2002) Heavy metal toxicity: cadmium permeates through calcium channels and disturbs the plant water status. Plant J 32:539–548

Perveen S, Samad A, Nazif W, Shah S (2012) Impact of sewage water on vegetables quality with respect to heavy metals in Peshawar Pakistan. Pak J Bot 44:1923–1931

Piotrowska A, Bajguz A, Godlewska-Zylkiewicz B, Czerpak R, Kaminska M (2009) Jasmonic acid as modulator of lead toxicity in aquatic plant *Wolffia arrhiza* (Lemnaceae). Environ Exp Bot 66 (3):507–513

Pourrut B, Perchet G, Silvestre J, Cecchi M, Guiresse M, Pinelli E (2008) Potential role of NADPH-oxidase in early steps of lead-induced oxidative burst in *Vicia faba* roots. J Plant Physiol 65 (6):571–579

Pourrut B, Shahid M, Dumat C, Winterton P (2011). Lead uptake, toxicity, and detoxification in plants. A reviews of environmental contamination and toxicology. Retrieved on 23/04/2020

Pouyat RV, Yesilorus ID, Russell-Anelli J, Neerchal NK (2007) Soil chemical and physical properties that differentiate urban land use and cover types. Soil Sci Soc Am J 1:1010–1019

Raab A, Schat H, Meharg AA, Feldmann J (2005) Uptake, translocation and transformation of arsenate and arsenite in sunflower (*Helianthus annuus*): Formation of arsenic–phytochelatin complexes during exposure to high arsenic concentrations. New Phytol 168:551–558

Raab A, Wright SH, Jaspars M, Meharg AA, Feldmann J (2007) Pentavalent arsenic can bind to biomolecules. Angew Chem Int Ed 46:2594–2597

Rahman H, Sabreen S, Alam S, Kawai S (2005) Effect of nickel on growth and composition of metal micronutrients in barley plants grown in nutrient solution. J Plant Nutr 28(3):393–404

Rahmati R, Khara J (2011) Effects of vesicular arbuscular mycorrhiza *Glomus intraradices* on photosynthetic pigments, antioxidant enzymes, lipid peroxidation, and chromium accumulation in maize plants treated with chromium. Turk J Biol 35(1):51–58

Rajkuma M, Sandhya S, Majeti P, Freitas H (2012) Perspective of plant associated microbes in heavy metal phytoremediation. Biotechnol Adv 30(6):1562–1574

Rastgoo L, Alemzadeh A, Afsharifar A (2011) Isolation of two novel isoforms encoding zinc- and copper-transporting P1BATPase from Gouan (*Aeluropus littoralis*). Plant Omics J 4 (7):377–383

Reddy VS, Reddy MV, Lee KK, Rao KPC, Srinivas ST (1996) Response of some soil meso and macro-fauna population of soil management during crop and fallow periods on semi-arid tropical alfisol (India). Eur J Soil Biol 32(3):123–129

Reichenauer TG, Germida JJ (2008) Phytoremediation of organic contaminants in soil and groundwater. ChemSusChem 1(8-9):708–717

Rejeb KB, Abdelly C, Savouré A (2014) How reactive oxygen species and proline face stress together. Plant Physiol Biochem 80:278–284

Renault SL, Nakata C, Sabra A, Davis I, Overton D (2007) Revegetation of tailing at Gunnar mine site, Manitoba (NTS 52L14) preliminary observation on plant growth in tailings amended with paper mill sludge. In: Report of activities 2006. Manitoba Science, Technology, Energy and Mines, Manitoba Geological Survey, pp 161–165

Riberro H, Mucha AP, Almeida CMR, Bordalo AA (2014) Potential of phytoremediation for the removal of petroleum hydrocarbons in contaminated salt marsh sediments. J Environ Manag 137:10–15

Roos P, Jakobsen I (2008) Arbuscular mycorrhiza reduces phytoextraction of uranium, thorium and other elements from phosphate rock. J Environ Radioact 99:811–819

Rufyikiri G, Thiry Y, Wang L, Delvaux B, Declerck S (2002) Uranium uptake and translocation by the arbuscular mycorrhizal fungus, *Glomus intraradices*, under root-organ culture conditions. New Phytol 156:275–281

Rufyikiri G, Huysmans L, Wannijna J, Hees MV, Leyval C, Jakobsen I (2004) Arbuscular mycorrhizal fungi can decrease the uptake of uranium by subterranean clover grown at high levels of Uranium in soil. Environ Pollut 130:427–436

Saba H, Jyoti H, Neha S (2013) Mycorrhizae and phytochelators as remedy in heavy metal contaminated land remediation. Int Res J Environ Sci 2(1):74–78

Sasaki A, Yamaji N, Yokosho K, Ma JF (2012) Nramp5 is a major transporter responsible for manganese and cadmium uptake in rice. Plant Cell 24:2155–2167

Satoh-Nagasawa N, Mori M, Sakurai K, Takahashi H, Watanabe A, Akagi H (2013) Functional relationship heavy metal P-type ATPases (OsHMA2 and OsHMA3) of rice (Oryza sativa) using RNAi. Plant Biotechnol 30:511–515

Schutzendubel A, Polle A (2002) Heavy metal signaling in plants: linking cellular and organismic responses. In: Hirt H, Shinozaki K (eds) Plant responses to abiotic stress. Springer, Berlin, pp 187–215

Sengar RS, Gautam M, Sengar RS, Sengar RS, Garg SK, Sengar K, Chaudhary R (2009) Lead stress effects on physiobiochemical activities of higher plants. Rev Environ Contam Toxicol 196:1–21

Sessitsch A, Kuffner M, Kidd P, Vangronsveld J, Wenzel W, Fallmann K, Puschenreiter M (2013) The role of plant-associated bacteria in the mobilization and phytoextraction of trace elements in contaminated soils. Soil Biol Biochem 60:182–194

Sewelam N, Oshima Y, Mitsuda N, Ohme-Takagi N (2014) A step towards understanding plant responses to multiple environmental stresses: a genome wide study. Plant Cell Environ 37:2024–2035

Shahid MA, Balal RM, Pervez MA (2014) Exogenous proline and proline-enriched *Lolium perenne* leaf extract protects against phytotoxic effects of nickel and salinity in *Pisum sativum* by altering polyamine metabolism in leaves. Turk J Bot 38(5):914–926

Sharma I (2012) Arsenic induced oxidative stress in plants. Biologia 67:447–453

Sharma P, Jha AB, Dubey RS, Pessaraldi M (2012) Reactive oxygen species, oxidative damage, and antioxidative defense mechanism in plant under stressful conditions. J Bot 12(3):1–26

Sheng XF, Xia JJ (2006) Improvement of rape plant (*Brassica napus*) growth and cadmium uptake by cadmium resistant bacteria. Chemosphere 64:1036–1042

Sheng XF, He L, Wang Q, Ye H, Jiang C (2008) Effects of inoculation of biosurfactant-producing Bacillus sp. J119 on plant growth and cadmium uptake in a cadmium amended soil. J Hazard Mater 155:17–22

Shukla D, Tiwari M, Tripathi RD, Nath P, Trivedi PK (2013) Synthetic phytochelatins complement a phytochelatin deficient Arabidopsis mutant and enhance the accumulation of heavy metal (loid)s. Biochem Biophys Res Commun 434(3):664–669

Singh R, Tripathi RD, Dwivedi S, Kumar A, Trivedi PK, Chakrabarty D (2010) Lead bioaccumulation potential of an aquatic macrophyte *Najas indica* are related to antioxidant system. Bioresour Technol 101:3025–3032

Sirichandra C, Gu D, Hu HC, Davanture M, Lee S, Djaoui M, Valot B, Zivy M, Leung J, Merlot S (2009) Phosphorylation of the Arabidopsis AtrbohF NADPH oxidase by OST1 protein kinase. FEBS Lett 583:2982–2986

Slatter KA (2013) Nickel accumulation and tolerance in Berkheya Codii and its application in phytoremediation. Master's Thesis, University of Kwazulu, Natal, South Africa

Solanki R, Dhankhar R (2011) Biochemical changes and adaptive strategies of plants under heavy metal stress. Biologia 66(2):195–204

Song X, Wong MD, Kawase E, Xi R, Ding BC, McCarthy JJ, Xie T (2004) Bmp signals from niche cells directly repress transcription of a differentiation-promoting gene, bag of marbles, in germline stem cells in the Drosophila ovary. Development 131(6):1353–1364

Sreelal G, Jayanthi R (2017) Review on phytoremediation technology for removal of soil contaminants. Indian J Sci Res 14(1):127–130

Steele MK, McDowell WH, Aitkenhead-Peterson JA (2010) Chemistry of urban, suburban, and rural surface waters. In: Aitkenhead-Peterson J, Volder A (eds) Urban ecosystem ecology, Agron. monogr. 55. ASA, CSSA, and SSSA, Madison, WI, pp 297–340

Susan L, Schantz SL, Gasior DM, Polverejan E, McCaffrey RJ, Sweeneys AM, Humphery HEB, Gardiner JC (2001) Impairments of memory and learning in older adults exposed to polychlorinated biphenyls via consumption of great lake fish. Environ Health Perspect 109:605–611

Szabados L, Savour A (2010) Proline: a multifunctional amino acid. Trends Plant Sci 15(2):89–97

Taghavi S, Weyens N, Vangronsveld J, Lelie D, Pirttilä AM, Frank AC (2011) Improved phytoremediation of organic contaminants through engineering of bacterial endophytes of trees. Endophytes of forest trees. Springer, Cham, pp 205–216

Teschler JK, Zamorano-Sánchez D, Utada AS, Warner CJ, Wong GC, Linington RG, Yildiz FH (2015) Living in the matrix: assembly and control of *Vibrio cholerae* biofilms. Nat Rev Microbiol 13:255–268

Thangavel P, Long S, Minocha R (2007) Changes in phytochelatins and their biosynthetic intermediates in red spruce (*Picea rubens Sarg*.) cell suspension cultures under cadmium and zinc stress. Plant Cell Tissue Organ Cult 88(2):201–216

Theodorakis CW, Bickham JW, Donnelly KC, Mc Donald TJ, Willink PW (2012) DNA damage in cichlid from an oil production facility in Guatemala. Ecotoxicology 21:496–511

Tomulescu IM, Radoviciu EM, Merca VV, Tuduce AD (2004) Effect of copper, zinc and lead and their combinations on the germination capacity of two cereals. J Agric Sci 15:1–8

Ton J, Flors V, Mauch-Mani B (2009) The multifaceted role of ABA in disease resistance transcription reprogramming. New Phytol 186:333–339

Tripathy RD, Srivastava S, Mishra S, Singh N, Tuli R, Gupta DK, Maathuis FJ (2007) Arsenic hazard, strategies for tolerance and remediation by plant. Trends Biotechnol 25:158–165

Udebuani AC, Ozoh PT (2007) Aspects of the chemistry of soils and Elaine indica growing on seven years oil spill site. Int J Trop Agric Food Syst 1(2):187–192

Udebuani AC, Okoli CI, Nwigwe HC, Ozoh PTE (2012) The value of animal manure in the enhancement of bioremediation processes in petroleum hydrocarbon contaminated agricultural soils. J Agric Technol 8(6):1935–1952

Upadhyaya H, Panda SK, Bhattacharjee MK, Dutta S (2010) Role of arbuscular mycorrhiza in heavy metal tolerance in plants: prospects for phytoremediation. J Phytology 2(7):16–27

Uraguchi S, Fujiwara T (2012) Cadmium transport and tolerance in rice: perspectives for reducing grain cadmium accumulation. Rice 5(5):1–8

Uroz S, Christophe C, Turpault MP, Frey-Klett P (2009) Mineral weathering by bacteria: ecology, actors and mechanisms. Trends Microbiol 17(8):378–387

Uzu G, Sobanka S, Sarret G, Munoz M, Dumat C (2010) Foliar lead uptake by lettuce exposed to atmospheric fallout. Environ Sci Technol 44:1036–1042

Van AB, Tehrani R, Schnoor J (2011) Endophyte-assisted phytoremediation of explosives in poplar trees by MethylobacteriumpopuliBJ001T. In: Pirttila AM, Frank AC (eds) Endophytes of forest trees. Springer, Cham, pp 217–234

Vander Ent A, Baker AJM, Reeves RD, Pollard AJ, Schat H (2013) Hyperaccumulators of metal and metalloid trace elements: farts and fiction. Plant Soil 362:319–334
Venturi V, Keel C (2016a) Signaling in the rhizosphere. Trend Plant Sci 21:187–198
Venturi V, Keel C (2016b) Signaling in the rhizosphere. Trends Plant Sci 21(3):187–198
Verma S, Nizam S, Verma PK (2013) Biotic and abiotic stress signaling in plants. Stress signaling in plants. Genom Proteom Persp 1:25–49
Weyens N, Lelie D, Taghavi S, Newman L, Vangronsveld J (2009) Exploiting plant-microbe partnerships for improving biomass production and remediation. Trends Biotechnol 27:591–598
Wu Z, Zhao X, Sun X, Tan Q, Tang Y, Nie Z, Qu C, Chen Z, Hu C (2015) Antioxidant enzyme systems and the ascorbate-glutathione cycle as contributing factors to cadmium accumulation and tolerance in two oil seed rape cultivars (*Brassica napus* L), under moderate cadmium stress. Chemosphere 138:526–536
Yamada K, Xu H-L (2000) Properties and application of an organic fertilizer inoculated with effective microorganisms. J Crop Prod 3(1):255–268
Yamaji N, Xia J, Mitani-Ueno N, Yokosho K, Ma JF (2013) Preferential delivery of zinc to developing tissues in rice is mediated by P-type heavy metal ATPase OsHMA2. Plant Physiol 162:927–939
Yan J, Tsuchihara N, Etoh T, Iwai S (2007) Reactive oxygen species and nitric acid are involved in ABA inhibition of stomata opening. Plant Cell Environ 30(10):1320–1325
Yi H-S, Yang JW, Ryu C-M (2013) ISR meets SAR outside: Additive action of the endophyte *Bacillus pumilus* INR7 and the chemical inducer, benzothiadiazole, on induced resistance against bacterial spot in field grown pepper. Front Plant Sci 4:1–122
Yu M, Tsunoda H, Tsunoda M (2011) Environmental toxicology: biological and health effects of pollutants, 3rd edn. CRC Press, Boca Raton
Zhang H, Chai V, Ye Z (2011) Single factor analysis of Chongqing index method of non-point pollution water stream. Public Commun Sci Technol 10:23–231
Zhang Z, Abuduwaili J, Jiang F (2013) Heavy metals in surface water in eastern, central and western Tianshan mountains, Central Asia. Asian J Chem 25(14):7883–7887
Zhang B, Matchinski EJ, Chen B, Ye X, Jing L, Lee K (2019) Marine oil spills - oil pollution, sources and effects. World Seas 2019:391–406
Zhao F, Ma J, Meharg A, McGrath S (2009) Arsenic uptake and metabolism in plants. New Phytol 181:777–794
Zhaoyong Z, Abuduwaili J, Fengqing J (2015) Heavy metal contamination, source and pollution assessment of surface water in the Tianshan mountain of China. Environ Monit Assess 187:13
Zhu YL, Zayed AM, Quian JH, De Souza M, Terry N (1999) Phytoaccumulation of trace elements by wetlands plants: II. Water hyacinth. J Environ Qual 28:339–344

Advanced Bioremediation Strategies for Mitigation of Chromium and Organics Pollution in Tannery

10

Manikant Tripathi, Durgesh Narain Singh, Nivedita Prasad, and Rajeeva Gaur

Abstract

Recent past has witnessed to increase in environmental pollution because of rapid urbanization and industrialization. Various organic and inorganic toxicants are present in tannery effluents such as metals and other xenobiotic compounds which cause imbalance to the ecosystem having carcinogenic effects threaten plants, human, and animals' health. Chromium is one of the major pollutants discharged from tanneries, is highly toxic, mutagenic, and carcinogenic in nature. There are several remedial measures for the removal of such toxicants. Physico-chemical approaches remove the pollutants but they are not cost-effective and eco-friendly. Microorganisms based treatment of toxic chemicals either in liquid or solid system is one of the most economic, effective, environment friendly, robust, and sustainable remediation strategy. Several microbes of different physicochemical orientation and plants may selectively be employed for such remedial measure of any type of toxic chemicals of industrial effluent. This chapter discusses the recent advances and challenges in bioremediation methods of tannery wastewater.

Keywords

Bioremediation · Chromium · Heavy metals · Tannery · Pollution

M. Tripathi · R. Gaur (✉)
Department of Microbiology, Dr. Rammanohar Lohia Avadh University, Ayodhya, Uttar Pradesh, India

D. N. Singh
Department of Zoology, University of Delhi, Delhi, India

N. Prasad
Department of Dairy Microbiology, Sam Higginbottom University of Agriculture Technology & Sciences, Prayagraj, Uttar Pradesh, India

© The Author(s), under exclusive licence to Springer Nature Singapore Pte Ltd. 2021

V. Kumar et al. (eds.), *Rhizobiont in Bioremediation of Hazardous Waste*,
https://doi.org/10.1007/978-981-16-0602-1_10

10.1 Introduction

In the past few years, industrialization and modernization produced many problems in the form of hazardous pollutants in the environment. Industrial processes insert various types of hydrocarbons, heavy metals, chlorinated phenols, biocides, and dyes to the environment (Garg and Tripathi 2011; Nicolopoulou-Stamati et al. 2016; Tripathi et al. 2019). These pollutants cause pollution in water, soil, and air resulting in harmful effects on environment and human health (Zhang et al. 2020). Chromium has contaminated all types of water resources (Szulczewski et al. 1997). There are several other industries such as chemical, iron, and steel producing bulk of chromium pollution (Chirwa and Wang 2000, 2005; Garg et al. 2012). The excessive use of hexavalent chromium (Cr^{6+}) in industries has caused substantial environmental pollution (Sultan and Hasnain 2007). Such waste is discharged into the ecosystem through leakage and inappropriate remediation methods (Palmer and Wittbrodt 1991). Chromium is listed as a priority pollutant by United States Environmental Protection Agency with discharge limit of 0.05 mg L^{-1} (U.S. EPA 1979). While the permissible limit for Cr^{6+} is 0.1 mg L^{-1} in India (Bhide et al. 1996). Chromium exists from −2 to +6 oxidation states (Avudainayagam et al. 2003); however, the most common oxidation states of Cr are +6 and + 3 (Garg et al. 2012). Cr^{6+} is toxic, carcinogenic, mutagenic, and teratogenic (Garg et al. 2013; Tripathi et al. 2011a, b, 2019). It is important to remove such toxicants or at least transform them to nontoxic form before they release into the environment. Our ecosystem is damaging due to discharge of improperly treated large quantities of heavy metals and organics containing toxic waste. Due to their bioaccumulation, persistence, and resistance to bioremediation, metal pollution has become hazardous to all living forms of our environment. To tackle the challenges due to Cr^{6+} pollution, a concerted effort should be undertaken involving both surveillance of its use and improvements in remediation processes (Garg et al. 2012).

Another major toxicant is pentachlorophenol, also discharged from tannery effluent which is highly toxic and recalcitrant (Srivastava and Thakur 2007; Thakur et al. 2001; Tripathi et al. 2014a, b). Due to its toxicity, US EPA listed PCP in the list of priority pollutants. According to the ISI, the standard limit for phenolics is 0.002 mg L^{-1} in surface waters (Tripathi and Garg 2013). Phenolic compounds are accumulated in biological food chains causing toxic effects (Garg et al. 2013). Thus, remediation of such pollutants from effluent is necessary. There are many strategies that have been used for preventing harmful effect of such pollutants up to certain level. Physical and chemical methods are being used to remediate these pollutants but due to some limitations such as cost and non-ecofriendly nature, it has not been applied successfully. Despite this, microbiological methods or bioremediation are currently applied to decrease the toxicity of pollutants from soil, water, and environment.

Bioremediation is the application of live forms of organisms, particularly microbes, to remove pollutants and transform them into innocuous forms in the environment (Garg et al. 2012). Microbe based remediation has been developed to degrade toxicants through various biosynthetic pathways. A number of bacteria,

fungi, algae, actinomycetes, etc. are being used for bioremediation. This process is facilitated by two ways, in situ (on site) and ex situ (away from site). Microbial systems are being introduced to the contaminated site to enhance the remediation process known as bioaugmentation (Vidali 2001) which are mechanized by bioreduction, biosorption, and bioaccumulation (Rehman et al. 2007). Bioreduction is another approach of bioremediation in which the toxic Cr^{6+} is reduced to Cr^{3+} using microbial enzyme chromate reductase (Tripathi and Garg 2014a, b). The main benefits of bioremediation over traditional methods include cost effective, less amounts of secondary pollutants, good efficiency, and regeneration of biomass for further use (Garg et al. 2013). This chapter discusses different advanced methods of bioremediation, and their mechanisms using potential microorganisms in the treatment of hexavalent chromium and organic pollutants from the tannery wastewater.

10.2 Physicochemical Characteristics of Tannery Wastewater

Tannery wastewater causes serious problems to ecosystem because of various toxic components. Such toxicants came in the environment through discharge from industries affecting almost all living systems. Some researchers discussed common characteristics of the organic pollutants (Yadav et al. 2016). There are several parameters like biological oxygen demand (BOD), chemical oxygen demand (COD), total dissolved solid (TDS), residual chlorine, sulphide, nitrate, phenol, total chromium along with other heavy metals, oil and grease were found above than the standard permissible levels of tannery wastewater (Table 10.1). Heavy metals cause serious toxicological concerns to human health (Davis et al. 2000; Yadav et al. 2017).

Both BOD and COD values indicate the level of organic pollution in wastewater (Tripathi et al. 2011a). Tiwari et al. (2012) used a bacterium, *Pediococcus acidilactici* B-25 strain for the removal of color, COD, and BOD of distillery wastewater. There are many inorganics such as Cr^{6+} along with other heavy metals which are not easily removed from the polluted sites and persist in the environment. Thus, it is very important to treat properly such toxicants from tannery effluent before discharge into the environment.

10.3 Chromium and Organics Pollution

Chromium and organics pollution may be due to several weathering of rocks, discharge of improperly treated industrial effluent such as tannery waste and leaching of soils (Oliveira 2012). However, contamination from oil spills, leakages, domestic, and industrial wastes contributes to organics pollution in the environment (Fig. 10.1). Cr^{6+}contamination in the environment adversely affects the soil microbial communities (Yadav et al. 2016).

It causes several health problems to living systems (Chandra et al. 2011; Turick et al. 1996). These contaminants are entering and increasing in our ecosystem

Table 10.1 General properties of the treated tannery wastewater (Source: Tripathi et al. 2011a)

Physicochemical parameter/heavy metal	Permissible limit[a]	Obtained value
pH	5.5–9.0	7.3 ± 0.15[b]
Temperature	<35 °C	34 ± 0.27
Total solid (mg L^{-1}) Total suspended solid (mg L^{-1}) Total dissolved solid (mg L^{-1})	– 600 2100	3468 ± 1.89 1102.25 ± 0.22 2366.62 ± 1.65
Total alkalinity (mg L^{-1})	–	340 ± 3.05
Total acidity (mg L^{-1})	–	201.33 ± 1.08
Residual chlorine (mg L^{-1})	1	5.17 ± 0.18
Hardness (mg L^{-1})	–	780.45 ± 1.02
Sulfide (mg L^{-1})	2.0–5.0	9.43 ± 0.20
Oil and grease (mg L^{-1})	10.0	19.86 ± 0.67
B.O.D. (mg L^{-1})	30.0	104.90 ± 0.25
C.O.D. (mg L^{-1})	250.0	490.93 ± 1.27
Total nitrogen (mg L^{-1})	100.0	30.64 ± 0.69
Nitrate (mg L^{-1})	10.0	15.09 ± 0.05
Phenol (mg L^{-1})	1–5.0	11.93 ± 0.17
Cr^{6+} (mg L^{-1}) Total-Cr (mg L^{-1})	0.1 2.0	1.26 ± 0.05 8.89 ± 0.74
Pb^{2+} (mg L^{-1})	0.1	0.47
Cu^{2+} (mg L^{-1})	3.0	0.006
As^{3+} (mg L^{-1})	0.2	0.39
Ni^{2+} (mg L^{-1})	3.0	0.72
Zn^{2+} (mg L^{-1})	5.0	0.36
Cd^{2+} (mg L^{-1})	2.0	0.002

[a]Permissible limits prescribed by United States Environment Protection Agency (USEPA) and Ministry of Environment and Forest (MOEF)
[b]Mean value ± SD

because of rapid industrialization and urbanization. There must be strict rules to overcome from pollution. Xenobiotics are synthesized chemicals that persist in the ecosystem for longer period at higher concentrations. They are recalcitrant compounds such as pentachlorophenol and synthetic dyes discharged from various industrial discharges (Garg et al. 2012; Garg and Tripathi 2011; Tripathi et al. 2019).

10.4 Toxicity of Chromium

Chromium of hexavalent nature is more toxic, mutagenic, and carcinogenic in aquatic systems (Losi et al. 1994; Lovely and Coates 1997; Pal et al. 2005; Ray and Ray 2009), whereas $Cr^{3+}$is innocuous form of chromium. The increased bioconcentration of metals and their toxicity to all the live forms show the urgent call for the treatment of these toxicants from the polluted soil and water. The metals are generally accumulated in living systems through the food (Perpetuo et al. 2011).

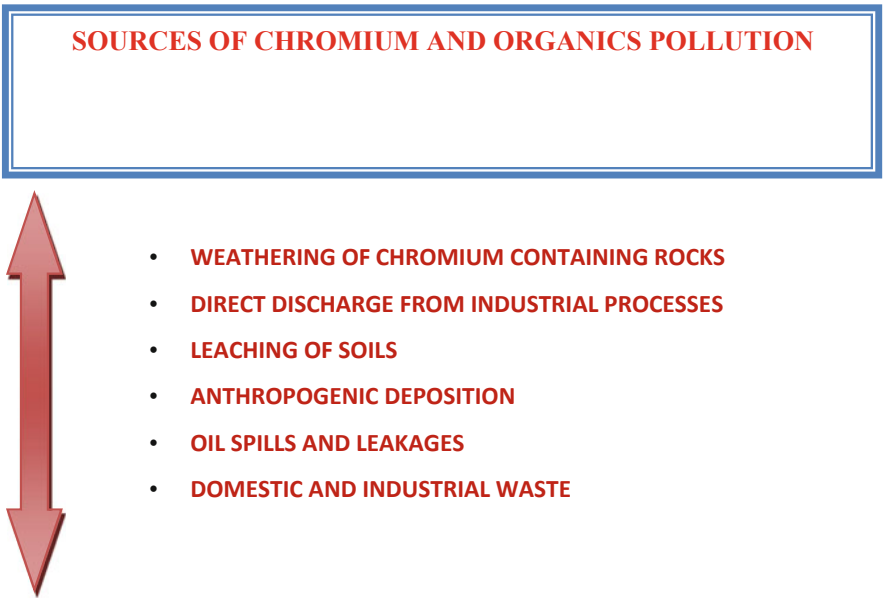


Fig. 10.1 Different sources of chromium and organics contamination in the environment

Heavy metal like Cr inhibits photosynthesis, growth and causes chlorosis in plants by hindering iron metabolism (Purakayastha and Chhonkar 2010; Upadhyay et al. 2017). Chromium affects various tissues in human and animals that include dermal, lung, liver, kidney, red blood cells, and spleen (Holmes et al. 2008). Kumar et al. (2013) reported adverse effects of heavy metals to human health. There are number of diseases such as respiratory and nephrotic ailments found in the workers of tannery industry (Maria et al. 1999).

10.5 Bioremediation

Bioremediation is one of the most important approaches for pollution mitigation. It offers the possibility of using indigenous or exogenous microbes to detoxify or degrade various toxicants that are hazardous to ecosystem. Bioremediation occurs aerobically or anaerobically. It removes pollutants which are detrimental to the environment by the application of phyto- and microbial remediation (Kumar et al. 2017). A number of bioremediation processes such as bioaugmentation, biostimulation, bioreduction, biosorption, bioaccumulation, immobilization, and phytoremediation are being used for Cr^{6+} remediation and organic pollutants.

Figure 10.2 shows the different strategies for Cr^{6+} and organic pollutants remediation from contaminated sites. These methods include physical, chemical, and biological along with modern approaches for treating contaminated sites. In general, bioremediation process can be performed by ex/in situ. In situ bioremediation

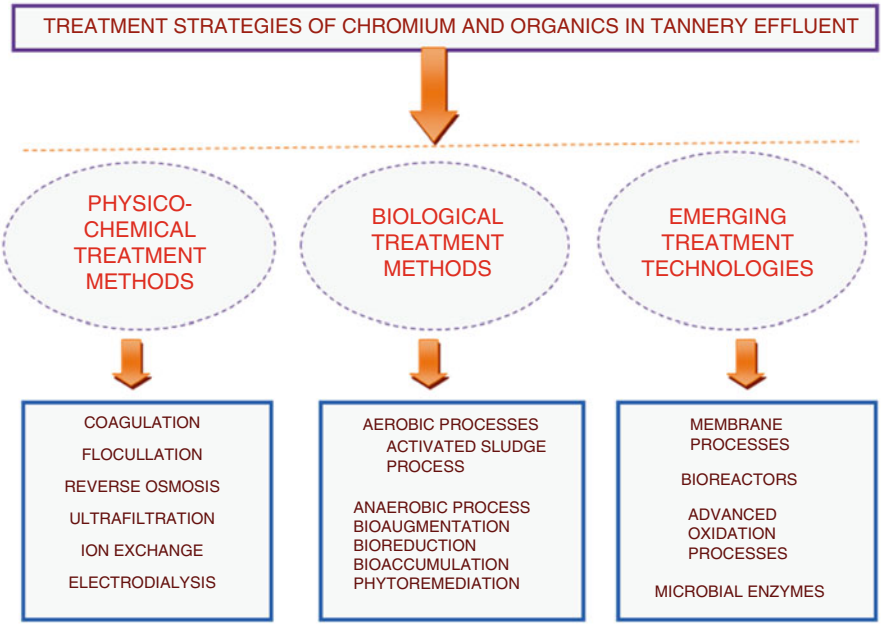


Fig. 10.2 Different methods for remediation of hexavalent chromium and organics from polluted sites

(bioventing, biosparging, phytoremediation) involves the treatment of contaminant on site of its origin. However, in ex situ bioremediation (composting, land fills, biopiles), treatment of pollutants occurs away from the contaminated origin sites that involve transportation.

Thus, in situ bioremediation is better option for treatment due to its cost effectiveness and feasibility.

It has been showed in many studies that microbes can interact with heavy metals ions (Cr^{6+}) for their removal (Garg et al. 2018; Ishibashi et al. 1990; Shen and Wang 1995; Upadhyay et al. 2017; Tripathi et al. 2018; Tripathi and Garg 2014a, b). The reduction of Cr^{6+} to $Cr^{3+}$is used to detoxify Cr^{6+} from polluted sites. Genetic engineering of microbial cells may change their characteristics in such a way that may help to bioremediation.

There are some important factors such as the use of low cost waste biomass, its immobilization and regeneration for opting bioremediation as a strategy for the removal of toxicants from industrial effluent (Quintelas et al. 2006; Garg et al. 2012; Tripathi et al. 2019). Also, there are various physicochemical and nutritional parameters that may affect the bioremediation of tannery waste (Fig. 10.3) which control the treatment process in the ecosystems that are polluted with Cr^{6+} and organic pollutants.

Different bioremediation approaches for mitigation of Cr^{6+} and organic pollutants are discussed below.

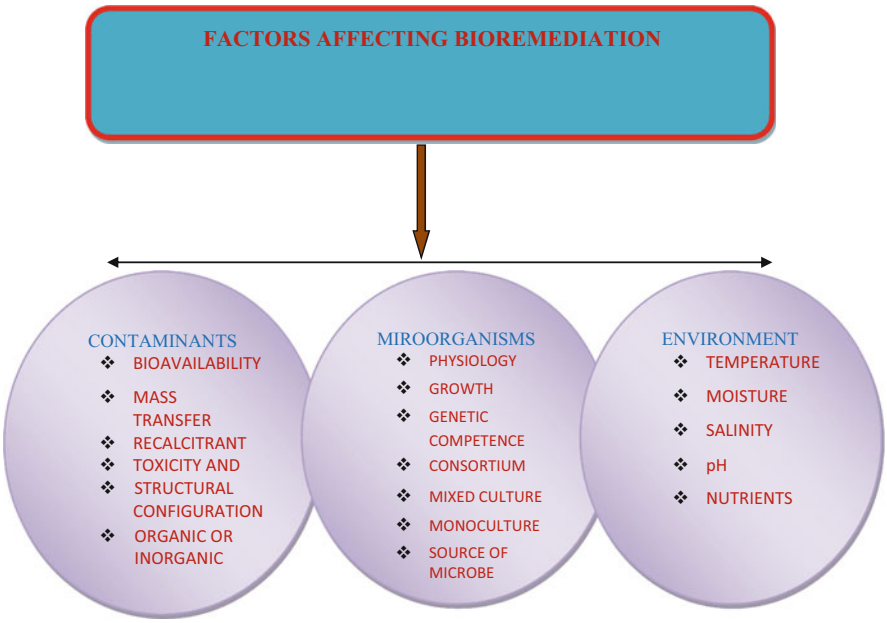


Fig. 10.3 Factors affecting bioremediation of Cr^{6+} and organic pollutants in tannery effluent

10.5.1 Mechanism of Cr^{6+} Removal by Microorganisms

Several microbes have been used with their applicability in Cr^{6+} bioremediation (Garg et al. 2013; Tripathi et al. 2011a, b, 2014a, b; Tripathi and Garg 2010, 2013). There are some important methods applied in heavy metal bioremediation by decreasing the solubility of metals by altering the pH, redox reaction, and adsorption from the contaminated sites. In redox reactions, heavy metals are transformed into the less toxic form that is less mobile and stable. The major bioremediation mechanisms of Cr^{6+} are biosorption, bioaccumulation, bioreduction, bioaugmentation, phytoremediation, and enzymatic transformation (Fig. 10.2). The efficiency of these techniques depends on several parameters that include the type and nature of organism used, the existing environmental factors, nutrients availability, and the concentration of pollutant present in that environment (Fig. 10.3).

10.5.1.1 Biosorption

It is an independent passive metabolic process in which physicochemical interaction occurs between metal species and the cellular components of microbial species (Shumate and Strandberg 1985). The biosorption process comprises different kinds of mechanisms that include physical adherence, ion exchange, and surface complexation, which differs based on the type of microorganisms used and method of processing (Srivastava and Dwivedi 2015). There are different biosorbent materials such as bacteria, yeast, algae, and fungi, which carry out the biosorption

process through several mechanisms, including ion exchange, redox processes, electrostatic interactions, surface complexation, and precipitation (Beiyuan et al. 2017). Different functional groups such as carboxyl, imidazole, sulfhydryl, amino, phosphates, etc. are present on biosorbent which interact with metal species (Garg et al. 2012). The selection of biosorbent material requires certain criteria that must be followed, including low cost and reusable biosorbent, rapid movement of metals, and effective separation from the solution (Kumar et al. 2016).

Microorganisms, due to their widespread presence, play significant role in transforming toxic heavy metals into nontoxic forms. Microbes act as effective biosorbents due to their small size for removal of such toxicants. The bacterial cell wall is the main barrier which save microbes from toxic heavy metals. The cell wall carries a natural negative charge and has various functional groups that are involved in the metal binding and also regulate their movement across the membrane. These bacteria contain carboxyl and phosphate groups present in their cell wall that acts as the main binding site for metal cations (Fomina and Gadd 2014; Ayangbenro and Babalola 2017). The type of interaction involves ion exchange, chemical, and physical processes (Garg et al. 2012). The cell wall of microbes consists of proteins, lipids, and polysaccharides (Dixit et al. 2015).

Various microbial groups such as bacteria, fungi, algae, actinomycetes, etc. are applied for biosorption of toxic hexavalent chromium by many researchers. Biosorption is carried out by dead and live cells (Srinath et al. 2002; Tripathi et al. 2011b). Several researchers used microorganisms for removal of Cr^{6+} (Garg et al. 2013; Park et al. 2005; Srinath et al. 2002; Tripathi et al. 2011b). The pH specificity also plays an important role in biosorption (Volesky 1990).

Generally, industrial effluents are characterized by coexistence of many types of toxic cationic and anionic species (Garg et al. 2012). Industrial effluents generally contain numerous cations and anions of metals/non-metals, the latter of which may impart assistance in binding of the concerned heavy metals. Thus, it is important to study the influence of toxicants mixtures on the growth of microbes when studying bioremediation strategies.

10.5.1.2 Bioaccumulation

It is energy-dependent, i.e., it uses the metabolic energy of bacteria to transport heavy metals by several processes like adsorption, intracellular accumulation, and bioprecipitation mechanisms. These mechanisms are reported to be related with the transport of heavy metals. Several researchers study the bioaccumulation of Cr^{6+} by different types of microorganisms (Congeevaram et al. 2007; Srivastava and Thakur 2007; Tripathi et al. 2011b). Parameswari et al. (2009) observed the efficacy of *Azotobacter chroococcum*, *Bacillus* sp., and *Pseudomonas fluorescens* for Cr^{6+} removal. However, biosorption, as a passive process, has several advantages over bioaccumulation. In biosorption, the simple physical method of recovery of heavy metal is achieved without breaking the biosorbents structural integrity, while bioaccumulation is a passive as well as active process in which cells get disrupted during the process.

10.5.1.3 Biostimulation

Nutritional amendment also enhances the process of bioremediation. Biostimulation process facilitates the growth of native microbes of the polluted site by providing nutrients, oxygen, surfactants, and pH alteration substances which are responsible to increase the bioremediation process (Li and Li 2011). Garg et al. (2018) studied the effect of nutrient addition on Cr^{6+} removal by adding carbon and nitrogen sources in diluted tannery effluent. They observed better removal efficiency than nutrients unaided effluent.

10.5.1.4 Bioaugmentation

In this approach, exogenous microbes are added to the population of native microbes in order to increase the capability of already existing microbes to remove the pollutants. The microbes that have naturally occurring catabolic genes or that are genetically modified can be used in this process. This process is affordable, efficient, and quick, making its way among remediation experts. Garg et al. (2016) reported better Cr^{6+} ability in *Pseudomonas* sp. augmented diluted effluent medium than unaugmented medium.

10.5.1.5 Bioreduction

The oxidation state of toxic metals is affected by the activities of microorganisms for the reduction of Cr^{6+} to Cr^{3+} (Asatiani et al. 2004; Farag and Zaki 2010; Ilias et al. 2011; Liu et al. 2008; Tripathi et al. 2011a). Bacteria that grow in high Cr^{6+} containing natural environment develop chromium resistance indicate that they have ability to reduce Cr^{6+}, thereby may be isolated such resistant strain directly from ecosystem (Liu et al. 2008). Tripathi and Garg (2014a, b) reported 74.5% reduction by indigenous bacterial isolate *B. cereus* at initial 200 mg Cr^{6+} L^{-1} within 48 h incubation in minimal salt medium. However, Garg et al. (2018) found that *P. putida* strain has the ability to survive and reduce chromate in tannery effluents. The isolate survived in the native diluted tannery effluent and reduced Cr^{6+}. However, supplementation with carbon and nitrogen sources enhanced the bioremediation of Cr^{6+} in native diluted effluent. The microbial mechanisms for Cr^{6+} reduction is a detoxification mechanism that occurs intracellularly with the help of enzyme chromate reductase (Tripathi and Garg 2014a, b).

10.5.1.6 Immobilization and Elution of Chromium

The cell biomass used for biosorption as well as bioaccumulation is loaded with metals, and desorption of the loaded metal separate metal from adsorbent for reuse in industry, and the regenrated biomass is suitable for next round(s) of biosorption which make cost effective bioremediation process (Garg et al. 2012). Agar, polyacrylamide, and alginate matrices have been used in several immobilization studies (Tripathi and Garg 2013). The elution of bound chromium from cell biomass depends on its ionic state. It is normally found that when chromium is bound in hexavalent state, its simple elution by acidic solutions is based on reduction to trivalent state, which is then subsequently released into the eluent fraction (Garg et al. 2012). Some researchers reported sulfuric acid (1.0 M) and found to be the

most efficient eluent (Srinath et al. 2003). Benazir et al. (2010) studied the chromium bioremediation efficiency in the consortium of *B. subtilis, P. aeruginosa,* and *S. cerevisiae* in immobilized and nonimmobilized cells. Tripathi and Garg (2013) also used immobilized cells of *B. cereus* with alginate for Cr^{6+} removal. Similarly, Garg et al. (2018) also used *Pseudomonas putida* for bioremediation of Cr^{6+} in raw diluted tannery effluent. Immobilized cells may be better option for bioremediation than free cells because free cells are more exposed to the toxicity of pollutants which may cause lesser bioremediation by them.

10.6 Methods for Removal of Organic Pollutants from Tannery Wastewater

10.6.1 Chemical Methods

10.6.1.1 Coagulation and Flocculation

The tannery wastewater contains different types of organic pollutants, solid matters, and toxic metal ions which impose serious threat to the environment when disposed off without treatment (Table 10.1). Some of the important organic pollutants present in wastewater are benzene, naphthalene sulfonates, and syntans (Lofrano et al. 2013). Syntans are synthetic tannins added to soften the leather (Lofrano et al. 2008). Syntans have complex structure composed of naphthalene-, phenol-, formaldehyde-acrylic resins and melamine (De Nicola et al. 2007; Lofrano et al. 2007; Munz et al. 2009). Besides, tannery wastewater contains the considerable amount of chromium, which is above the permissible limit of 0.1 mg L^{-1}. The different types of inorganic coagulants have been applied for the coagulation and removal of organic pollutants, total solids, and toxic metal ions from tannery wastewater before proceeding for biological treatment (Lofrano et al. 2013). Different coagulants act differently in terms of reduction in organic load (COD), BOD, total dissolved solid, suspended solids, and toxic metal ions such as chromium (Ates et al. 1997; Kabdasli et al. 1999; Song et al. 2004; Lofrano et al. 2006). Coagulants are effective at specific pH that depends on the properties of wastewater (TE) as well nature and concentration of coagulants (Song et al. 2004). Using $FeSO_4$, $FeCl_3$, and alum, more than 99% of chromium and 40–70% of COD was removed from the wastewater of leather tanning (Kabdasli et al. 1999). In another study, only 30–37% of total COD and 74–99% of chromium were removed when 800 mg $L^{-1}$of alum was used as coagulants (Song et al. 2004). Nevertheless, chemical treatment methods have been effective in limited application due to generation of TE at very large scale that requires huge quantity of chemicals increasing the pollution which limits the application of chemical treatment method.

10.6.2 Biological Treatment

Biological treatment method involves activities of mixed microbial communities to remove organic pollutants from TE. It is a friendly and less-expensive alternative to chemical treatment. However, high concentration of tannins, toxic metal ions, and persistence organic compounds hampers the microbial activities (Lofrano et al. 2013). Biological treatment processes have been categorized into aerobic or anaerobic process. This has been further sub-divided into activate sludge, anaerobic stirred tank reactors, or attached biofilm process.

10.6.2.1 Aerobic Processes

During aerobic treatment, tannery wastewater is mixed with aerobic microorganisms in the presence of oxygen. Soluble, suspended, and colloidal organic pollutants that contribute to BOD are metabolized by microorganisms leading to production of carbon dioxide and decrease in the level of BOD. Production of excess microbial biomass during the process of biodegradation is a major drawback of aerobic process. Besides higher concentration of tannins, toxic metal ions and persistence organic compounds inhibit the biological treatment process (Lofrano 2013). In a study, growth of heterotrophic bacteria was significantly inhibited in the presence of 10 mg L^{-1} Cr (VI) (Stasinakis et al. 2002). A conventional sequencing batch reactor (SBR) has specialized architecture to support various group of microorganisms for effective biological treatment processes (Farabegoli et al. 2004; Ganesh et al. 2006). The most commonly used aerobic biological treatment processes are conventional activated sludge processes and trickle filters.

Activated Sludge Processes (ASP)

The ASP was described first in the year 1914 by Arnold and Locker. In ASP, wastewater that has undergone primary treatment is treated with the flocculated suspension of mixed microbial population within aerated and agitated reactor. It is a two-step process, biological treatment, and secondary settlement. The biological treatment is carried in aerated tanks containing flocculated suspension of diverse microorganisms. In the aerated tank, microorganisms grow and clump together to form a stable flocs, activated sludge. The different types of microorganisms that are involved in ASP include nitrifying, denitrifying, carbon oxidizers, fungi, protozoans, and algae. The species of *Acinetobacter* and *Zoogloea ramigera* are important microorganisms that play a key role in formation of flocs by production of polysaccharide gels. The microflora of activated sludge must be capable of producing all enzymes that can potentially degrade soluble as well insoluble pollutants. After flocs formation, effluent is passed into a secondary settlement tanks where flocculated microorganisms settle down to form a secondary sludge. Most often, after removal of secondary sludge, supernatant is disposed, but sometime tertiary treatment is required to remove the inorganic nutrients.

Trickle Filters

In aerobic trickle filter technique, microbial biofilm is formed on an inert support material placed within a bioreactor. Effluent is continuously sprayed over the microbial biofilm and percolates down the filter bed. While passing through the bed, organic matter is degraded by the microorganisms in the biofilm. As process continues, microorganisms grow and thickness of biofilm increases penetrating downward. At a point, when threshold thickness is achieved, concentration of oxygen drops at the surface of the biofilm and decrease in the biomass called sloughing occurs. Within filter, microbial population varies, a diverse range of microorganisms are present at top including bacteria, fungi, algae, and protozoan. Within filter, carbon oxidizing microorganisms dominate, while nitrifiers are predominant group present at the bottom of the bed. For efficient operation, larger the surface area of inert material, greater would be the concentration of biomass and thus, faster rate of degradation. Secondly, large void volume is required for efficient oxygenation and to prevent the clogging while passage of water through the filter bed. Trickle filter operates under two modes, low rate and high rate filter. Low rate filter consists of stone or other denser medium that have low surface area but high density, while high rate filter uses plastic material having large void volume and high surface area.

10.6.2.2 Anaerobic Biological Treatment

Anaerobic treatment processes of sludge and heavily polluted wastewater involve the activity of facultative and obligate anaerobic microorganisms that degrade organic pollutants in the absence of oxygen. Anaerobic degradation of organic pollutants is accompanied with the production of CO_2, biomass, and energy in the form of methane. The three different groups of microorganisms are involved in this process. The fermentative or hydrolytic bacteria secrete extracellular enzymes that degrade complex polymers (polysaccharide, proteins, and lipid) to generate CO_2, H_2, methanol, and volatile fatty acids (VFAs), viz. acetic, butyric, and propionic acid. The acetogenic bacteria metabolize the end product of fermentative bacteria into acetic acid, CO_2, and H_2. The methanogenic bacteria are the terminal member in the process of anaerobic degradation. The acetotrophs are group of methanogens that causes the breakdown of acetic acid into methane and CO_2, while hydrogenotroph mediates CO_2 reduction coupled to oxidation of H_2 to generate methane. The anaerobic treatment processes are mainly carried out in simple mixed sludge reactor, upflow anaerobic sludge blanket reactors, anaerobic filters (AFs) that consist of upflow and down-flow AFs, and anaerobic baffled reactor (Lofrano 2013; Lefebvre et al. 2006; El-Sheikh et al. 2011; Zupancic and Jemec 2010).

10.6.3 Advanced Treatment Technologies

10.6.3.1 Membrane Technologies

The use of membrane technologies for treating tannery effluent is a cost-effective treatment system of chromium contaminated water. Previous studies have

demonstrated that ultrafiltration and nano-filtration can be efficiently used in tanning industry for the recovery of chromium and reducing pollutant load (Ashraf et al. 1997; Cassano et al. 2001). Moreover, refractory organic compounds (sulfate and chloride) have been removed by reverse osmosis with a plane membrane (De Gisi et al. 2009). In addition, membrane bioreactor (MBR) has emerged as an alternative to activated sludge process (ASP), as no additional settling tank is required for wastewater treatment. However, the main limitation of membrane technology is clogging of membrane (Lofrano et al. 2013).

10.6.3.2 Oxidation Processes (OPs)

In recent past, role of different oxidation processes (OPs) in treatment of tannery wastewater has been well documented. Treatment method that involves OPs uses strong oxidants (H_2O_2, O_3,) and/or catalysts (TiO_2, Fe, Mn) (Schrank et al. 2004). The basic principles of oxidation processes the production of hydroxyl radicals (a powerful oxidants) that causes rapid but unselective oxidation of broad range of organic compounds leading to the reduction in the COD level. Some examples of OPs include Fenton oxidation, photooxidation, ozone oxidation, and photocatalysis (Lofrano et al. 2013). The selection of optimum OPs wastewater treatment requires proper assessment. The heavily polluted wastewaters are pre-treated before the application of OPs (Schrank et al. 2004).

10.6.3.3 Bioreactor System in Bioremediation

The vessel system which is generally known as fermenter or bioreactor provides a controlled and desired levels either physicochemical or nutritional parameters or both for the growth of a microorganism alone or in combinations at optimum level. Tannery effluent is a serious environmental problem. Khan et al. (2020) also studied the bioremediation of chromium using pilot scale sand bed bioreactor.

The development of bioreactor technology can change any process parameters economical. Bioreactor technology may depend upon the microorganisms and nature of the effluent. Bioreactor design is one of the important components in bioprocess engineering (Gaur et al. 2017). In spite of such development, still there is lack of efficient bioreactor system for effective treatment. Bioreactor system for treatment of tannery effluent through specific architecture and design specially Degrimond, Sulzer, and Aquatech has been successfully used for the treatment of such waste from industries. But these technologies must be updated on the ground of efficient recycling of active/alive microbial biomass transfer, proper treatment/recycling of heavy metals along with use of microbial consortium in a specialized vessel system within large bioreactors where entirely different environment is created for effective degradation of aromatic hydrocarbon or other xenobiotic compounds. To achieve the above parameters, any bioreactor system is optimized on the basis of these parameters either fed batch or continuous system. Most of the bioreactor for such work is designed for continuous bioremediation process including the following parameters:

1. Substrate utilization rate, where variety of substrates have been used from simple to complex requires different amount of enzymes, biomass, and retention period. These factors must be optimized in the labs and may be designed in the same bioreactor in multiple vessel systems having specialized microbial consortium, which specially degrade xenobiotic compounds, further this vessel effluent should be passed to the vessel where simple organic compounds easily utilized leading to some other organic compounds that will further degraded as long retention period will facilitate higher degradation.
2. Another parameter is biomass production and its recycling outlets with in a vessel where biomass is recycled in the initial vessel to achieve active biomass using gravity based recycling outlet as live cells are heavier, but microbial flocculation of dead or live nature must be evaluated prior to develop design/architecture.
3. This component is important but difficult to maintain, i.e., microbial metabolites mainly in the form of enzymes which act on xenobiotic/simple organic matter decomposition for effective bioremediation. These parameters generally affected by the variation of substrate concentration which generally vary in bulk treatments. For this, the temperature tolerant, aero-tolerant, acid, and alkali-tolerant with high and low substrate concentration tolerant may be isolated and used in such bioreactors. Gaur and Tiwari (2015) isolated such strains from natural ecosystem and used for the production of amylases and cellulases for effective degradation of lignocellulosics and starchy materials at very high substrate concentration as these parameters are very essential. Nature is a rich reservoir of microorganisms, therefore any desired microbial system are available, only isolation and optimization can solve this goal efficiently.
4. The ultimate effects can be minimized by designing and architecture of an effective bioreactor system. For example, most of the industrial effluent contains heavy metals that must be separated from the water bodies otherwise contaminate ground water, pond, river water, soil. It affects crops as well as human and animal health. The heavy metals are not metabolized by microbial system. Most of the microorganisms can only change its oxidation state or accumulate on the cell surface/membrane only up to some extent and further release after the death of microorganisms and their viable cells again accumulate, therefore cannot be efficiently removed from the system. Therefore, phytoremediation for heavy metal removal from aquatic system is the effective measure for the treatment because it absorbs high flux of almost all types of metals from the effluent. Various plants of aquatic origin have been grown in polluted sites and after removal of the plants from the contaminated sites, thereafter burned in furnace to get the ashes of metals for extraction. Thus, this approach must be designed in such a way the bioreactor treated effluents should be passed through such ponds attached in series by removal of weeds continuously. This is only way of effective removal of toxic heavy metals from industrial effluent especially from tanneries. The role of bioreactor in bioremediation requires upgradation in their design in which multivessel system designed in such a way that original microbial biomass should be maintained for longer period monitored by specific device and reloading of fresh culture without restricting the process. Thus, a variety of

specific consortia are required for the treatment of intermediates of the xenobiotic compounds efficiently within 48–72 h; therefore, size of the bioreactor, retention period of the effluent along with the requirement of oxygen or without oxygen can be created depending on the nature of microbial communities required for bioremediation. The main problems associated to this are blockage of pores, pipe, lives and hydrolic load which must be evaluated accordingly.

10.7 Future Prospects and Challenges in Bioremediation

Industrialization and urbanization are the social need of every country, but its proper management is equally essential and need of the hour. Industrial effluent of distillery, tannery, pulp and paper industries is highly toxic due to presence of color compounds and complex organic compounds along with heavy metals. It has been proved that bioremediation is the ultimate alternative over the physical and chemical approaches because of the cost effective as well as ecofriendly means. The management of biosystem for efficient treatment requires certain technology and management of microbial system. The microbial application strategies with combinations of microbes at different stages is the most essential part of this area. Xenobiotic compounds are also treated by co-metabolism in which some specific group converts the complex form to simple form without utilizing the original compound for carbon and energy source. The converted compound is metabolized by another group of microorganisms. Therefore, the selection of such microorganisms which can co-exist without any negative interaction with them and ability to utilize different carbon and nitrogen sources via different metabolic pathways is necessary. Such combinations are long lasting and effective for bulk treatment at industrial scale. Another important aspect is the use of thermotolerant/thermophilic microorganisms at large scale treatment of effluent in bioreactor as temperature increases from 5° to 10° C. Furthermore, the selection of microbial combination in different stages in bioreactor is another important aspect which is totally based on the organic and inorganic load of the effluent and the microbial nature. In this process, proteolytic, lipolytic along with chemolithotrophic groups are being used in combinations, because at this level, the chemoorganotrophs utilize all proteins, lipids, and fats, as keratinophilic microbial combination will liquefy the hair from follicles and short hairs present in the effluent. In this stage, large closed jacket of non-reactive metals is required in order to reduce the putrefaction odors as well as other gaseous compositions. This stage may also release several pathogenic microorganisms especially for bacteria and some surface growing fungi which may cause aeroallergenic diseases. This stage has high nutritional effluent which generates bulk of microbial groups, therefore, close jacket treatment using airlift or hydrodynamic fermenter models may be recommended. At this stage, 24–48 h retention period cuts the BOD and COD by 75 to 80% along with other easily available carbohydrate, proteins, lipids, and other minerals. A huge microbial biomass and some of xenobiotic compounds along with the inorganic components especially heavy metals like chromium, arsenic, or other may be down streamed along with open pond system for remediation. The microbes

which have capability to produce peroxidases, phenoxidases, laccases, mono-, dioxygenases will be used to eliminate tannin, oils, paint compounds. Further, heavy metals may be extracted through phytoremediation within 5–10 days in small oxidation ponds attached in series of 4–5 numbers depending on the capacity of industry. The bioremediation with proper management under the supervision of microbiologist is always essential because fermentaion kinetics norms at various stages in bioreactor is very essential. Microbial system is much diversified, therefore, regular isolation and characterization of microorganisms is required to find a better strain of the diversified level, as microbial diversity is abundant and newer strains always reform through recombination process in the natural ecosystem through transformation, conjugation, and transduction especially in bacteria.

Since the microbial handling especially the cultivation without contamination and monitoring its population and application of various combinations of consortia requires strict monitoring and everyday observation under microscope regarding the existence of consortia as well as their norms set by processing and downstreamed products required for the treatment process. There are some major challenges in bioremediation such as understanding the nature of chemical compound means simple or complexity in structure, selection of potential microbial strain, and the management of environmental conditions. Further, the bioremediation requires update in the area of bioreactor design and architecture alongwith multivessel, and multi-steps bioremediation with specific group of microorganisms depending on the nature of effluents in bulk treatment. Most of the industries release bulk liquid waste which contains high organic and inorganic loads. The organic load can be best treated by using various groups of microorganisms especially those which have high capability to degrade xenobiotic compounds. Further the heavy metals of the effluent should also be remediated using different microbial system. The remedial measure is not only based on the capability of the microorganisms but also based on the design and protocol for specific effluents treatment. Such challenges require space, microbial quality, microbial differentiation, aerobic and anaerobic situations for effective remediation. The microorganisms having capability of producing degradative enzymes, etc., mono and/or dioxygenases, laccases, peroxidases by different microbial groups may be used in consortium of aerobic to anaerobic as well as mesophilic to thermophilic origin in large bioreactors.

10.8 Conclusion

Bioremediation based treatment of xenobiotic compounds either in liquid or a solid system is one of the most economic, eco-friendly, and safe method. The most diversified microbial groups in consortium have been suggested for an efficient bioremediation process. The bulk quantities of industrial solid and liquid wastes are being treated with naturally occurring microorganisms. The microbes which degrade xenobiotic compounds are limited in soil and water ecosystem, therefore, must be deliberately introduced during the treatment process. The initial population follows the co-metabolism process, through which the intermediate compounds

again initiate another group of microbial process which further ultimately reduce the time limit as well as productivity of the remediation process, the deliberate introduction of some specific microbial inoculum in the ratio of 2–5% having population 50×10^6 cfu of each group depending on the nature of xenobiotic compound is suggested. In this approach, the chemical nature of xenobiotic compounds and metabolic pathways alongwith their intermediate are to be known for effective bioremediation process. Further this remedial measure requires appropriate bioreactor technology in multivessel continuous fermentation having different concentration gradients can be facilitated through airlift and hydrodynamic architecture of bioreactor. The gases released from such process are CO_2, SO_2, NO_2, and CH_4 which can be utilized for the use to reduce the air pollution. Such approach will be safe for soil, water, and air for sustainable environment. The efficient microbial groups, especially bacteria are the dominating flora of such process as they are fast multiplying and able to grow at wide range of temperature and from aerobic, facultative to anaerobic conditions, while fungi are slow growing as well as mostly aerobic but some anaerobic fungi have also been identified but very limited. The quick multiplication in all the conditions, bacteria is the dominating and potential microorganisms. The downstream processing is also not required in such process; therefore, bacteria are more appropriate than any existing microbes. The tannery effluent generally has more color compounds of aromatic hydrocarbons origin which requires higher population of specific bacteria which produce certain enzymes like mono-dioxygenases, laccases as well as peroxidase essentially required for beta keto adipic, mandelate or meta cleavage pathways where catechol and other intermediates of aromatic hydrocarbons are degraded to super compounds like muconic acid, muconolactone to pyruvate. Leading to complete degradation of xenobiotics.

References

Asatiani NV, Abuladze MK, Kartvelishvili TM, Bakradze NG, Sapojnikova NA, Tsibakhashvili NY, Tabatadze LV, Lejava LV, Asanishvili LL, Holman H (2004) Effect of Cr (VI) action on *Arthrobacter oxydans*. Curr Microbiol 49:321–326

Ashraf CM, Ahmad S, Malik MT (1997) Supported liquid membrane technique applicability for removal of chromium from tannery wastes. Waste Manag 17:211–218

Ates E, Orhon D, Tunay O (1997) Characterization of tannery wastewaters for pretreatment selected case studies. Water Sci Technol 36:217–223

Avudainayagam S, Meghara A, Owens G, Kookana RS, Chittleborough D, Naidu R (2003) Chemistry of chromium in soils with emphasis, on tannery waste sites. Rev Environ Contam Toxicol 178:53–91

Ayangbenro AS, Babalola OO (2017) A new strategy for heavy metal polluted environments: a review of microbial biosorbents. Int J Environ Res Public Health 14(1):94

Beiyuan J, Awad YM, Beckers F, Tsang DC, Ok YS, Rinklebe J (2017) Mobility and phytoavailability of as and Pb in a contaminated soil using pine sawdust biochar under systematic change of redox conditions. Chemosphere 178:110–118

Benazir JF, Suganthi R, Rajvel D, Pooja MP, Mathithumilan B (2010) Bioremediation of chromium in tannery effluent by microbial consortia. Afr J Biotechnol 9(21):3140–3143

Bhide JV, Dhakephalkar PK, Paknikar KM (1996) Microbiological process for the removal of Cr (VI) from chromate-bearing cooling tower effluent. Biotechnol Lett 18:667–672
Cassano A, Molinari R, Romano M, Drioli E (2001) Treatment of aqueous effluent of the leather industry by membrane processes. A review. J Membr Sci 181:111–126
Chandra R, Bharagava RN, Kapley A, Purohit HJ (2011) Bacterial diversity, organic pollutants and their metabolites in two aeration lagoons of common effluent treatment plant (CETP) during the degradation and detoxification of tannery wastewater. Bioresour Technol 102:2333–2341
Chirwa EMN, Wang YT (2000) Simultaneous chromium (VI) reduction and phenol degradation in an anaerobic consortium of bacteria. Water Res 33:2376–2384
Chirwa EMN, Wang YT (2005) Modeling hexavalent chromium reduction and phenol degradation in a coculture biofilm reactor. ASCE J Environ Eng 131(11):1495–1506
Congeevaram S, Dhanarani S, Park J, Dexilin M, Thamaraiselvi K (2007) Biosorption of chromium and nickel by heavy metal resistant fungal and bacterial isolates. J Hazard Mater 146:270–277
Davis TA, Volesky B, Vieira RHSF (2000) Sargassum seaweed as biosorbent for heavy metals. Water Res 34:4270–4278
De Gisi S, Galasso M, De Feo G (2009) Treatment of tannery wastewater through the combination of a conventional activated sludge process and reverse osmosis with a plane membrane. Desalination 249:337–342
De Nicola E, Meriç S, Gallo M, Iaccarino M, Della Rocca C, Lofrano G et al (2007) Vegetable and synthetic tannins induce hormesis/toxicity in sea urchin early development and in algal growth. Environ Pollut 146:46–54
Dixit R, Malaviya D, Pandiyan K, Singh UB, Sahu A, Shukla R, Paul D (2015) Bioremediation of heavy metals from soil and aquatic environment: an overview of principles and criteria of fundamental processes. Sustainability 7(2):2189–2212
El-Sheikh Mahmoud A, Hazem I, Saleh J, Flora R, Mahmoud R, El-Ghany A (2011) Biological tannery wastewater treatment using two stage UASB reactors. Desalination 276:253–259
Farabegoli G, Carucci A, Majone M, Rolle E (2004) Biological treatment of tannery wastewater in the presence of chromium. J Environ Manage 71:345–349
Farag S, Zaki S (2010) Identification of bacterial strains from tannery effluent and reduction of hexavalent chromium. J Environ Biol 31(5):877–882
Fomina M, Gadd GM (2014) Biosorption: current perspectives on concept, definition and application. Bioresour Technol 160:3–14
Ganesh R, Balaji G, Ramanujam RA (2006) Biodegradation of tannery wastewater using sequencing batch reactor—respirometric assessment. Bioresour Technol 97:1815–1821
Garg SK, Tripathi M (2011) Strategies for decolorization and detoxification of pulp and paper mill effluent. Rev Environ Contam Toxicol 212:113–136
Garg SK, Tripathi M, Srinath T (2012) Strategies for chromium bioremediation of tannery effluent. Rev Environ Contam Toxicol 217:75–140
Garg SK, Tripathi M, Singh SK, Singh A (2013) Pentachlorophenol dechlorination and simultaneous Cr^{6+} reduction by *Pseudomonas putida* SKG-1 MTCC (10510): characterization of PCP dechlorination products, bacterial structure, and functional groups. Environ Sci Pollut Res Int 20 (4):2288–2304
Garg SK, Singh K, Tripathi M (2016) Optimization of process variables for hexavalent chromium biosorption by psychrotrophic *Pseudomonas putida* SKG-1 isolate. Desal Water Treat 57:19865–19876
Garg SK, Garg S, Tripathi M, Singh K (2018) Microbial treatment of tannery effluent by augmenting psychrotrophic Pseudomonas putida isolate. Environ Poll Prot 3:23–39
Gaur R, Singh A, Tripathi A, Singh R (2017) Bioreactor. In: Singh RL (ed) Principles and applications of environmental biotechnology for a sustainable future. Springer, Singapore
Gaur R, Tiwari S (2015) Isolation, production, purification and characterization of an organic-solvent-thermostable alkalophilic cellulase from Bacillus vallismortis RG-07. BMC Biotechnol 15:19

Holmes AL, Wise SS, Wise JP Sr (2008) Carcinogenicity of hexavalent chromium. Indian J Med Res 128:353–372

Ilias M, Rafiqullah IM, Debnath BC, Mannan KSB, Hoq MM (2011) Isolation and characterization of chromium (VI)-reducing bacteria from tannery effluents. Indian J Microbiol 51(1):76–81

Ishibashi Y, Cervantes C, Silver S (1990) Chromium reduction in *Pseudomonas putida*. Appl Environ Microbiol 56:2268–2270

Kabdasli I, Tunay O, Orhon D (1999) Wastewater control and management in a leather tanning district. Water Sci Technol 40:261–267

Khan P, Pujara K, Murugavelh S, Mohanty K (2020) Bioremediation of chromium using a laboratory-scale sand bed reactor. In: Shah M, Banerjee A (eds) Combined application of physico-chemical & microbiological processes for industrial effluent treatment plant. Springer, Singapore. https://doi.org/10.1007/978-981-15-0497-6_13

Kumar S, Srivastava S, Gaur R (2013) Increasing antibiotic resistance in microbial consortium and human health hazards by heavy metals exposure. Int J Biomed Health Sci 3(1):45–50

Kumar M, Kumar V, Varma A, Prasad R, Sharma A, Pal A, Arshi A, Singh J (2016) An efficient approach towards the bioremediation of copper, cobalt and nickel contaminated field samples. J Soil Sediment 17(4):2118. https://doi.org/10.1007/s11368-016-1398-1

Kumar V, Kumar M, Sharma S, Prasad R (2017) Probiotics in agroecosystem. Springer, Singapore

Lefebvre O, Vasudevan N, Torrijosa M, Thanasekaran K, Moletta R (2006) Anaerobic digestion of tannery soak liquor with an aerobic post-treatment. Water Res 40:1492–1500

Li YY, Li B (2011) Study on fungi-bacteria consortium bioremediation of petroleum contaminated mangrove sediments amended with mixed biosurfactants. In: Advanced materials research. Trans Tech Publications, Zurich, pp 1163–1167

Liu YG, Pan C, Xia WB, Zeng GM, Zhou M, Liu YY, Ke J, Huang C (2008) Simultaneous removal of Cr (VI) and phenol in consortium culture of *Bacillus anthracis* and *Pseudomonas putida* Migula (CCTCC AB92019). Trans Nonf Met Soc China 18:1014–1020

Lofrano G, Belgiorno V, Gallo M, Raimo A, Meriç S (2006) Toxicity reduction in leather tanning wastewater by improved coagulation flocculation process. Global NEST J 8:151–158

Lofrano G, Meric S, Belgiorno V, Napoli RMA (2007) Fenton's oxidation of various based synthetic tannins (syntans). Desalination 211:10–21

Lofrano G, Aydin E, Russo F, Guida M, Belgiorno V, Meric S (2008) Characterization, fluxes and toxicity of leather tanning bath chemicals in a large tanning district area (IT). Water Air Soil Pollut 8:529–542

Lofrano G, Meric S, Zengin GE, Orhon D (2013) Chemical and biological treatment technologies for leather tannery chemicals and wastewaters: a review. Sci Total Environ 461:265–281

Losi ME, Amrhein C, Frankenberger WT (1994) Environmental biochemistry of chromium. Rev Environ Contam Toxicol 36:91–121

Lovely DR, Coates JD (1997) Bioremediation of metal contamination. Curr Opin Biotechnol 8:285–289

Maria MV, Bertha AR, Carlos GSJ (1999) Health deterioration by chromium in workers of a tannery unit. Tata McGraw-Hill, New Delhi, pp 725–730

Munz G, De Angelis D, Gori R, Mori G, Casarci M, Lubello C (2009) The role of tannins in conventional angogated membrane treatment of tannery wastewater. J Hazard Mater 164:733–739

Nicolopoulou-Stamati P, Maipas S, Kotampasi C, Stamatis P, Hens L (2016) Chemical pesticides and human health: the urgent need for a new concept in agriculture. Front Public Health 4:148. https://doi.org/10.3389/fpubh.2016.00148

Oliveira H (2012) Chromium as an environmental pollutant: insights on induced plant toxicity. J Bot 2012:375843. https://doi.org/10.1155/2012/375843

Pal A, Dutta S, Paul AK (2005) Reduction of hexavalent chromium by cell-free extract of *Bacillus sphaericus* AND 303 isolated from serpentine soil. Curr Microbiol 66:327–330

Palmer CD, Wittbrodt PR (1991) Processes affecting the remediation of chromium-contaminated sites. Environ Health Perspect 92:25–40

Parameswari E, Lakshmanan A, Thilagavathi T (2009) Biosorption of chromium (VI) and nickel (II) by bacterial isolates from an aqueous solution. Electronic J Environ Agri Food Chem 8 (3):150–156

Park D, Yun Y-S, Park JM (2005) Use of dead fungal biomass for the detoxification of hexavalent chromium: screening and kinetics. Process Biochem 40:2559–2565

Perpetuo EA, Souza CB, Nascimento CAO (2011) Engineering bacteria for bioremediation. In: Progress in molecular and environmental bioengineering-from analysis and modeling to technology applications. IntechOpen, London

Purakayastha TJ, Chhonkar PK (2010) Phytoremediation of heavy metal contaminated soils. In: Soil heavy metals. Springer, Berlin, Heidelberg, pp 389–429

Quintelas C, Sousa E, Silva F, Neto S, Tavares T (2006) Competitive biosorption of ortho-cresol, phenol, chlorophenol and chromium (VI) from aqueous solution by a bacterial biofilm supported on granular activated carbon. Process Biochem 41:2087–2091

Ray Arora S, Ray MK (2009) Bioremediation of heavy metal toxicity-with special reference to chromium. Al Ameen J Med Sci 2(2):57–63

Rehman A, Shakoori FR, Shakoori AR (2007) Heavy metal resistant *Distigma proteus* (Euglenophyta) isolated from industrial effluents and its possible role in bioremediation of contaminated wastewaters. World J Microbiol Biotechnol 23:753–758

Schrank SG, José HJ, Moreira RFPM, Schroder HF (2004) Elucidation of the behaviour of tannery wastewater under advanced oxidation conditions. Chemosphere 56:411–423

Shen H, Wang YT (1995) Modeling simultaneous hexavalent chromium reduction and phenol degradation by a defined coculture of bacteria. Biotechnol Bioeng 48:606–616

Shumate SE, Strandberg GW (1985) Accumulation of metals by microbial cells. In: Moo-Young M, Robinson CW, Howell JA (eds) Comprehensive biotechnology. Pergamon Press, New York, pp 235–247

Song Z, Williams CJ, Edyvean RGJ (2004) Treatment of tannery wastewater by chemical coagulation. Desalination 164:249–259

Srinath T, Verma T, Ramteke PW, Garg SK (2002) Chromium (VI) biosorption and bioaccumulation by chromate resistant bacteria. Chemosphere 48:427–435

Srinath T, Garg SK, Ramteke PW (2003) Biosorption and elution of chromium from immobilized *Bacillus coagulans* biomass. Indian J Exp Biol 41:986–990

Srivastava S, Dwivedi AK (2015) Biological wastes the tool for biosorption of arsenic. J Bioremed Biodegr 7:1–3

Srivastava S, Thakur IS (2007) Evaluation of biosorption potency of *Acinetobacter* sp. for removal of hexavalent chromium from tannery effluent. Biodegradation 18:637–646

Stasinakis AS, Mamais D, Thomaidis NS, Lekkas TD (2002) Effect of chromium (VI) on bacterial kinetics of heterotrophic biomass of activated sludge. Water Res 36:3342–3350

Sultan S, Hasnain S (2007) Reduction of toxic hexavalent chromium by *Ochrobactrum intermedium* strain SDCr-5 stimulated by heavy metals. Bioresour Technol 98(2):340–344

Szulczewski MD, Helmke PA, Bleam WF (1997) Comparison of XANES analysis and extractions to determine chromium speciation in contaminated soils. Environ Sci Technol 31:2954–2959

Thakur IS, Verma P, Upadhyaya KC (2001) Involvement of plasmid in degradation of pentachlorophenol by *Pseudomonas* sp. from a chemostat. Biochem Biophys Res Commun 286:109–113

Tiwari S, Rai P, Yadav SK, Gaur R (2012) A novel thermotolerant *Pediococcus acidilactici* B-25 strain for color, COD, and BOD reduction of distillery effluent for end use. Environ Sci Pollut Res 20:4046–4058

Tripathi M, Garg SK (2010) Studies on selection of efficient bacterial strain simultaneously tolerant to hexavalent chromium and pentachlorophenol isolated from treated tannery effluent. Research J Microbiol 5(8):707–716

Tripathi M, Garg SK (2013) Co-remediation of pentachlorophenol and Cr^{6+} by free and immobilized cells of native *Bacillus cereus* isolate: spectrometric characterization of PCP dechlorination products, bioreactor trial and chromate reductase activity. Process Biochem 48:496–509

Tripathi M, Garg SK (2014a) Dechlorination of chloroorganics, decolorization and simultaneous bioremediation of Cr6+ from real tannery effluent employing indigenous Bacillus cereus isolate. Environ Sci Pollut Res Int 21(7):5227–5241

Tripathi M, Garg SK (2014b) Response surface modeling for co-remediation of Cr^{6+} and pentachlorophenol by *Bacillus cereus* RMLAU1: bioreactor trial and structural and functional characterization by SEM-EDS and FT-IR analyses. Biorem J 18:328–344

Tripathi M, Vikram S, Jain RK, Garg SK (2011a) Isolation and growth characteristics of chromium (VI) and pentachlorophenol tolerant bacterial isolate from treated tannery effluent for its possible use in simultaneous bioremediation. Indian J Microbio 51(1):61–69

Tripathi M, Mishra SS, Tripathi VR, Garg SK (2011b) Predictive approach for simultaneous biosorption of hexavalent chromium and pentachlorophenol degradation by *Bacillus cereus* RMLAU1. Afr J Biotechnol 10(32):6052–6061

Tripathi M, Upadhyay SK, Kaur M, Kaur K (2018) Toxicity concerns of hexavalent chromium from tannery waste. J Biotechnol Bioeng 2:40–44

Tripathi M, Kumar S, Yadav SK, Pandey R, Tripathi P (2019) Modern biological methods for treatment of tannery effluent. In: Tripathi M (ed) Microbial treatment strategies for waste management. OMICS International, London

Turick CE, Apel WA, Carmiol NS (1996) Isolation of hexavalent chromium reducing anaerobes from hexavalent chromium contaminated and non-contaminated environments. Appl Microbiol Biotechnol 44:683–688

U.S. EPA (1979) Economics of wastewater treatment alternatives for the electroplating industry. In: U.S. EPA technology transfer report, Environment Protection Agency 625/5-79-016, June, U.S. Environmental Protection Agency, Washington, DC

Upadhyay N, Vishwakarma K, Singh J, Mishra M, Kumar V, Rani R, Mishra RK, Chauhan DK, Tripathi DK, Sharma S (2017) Tolerance and reduction of chromium (VI) by *Bacillus* sp. MNU16 isolated from contaminated coal mining soil. Front Plant Sci 8:778–791. https://doi.org/10.3389/fpls.2017.00778

Vidali M (2001) Bioremediation. An overview. Pure Appl Chem 73(7):1163–1172

Volesky B (1990) Biosorption and biosorbents. In: Volesky B (ed) Biosorption of heavy metals. CRC, Boca Raton

Yadav A, Mishra S, Kaithwas G, Raj A, Bharagava RN (2016) Organic pollutants and pathogenic bacteria in tannery wastewater and their removal strategies. Micr Environ Man 5:101–127

Yadav KK, Gupta N, Kumar V, Singh JK (2017) Bioremediation of heavy metals from contaminated sites using potential species: a review. Indian J Environ Prot 37(1):65

Zhang W, Lin Z, Pang S, Bhatt P, Chen S (2020) Insights into the biodegradation of lindane (γ-hexachlorocyclohexane) using a microbial system. Front Microbiol 11:522

Zupancic GD, Jemec A (2010) Anaerobic digestion of tannery waste: semi-continuous and anaerobic sequencing batch reactor processes. Bioresour Technol 101:26–33

Current Approaches in Bioremediation of Toxic Contaminants by Application of Microbial Cells; Biosurfactants and Bioemulsifiers of Microbial Origin

11

Amrita Kharangate-Lad and Nezlyn Cressida D'Souza

Abstract

The increase in global human population has resulted in swift and extensive urbanization and industrialization. These anthropogenic activities along with natural phenomena result in the release of toxic compounds in the environment. These toxic compounds are recalcitrant in nature and accumulate in the environment, contaminating the soil and aquatic ecosystems. They pose a risk to human health and ecosystem through the contamination of drinking water, ingestion through the food chain and reduction in water and food quality. Microorganisms such as bacteria, fungi, yeast and algae possess various mechanisms that metabolize and detoxify these toxic pollutants. In this chapter, we emphasize the use of these microorganisms for bioremediation of toxic pollutants like heavy metals such as Cd, Hg, Pb, Zn, Cu and others; polyaromatic hydrocarbons and petroleum-based hydrocarbons; plastic polymers and recalcitrant dyes and agro-based compounds. Apart from naturally occurring microorganisms, genetically engineered microorganisms have been designed to degrade these recalcitrant toxic compounds. Bioremediation using both these natural and genetically engineered microbes is an economic and eco-friendly alternative to conventional physicochemical technologies.

Keywords

Biosurfactants · Bioemulsifiers · Hydrocarbons · Microbes · Toxic pollutants

A. Kharangate-Lad (✉)
Department of Biochemistry, School of Chemical Sciences, Goa University, Goa, India

N. C. D'Souza
Department of Post Graduate Studies in Food Technology, Carmel College of Arts, Science and Commerce, Goa, India

© The Author(s), under exclusive licence to Springer Nature Singapore Pte Ltd. 2021

V. Kumar et al. (eds.), *Rhizobiont in Bioremediation of Hazardous Waste*,
https://doi.org/10.1007/978-981-16-0602-1_11

11.1 Introduction

Environmental pollution from toxic metals, organic pollutants and other hazardous materials has affected the natural ecosystem and human health. Anthropogenic activities like industrialization, mismanagement of toxic waste and natural activities like hurricanes, storms and volcanic eruptions are responsible for the discharge of toxic pollutants into the environment. Due to the expense and inefficiency of chemical methods, bioremediation using nanoparticles, microorganisms or their components is an eco-friendly and economical alternative for reclaiming the environments that are contaminated with toxic pollutants.

Bioremediation is detoxification of toxic xenobiotic compounds using living organisms including plants (phytoremediation) and microorganisms such as algae, bacteria and fungi (microbial remediation). The toxic compounds usually include pesticides, plastics, polyaromatic hydrocarbons (PAHs), heavy metals and toxic metal contaminants discharged in soil and aquatic environments due to anthropogenic activities (Das and Dash 2014). Due to the interaction between air, water and land, the toxic pollutants move in the environment and are transported beyond geographical boundaries by air and water currents (Fig. 11.1).

11.2 Microbial Cells in Bioremediation of Toxic Pollutants

Microorganisms are extensively studied for their role in bioremediation of toxic pollutants. The indigenous bacteria from contaminated sites are stimulated by providing optimum conditions of growth such as pH and nutrients such as phosphorous and sulphur by addition of compost and biochar (Ojuederie and Babalola 2017). This stimulates the microorganisms and makes the environment more favourable for bioremediation enabling the microbes to metabolize the toxic pollutants more efficiently (Das and Dash 2014). The efficacy of biodegradation of the toxic pollutants during bioremediation therefore depends on the nutrient availability, oxygen, temperature and pH of the surrounding environment. These factors influence the chemistry of the pollutant such as viscosity and volatility thereby affecting the bioavailability of the toxic pollutant to the microorganisms.

11.3 Factors Affecting Bioremediation

The factors that govern the efficiency of the microbial bioremediation are of two types: abiotic and biotic factors. The abiotic factors include environmental influences such as soil type, oxygen content, temperature, pH, presence of electron acceptors, nutrients and metal ions.

The metabolic abilities of the microorganisms and the physicochemical properties of the pollutant are the major properties that determine the fate of the target pollutant. Environmental factors like soil structure and site characteristics, pH, temperature, moisture, redox potential, oxygen content and availability of nutrients affect the

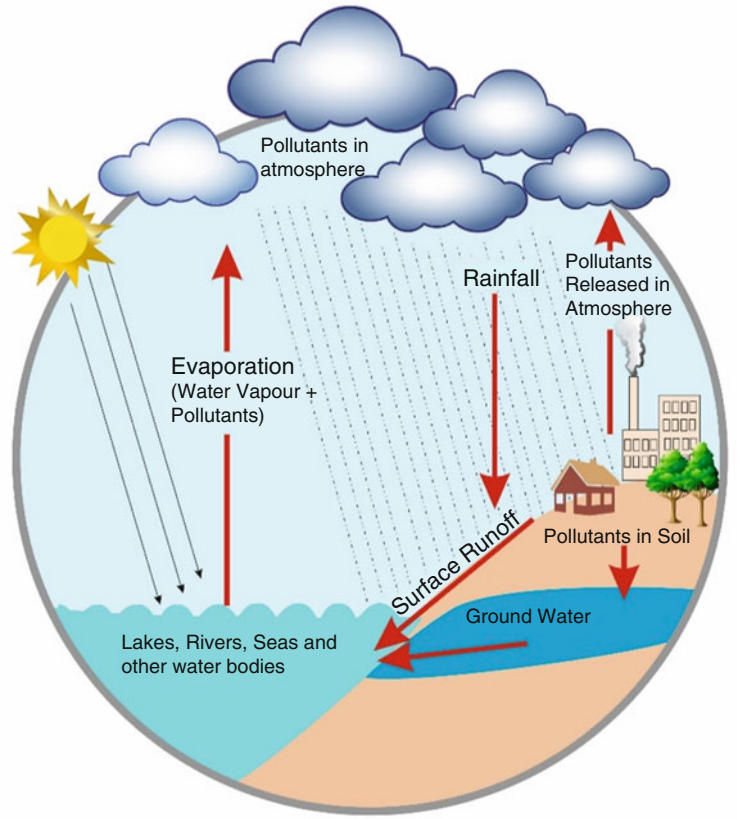


Fig. 11.1 Movement of toxic pollutants in the three spheres of the environment: lithosphere, hydrosphere and atmosphere

growth and interaction of the microorganisms with the pollutant (Fig. 11.2). Whereas the physicochemical properties such as the structure and toxicity of the pollutant govern the bioavailability of the compound to the microorganisms.

11.3.1 Availability of Nutrients

Essential nutrients, mainly nitrogen and phosphorus play a crucial role in microbial growth, reproduction and degradation of the toxic pollutant. Supplementing microorganisms with these essential nutrients has been reported to significantly impact the metabolic activity and increase the degradative capacity of microorganisms in the cold environments since biodegradation in cold environment is limited due to lack of nutrient availability. Similar improvement in degradation of hydrocarbons was reported on addition of nutrients (Abatenh et al. 2017).

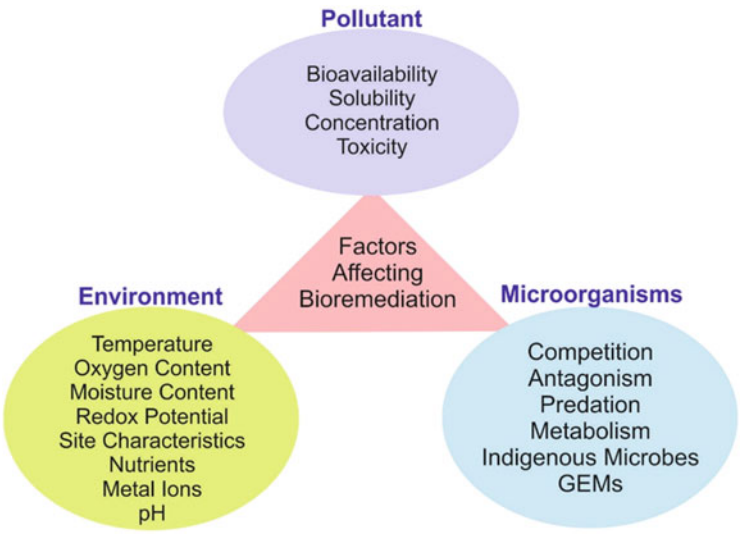


Fig. 11.2 Factors affecting microbial bioremediation

11.3.2 Temperature

Temperature is the most vital factor that determines the survival of the microorganism as well as the bioavailability of the pollutant. In colder regions of the Arctic, it becomes difficult to employ microorganisms for a cleanup as the sub-zero temperature freezes the microbial transport channels and the cytoplasm rendering the microbe metabolically inactive (Abatenh et al. 2017). All enzymes have an optimum temperature below and above which the rate of conversion for the pollutant will not be as effective as at optimum temperature. The metabolic activity of a microorganism increases with the increase in temperature. At a specific temperature the metabolic activity reaches a maximum which is known as the optimum temperature. The metabolic activity of microorganisms is slow at temperatures below and above the optimum temperature. Thus, temperature either increases or decreases the rate of bioremediation as it directly influences physiological activities of the microbes.

11.3.3 Oxygen Content

Oxygen requirement of microorganisms differs depending upon the nature of the microorganisms and widely affects their ability to degrade complex compounds. Biological degradation of various complex compounds has been carried out by both aerobic and anaerobic microorganisms (Abatenh et al. 2017). However, presence of oxygen is significant for the degradation of hydrocarbons by the enzymes oxygenases.

11.3.4 Moisture Content

Availability of water is an important factor as most microorganisms have ion transfer mechanisms at the cell surface level. The uptake of these ions depends upon their solubility in water. Moisture around the cells renders the pollutant more accessible for biosorption by microbial cells (Abatenh et al. 2017). Moisture influences the osmotic pressure, pH and the kind and amount of solubility of nutrients and pollutant; therefore, it directly influences the rate of degradation of the pollutant.

11.3.5 pH of Soil

The pH of the surrounding environment affects the growth and survival of the microorganism as it has no means of adjusting its inherent pH to that of surroundings. The pH also affects the structure and characteristics of the pollutant and thus its bioavailability to the microorganisms. A pH of 6.5–8.5 is optimal for biodegradation in most terrestrial and aquatic ecosystems (Abatenh et al. 2017).

11.3.6 Site Characterization

A detailed study of the site of contamination is needed to decide the best bioremedial strategies when employing microorganisms. It is necessary to study the extent of contamination in the vertical and horizontal zones of the site in addition to the abiotic parameters of the site (Abatenh et al. 2017). This helps determine the techniques to be used for sampling and analysis.

11.3.7 Metal Ions

Metals ions form an integral part of the biochemical components of the microorganisms. They are necessary in small amounts either in biosynthesis of new cell components or for carrying out metabolic activities. Limitation of these essential metal ions is known to have adverse effects on the rate of biodegradation of a compound. Microorganisms therefore have evolved strategies such as production of siderophores and metallothionein proteins to acquire these metal ions from the environment (Davis et al. 2003).

The microorganisms degrading the pollutant often face competition (from other microorganisms for carbon and energy sources), antagonistic interactions (from bacteriocins) and predation (from bacteriophages and protozoa). These negative interactions result in a decrease in production of enzymes by the microorganisms as well as it reduces the population of effective microbes responsible for degradation of the pollutants. These affect the degradative capacity of the microorganisms towards the toxic pollutant (Abatenh et al. 2017). Furthermore, the microorganism

needs to maintain its ability to degrade the pollutant without undergoing changes at a gene level (mutations) that may cause it to lose its affinity to the target pollutant.

11.4 Types of Microbial Bioremediation

Bioremediation techniques can be carried out by either in-situ or ex-situ approach. The in-situ treatment involves treating of the contaminated area without excavation of the contaminated site. In-situ treatment uses processes like biostimulation, bioattenuation, bioaugmentation, bioventing and biosparging. In-situ treatments are usually more desirable as it involves less cost and prevents disturbance of the environment. However, it faces limitations due to its inability to penetrate desired depth. Therefore, to make it more desirable diffusion of oxygen is allowed by means of external pipes and pump systems.

Ex-situ involves excavation of the soil from contaminated area. It mainly involves two major processes: the solid phase and slurry phase systems. The solid phase systems involve approaches such as biopiles, landfarming and composting (Fig. 11.3). The slurry phase system uses the bioreactor technique (Abatenh et al. 2017; Kumar et al. 2018a).

11.4.1 Biostimulation

Biostimulation involves the injection of nutrients at the site of contamination in order to stimulate the indigenous and naturally occurring microbial population. This involves the use of minerals, fertilizers, compost and growth supplements and providing environmental conditions such as pH, temperature and oxygen for

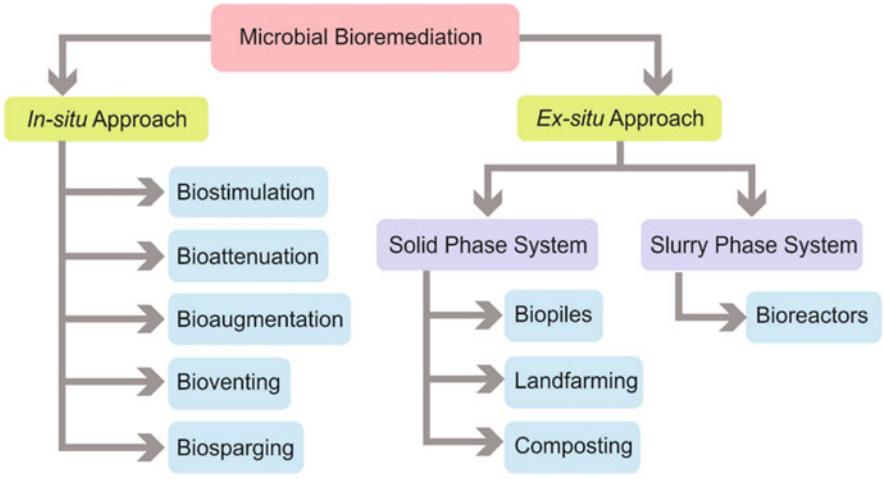


Fig. 11.3 Approaches in microbial bioremediation

optimum functioning of metabolic processes. The presence of small amounts of the pollutant can also trigger enzyme operons required in bioremediation (Abatenh et al. 2017). These nutrients provide the basic elements such as carbon, nitrogen and phosphorous that are needed for cell biomass and energy to produce enzymes that degrade the pollutant (Kumar et al. 2018a).

11.4.2 Bioattenuation

Bioattenuation or natural attenuation is the eradication of pollutant from the surrounding environment. Biologically it involves aerobic and anaerobic biodegradation; plant, animal or microbial uptake. Physical processes (advection, dispersion, dilution, diffusion, volatilization, sorption/desorption) result in clean up of the pollutant, and chemical mechanisms (complexation and ion exchange) result in abiotic transformation. Bioattenuation relies on nature to clean up the environmental pollutant. Microorganisms metabolize the pollutant as a source of carbon and energy converting them into water and harmless gases. Soil particles interact with the pollutant binding to it strongly and keeping them from entering the groundwater. The movement of pollutant through soil and into groundwater results in dilution of the pollutant. Volatile pollutants can evaporate from soil on exposure to sunlight and air (Abatenh et al. 2017). If bioattenuation has not completely cleared the pollutant, then bioremediation using biostimulation or bioaugmentation can be considered (Kumar et al. 2018a).

11.4.3 Bioaugmentation

Microorganisms that have a capacity to degrade the target pollutant are added to augment the biodegradative capacity of the natural and indigenous microbial populations at the contaminated site. GEMS or genetically engineered microorganisms are microbes that are collected from site of bioremediation and genetically modified to increase the efficiency of degradation. This technique has been specifically proven successful for chlorinated ethenes, such as tetrachloroethylene and trichloroethylene and ensures complete removal of these contaminants from the contaminated sites or their conversion to non-toxic forms (Abatenh et al. 2017; Kumar et al. 2018a).

11.4.4 Bioventing

Vents or wells in the soil are engineered to carry oxygen and nutrients to the soil to stimulate the growth of either the natural microorganisms or the introduced microorganisms. It can only be used for compounds that undergo aerobic degradation such as fuel residuals, volatile compounds and petroleum hydrocarbons (Abatenh et al. 2017; Sutar and Kumar 2012).

11.4.5 Biosparging

Biosparging refers to injecting air under pressure to increase the level of oxygen in groundwater for stimulating the indigenous population of microbes to degrade the contaminants. Biosparging enhances the interaction in the saturation zone and therefore increases the contact between soil and groundwater (Abatenh et al. 2017).

11.4.6 Biopiles

Soils contaminated with the pollutants are piled to form mounds and air is supplied to the biopile system by means of pumps. This enhances the microbial activity through microbial respiration resulting in efficient degradation of pollutants. This is a commonly used technique for aerobic degradation of petroleum pollutants (Abatenh et al. 2017; Sutar and Kumar 2012).

11.4.7 Landfarming

In landfarming, the contaminated soil is excavated, spread over an area and periodically tilled until pollutants are degraded. Tilling stimulates indigenous microorganisms and facilitates aerobic degradation of contaminants. This technique has limitations as it is effective upto10–35 cm of soil (Sutar and Kumar 2012). Efficient cleaning ability and low maintenance and monitoring costs make it a feasible option for bioremediation.

11.4.8 Composting

In this technique contaminated soil is mixed with known proportions of organic compost, manure or agricultural waste. These organic materials allow and support microbial population that degrades the contaminants (Kumar et al. 2018a; Sutar and Kumar 2012). The elevated temperature generated during composting is characteristic of this process.

11.4.9 Bioreactor

It involves the use of slurry reactors or aqueous reactors. The contaminated soil, sediment or sludge or contaminated water is introduced in the reactor (Kumar et al. 2018a; Sutar and Kumar 2012). A slurry bioreactor mixes the contaminants with water and gas to facilitate biodegradation by the indigenous microorganisms. The disadvantages include excavation and pre-treatment of the contaminated soil or water before being introduced into the bioreactor which is economically expensive.

11.5 Mechanisms of Interaction Between Microbial Cells and the Metal Pollutant

Heavy metals such as mercury, cadmium, nickel, cobalt, chromium, arsenic, lead have found their way into the environment due to natural and anthropogenic activities. For potential application of microbial cells in bioremediation, the microbial cells should not be inhibited by the toxic pollutant and should possess either one or more of the metal pollutant processing mechanisms (Kumar et al. 2016b). These mechanisms include uptake of the metal by means of metallothionein or metal sequestering proteins or by acquisition and interaction with the toxic pollutants by means of extracellular polymers (extracellular polymeric substances (EPS), biofilms, capsules, slime or sheath), biosorption into the cell membrane, intracellular assimilation, mobilization and immobilization, bioaccumulation, complexing and precipitation of the metal, efflux, reflux and release of the detoxified or transformed metal pollutant (Fig. 11.4). On uptake, the metal pollutant may be processed in mechanisms either dependent on the metabolic pathway of the organism or independently by using the metal pollutant processing mechanisms (Das and Dash 2014).

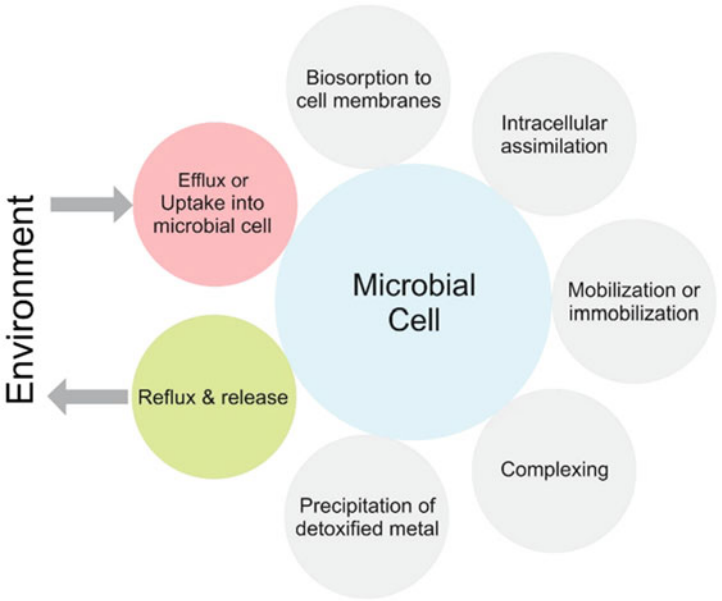


Fig. 11.4 Mechanisms possessed by microorganisms for dealing with metals and metal pollutants in the environment

11.6 Bioremediation of Toxic and Heavy Metals by Microorganisms

Bioremediation of heavy metals has been reported using bacteria, fungi and algae (Table 11.1). Microbial cells are negatively charged owing to the presence of negatively charged groups like hydroxyl groups, phosphate groups, carbonyl groups, sulphate groups and uronic acid of carboxyl groups on the surface of the bacterial cell wall. These bind to the heavy metal ions resulting in biosorption. *Enterobacter cloacae* has been reported to chelate cadmium, copper and cobalt. *Rhodobium marinum* NW16, *Rhodobacter sphaeroides* KMS24, purple non-sulphur bacteria have exhibited potential to remove zinc, copper, cadmium and lead from contaminated environment by bioaccumulation and precipitation (Panwichian et al. 2011). Research studies show that *Desulfovibrio desulfuricans,* a *s*ulphate-reducing bacterium can convert sulphate to hydrogen sulphate. This hydrogen sulphate reacts with heavy metals such as Zn and Cd and transforms them into insoluble forms of these metal sulphides (Chibuike and Obiora 2014).

Reports on viable and dead cells of *Mucor rouxii* demonstrated their ability to absorb cadmium, lead, zinc and nickel. It also established that the viable cells were more effective at low pH and optimum biosorption was achieved by the dead biomass and live cells above a pH of 4.0 (Yan and Viraraghavan 2003). Yeast *Saccharomyces cerevisiae* is used in bioremediation of contaminated wastewaters and is reported to remove toxic metals by biosorption. Detoxifying mechanisms like mobilization, immobilization and transformation by using metal-binding peptides called phytochelatins have been studied and reported in yeasts like *Schizosaccharomyces pombe* and *Candida* sp. (Bahafid et al. 2017; Wifak et al. 2017). Some strains of yeast such as *Hansenula polymorpha, Saccharomyces cerevisiae, Pichia guilliermondii, Rhodotorula pilimanae, Rhodotorula mucilage* and *Yarrowia lipolytica* have exhibited conversion of Chromium (VI) to Chromium (III) (Chatterjee et al. 2012; Ksheminska et al. 2008).

The large biomass of algae allows them a greater biosorption capacity in comparison to both bacteria and fungi (Mustapha and Halimoon 2015). Burdin (1985) reported ability of the algae to bioaccumulate heavy metals such as aluminium, cadmium, chromium, cobalt, copper, gold, lead, manganese, nickel, silver, tin and zinc. Many marine algae such as *Durvillaea potatorum, Ecklonia radiata* and *Laminaria japonica* have been reported to exhibit a higher biosorption capacity for heavy metals in comparison with zeolites or activated carbon sorbents (Kumar et al. 2013). Brown marine algae was studied to be effective in bioremediation of Cd, Ni and Pb due to presence of carboxyl, sulphonate, amino and sulphydryl groups on its surface (Davis et al. 2003). *Euglena gracilis*, a single celled alga has been reported for the bioaccumulation of Zn and *Chlorella vulgaris* and *Scenedesmus acutus* have been studied for bioaccumulation of Zn, Cr and Cd (Travieso et al. 1999). Biosorption of cadmium ions by *Spirulina platensis* has been demonstrated by using its dry biomass (Al-Homaidan et al. 2015). Marine algae have also shown to react differently to cadmium: *Tetraselmis suecica* exhibited affinity for cadmium, *Gracilaria fisheri* accumulated cadmium (II) and copper (II) while *Dunaliella salina*

Table 11.1 Microorganisms used in bioremediation of toxic metals at contaminated sites

Toxic Metal degrading microorganisms		
Microorganism	Pollutant	Reference
Bacteria		
Acidithiobacillus ferrooxidans	Cu	Rehan and Alsohim 2019
Alcaligenes sp.	Pb	Acosta-Rodríguez et al. 2018
Bacillus cereus strain XMCr-6 *Bacillus cereus*	Cr (VI)	Kanmani et al. 2012; Dong et al. 2013; Coelho et al. 2015
Bacillus megaterium	Ni	Acosta-Rodríguez et al. 2018; Igiri et al. 2018
Bacillus pumilus	Cd, Pb	Fulke et al. 2020
Bacillus subtilis	Cr (VI)	Balamurugan et al. 2014
Bacillus subtilis, Bacillus cereus	Cobalt, cadmium, zinc	Abdelatey et al. 2011
Bordetella sp.	Cadmium	Abou-Shanab et al. 2003
Desulfovibrio desulfuricans	Cr (VI), Cu, Ni	Igiri et al. 2018
Enterobacter cloacae B2-DHA	Cr (VI)	Rahman et al. 2015
Enterobacter cloacae	Cu, Cd, Co	Iyer et al. 2005
Frankia	Cu	Rehan and Alsohim 2019
Kocuria flava	Cu	Coelho et al. 2015
Pseudomonas aeruginosa	Organic and inorganic Hg	De et al. 2008; Das and Dash 2014
Pseudomonas putida	Cr (VI)	Balamurugan et al. 2014
Pseudomonas sp..	Phenols and aromatic compounds	Selvaratnam et al. 1997
Pseudomonas sp.	Co, Cd, Zn	Abou-Shanab et al. 2003
Pseudomonas veronii	Cd, Zn, Cu	Vullo et al. 2008; Coelho et al. 2015
Rhodobium marinum NW16, *Rhodobacter sphaeroides* KMS24	Cd, Cu, Pb, Zn	Panwichian et al. 2011
Sporosarcina ginsengisoli	As (III)	Achal et al. 2012; Coelho et al. 2015
Staphylococcus aureus	Chromate	Aguilar-Barajas et al. 2008
Vibrio harveyi	Cd, Pb	Mire et al. 2004; Abd-Elnaby et al. 2011
Fungi		
Aspergillus fumigatus	Pb	Kumar Ramasamy et al. 2011
Aspergillus niger	Zn, Hg, Co, Pb, Cd, Cu, Ni	Acosta-Rodríguez et al. 2018
Aspergillus versicolor	Ni, Cu	Coelho et al. 2015; Tastan et al. 2010
Aspergillus versicolor	Ni, Cu	Tastan et al. 2010; Coelho et al. 2015
Coprinopsis atramentaria	Cd, Pb	Igiri et al. 2018
Gloeophyllum sepiarium	Cr (VI)	Achal et al. 2011
Mucor rouxii	Pb, Cd, Ni, Zn	Yan and Viraraghavan 2003

(continued)

Table 11.1 (continued)

Toxic Metal degrading microorganisms		
Microorganism	Pollutant	Reference
Penicillium chrysogenum	Cr (VI)	De et al. 2008
Penicillium sp.	Pb	Igiri et al. 2018
Pleurotus ostreatus HAAS	Pb, Cd, Cr	Acosta-Rodríguez et al. 2018
Rhizopus oryzae (MPRO)	Cr (VI)	De et al. 2008; Sukumar 2010
Rhizopus stolonifer	Pb, Cd, Cu, Zn	Acosta-Rodríguez et al. 2018
Yeast		
Candida sp.	Ni, Zn, Pb, Cd, Cu, Co, Hg, Ag, As	De et al. 2008; Acosta-Rodríguez et al. 2017; Igiri et al. 2018
Saccharomyces cerevisiae	Pb, Cd	Farhan and Khadom 2015; Bahafid et al. 2017
Schizosaccharomyces pombe	Cu	Bahafid et al. 2017
Algae		
Chlorella vulgaris	Zn, Cd, Cu, Pb, Tributylin (TBT)	Travieso et al. 1999; De et al. 2008
Euglena gracilis	Zn	Travieso et al. 1999
Hydrodictyon, Oedogonium and *Rhizoclonium* sp.	As	Coelho et al. 2015; Srivastava and Dwivedi 2015
Rhodotorula mucilaginosa	Hg, Cu, Pb	Acosta-Rodríguez et al. 2018
Scenedesmus acutus	Cd, Zn, Cr	Travieso et al. 1999
Spirogyra sp. and *Cladophora* sp.	Pb (II), Cu (II)	Lee and Chang 2011; Coelho et al. 2015
Spirogyra sp. and *Spirulina* sp.	Cr Cu, Fe, Mn, Zn	Mane and Bhosle 2012; Coelho et al. 2015
Spirulina platensis	Cd	Al-Homaidan et al. 2015
Bacterial consortium		
Acinetobacter sp. and *Arthrobacter* sp.	Cr	De et al. 2008
Viridibacillus arenosi B-21, *Sporosarcina soli* B-22, *Enterobacter cloacae* KJ-46 and *E. cloacae* KJ-47	Lead, cadmium, copper	Kang et al. 2016

exhibited tolerance to cadmium. *Chlamydomonas* produces phytochelatins which sequester many metals and they have potential application in bioremediation of heavy metals (Kumar et al. 2013).

Pseudomonas sp. have been reported to degrade a wide range of toxic compounds including compounds of cobalt, zinc, cadmium; organic and inorganic mercury; phenols and other aromatic compounds and tributyltin in the aquatic environments. At low concentration of heavy metals, *Vibrio harveyi* which is a common bacterium of the saline environment exhibited bioaccumulation of cadmium (Abd-Elnaby et al. 2011) and precipitation of divalent lead into lead phosphate (Mire et al. 2004; Rehan and Alsohim 2019). Bacteria such as *Citrobacter freundii* avoid toxicity of metals by converting divalent lead to lead phosphate. Other bacteria such as *Acidithiobacillus*

ferrooxidans and *Frankia* detoxify copper by precipitating the metal by forming metal phosphate complexes (Rehan and Alsohim 2019).

The ability of bacteria to produce EPS is an important feature in metal sequestration and therefore in bioremediation. Exopolysaccharides produced by bacteria protect it against environmental stresses such as salinity, heavy metal toxicity, desiccation, presence of antibiotics, etc. Bacterial EPS such as alginate from *Pseudomonas aeruginosa* and *Azotobacter vinelandii*, sphingans from *Sphingomonas paucimobilis*, hyaluronan from *Pseudomonas aeruginosa*, *Pasteurella multocida* and attenuated strains of *Streptococci*, xanthan from *Xanthomonas campestris*, galactopol from *Pseudomonas oleovorans* and fucopol from *Enterobacter* A47 are some of the heteropolysaccharides that have potential applications in metal sequestration and reduction of metal from contaminated sites (Gupta and Diwan 2016). The bacteria, *Rhodobium marinum* NW16, *Rhodobacter sphaeroides* KMS24 were found to be more efficient in the removal of heavy metals from contaminated shrimp ponds when incubated for production of EPS (Panwichian et al. 2011).

Bioremediation of heavy metals is more efficient when a consortium of bacterial strains is used in comparison with a single strain. Kang et al. (2016) reported that a bacterial consortium containing *Viridibacillus arenosi* B-21, *Sporosarcina soli* B-22, *Enterobacter cloacae* KJ-46 and *E. cloacae* KJ-47 were more effective in bioremediation of soil contaminated with Pb, Cd and Cu due to the synergistic effect of bacterial consortium. The bacterial consortium showed greater resistance to the heavy metals in comparison to using a single strain. Bioremediation studies using consortium of marine bacteria exhibited efficient removal of mercury in the bioreactor (De et al. 2008). Therefore, a consortium of microbial isolates is metabolically more effective in biosorption of metals and therefore more potent in field applications (Table 11.1).

11.7 Microbial Mechanism of Degradation of Hydrocarbon Pollutants

Hydrocarbon pollutants are mainly of two types: polycyclic aromatic hydrocarbons and petroleum-based hydrocarbons (crude oil-based hydrocarbon). Polycyclic aromatic hydrocarbons are unsaturated hydrocarbons that contain two or more aromatic rings. These are generated by incomplete combustion of organic material such as wood, petroleum, coal, natural gas. Crude oil-based hydrocarbons or petroleum hydrocarbons usually include the *n*-alkanes and cyclohexanes which are saturated hydrocarbons (Kumar et al. 2018b). These are found to contaminate the soil and water due to spillages from oil tankers, shipping activities, storm water and industrial discharge. The degradation pathway employed by microorganisms for the degradation of these hydrocarbons and most of the organic pollutants involves the oxidation of the pollutant by cell oxygenases and peroxidases (Das and Dash 2014). The resulting catechol in case of PAHs and primary alcohols in case of crude oil-based hydrocarbons undergo degradation by the peripheral pathways of the cell forming intermediates that enter the central intermediary pathway like the Tricarboxylic acid

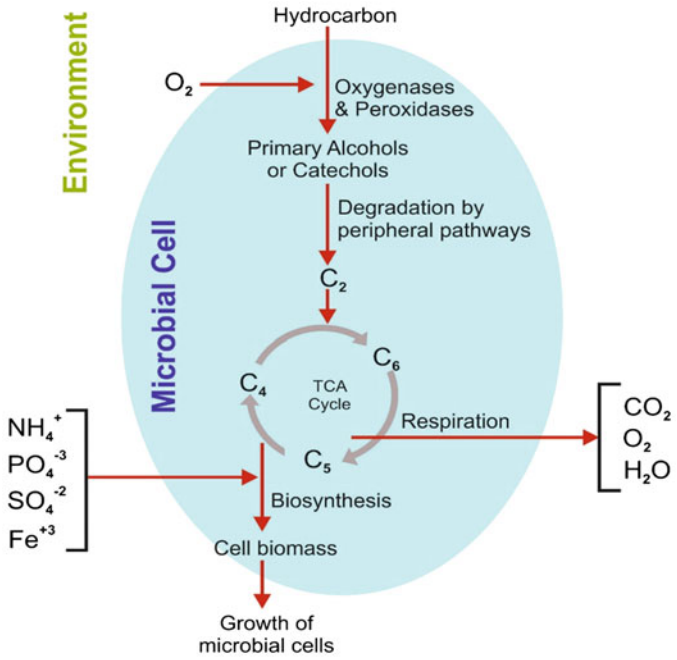


Fig. 11.5 Biodegradation of hydrocarbon compounds by microorganisms

pathway (TCA) (Fig. 11.5). The central precursor molecules of the TCA cycle (acetyl-CoA, succinate, pyruvate) then enter the biosynthesis pathway for sugar synthesis by gluconeogenesis and by formation of cell biomass.

In the biodegradation of hydrocarbons, the genera *Pseudomonas* is found to be the most prominent member that is capable of degrading wide number of polyaromatic hydrocarbons and petroleum hydrocarbons. *Pseudomonas stutzeri* was found to be a very dominant organism in the petroleum pipelines which had an ability to utilize aromatic hydrocarbons such as toluene, phenol, xylene and naphthalene.

11.7.1 Bioremediation of Polyaromatic Hydrocarbons by Microorganisms

Polyaromatic hydrocarbons are of environmental concern owing to their persistence in nature and their toxigenic, mutagenic and carcinogenic properties. PAHs include recalcitrant compounds such as naphthalene, benzopyrene, phenanthrene, anthracene, etc. Many bacteria, fungi and algae have been studied for their ability to metabolize and degrade these PAHs (Bhatia et al. 2018). Table 11.2 shows the list of bacterial, fungal and algal microorganisms that have the potential to degrade polyaromatic hydrocarbons. The bioremediation potential of the microorganisms

Table 11.2 Microorganisms used in bioremediation of polyaromatic hydrocarbons (PAHs)

Polyaromatic hydrocarbon degrading microorganisms		
Microorganism	Polyaromatic hydrocarbon (PAH)	Reference
Bacteria		
Achromobacter xylosoxidans DN002	Mono and poly aromatic hydrocarbons	Xu et al. 2018
Cycloclasticus sp.	Naphthalene, Phenanthrene, pyrene	Ghosal et al. 2016; Bhatia et al. 2018
Lutibacterium anuloederans	Phenanthrene	Chung and King 2001; Das and Dash 2014
Mycobacterium sp.	Naphthalene, Phenanthrene	Ghosal et al. 2016; Bhatia et al. 2018
Neptunomonas naphthovorans	Naphthalene	Hedlund et al. 1999; Das and Dash 2014
Pseudomonas sp.	Naphthalene, Phenanthrene	Ghosal et al. 2016; Bhatia et al. 2018
Sphingomonas paucimobilis EPA505	Phenanthrene	Das and Dash 2014; Ghosal et al. 2016
Fungi		
Aspergillus *terreus*	Pyrene, Benzopyrene, Phenanthrene	Capotorti et al. 2004; Capotorti et al. 2005; Cerniglia and Sutherland 2010
Cunninghamella elegans	Naphthalene, anthracene, phenanthrene	Cerniglia and Sutherland 2010
Fusarium sp.	Benzopyrene	Cerniglia and Sutherland 2010
Ganoderma lucidum	Phenanthrene, pyrene	Agrawal et al. 2018
Irpex lacteus	Pyrene	Cajthaml et al. 2008
Phanerochaete chrysosporium	Fluorene	Cerniglia and Sutherland 2010
Phanerochaete sordida	Creosote	Cerniglia and Sutherland 2010
Pleurotus ostreatus	Creosote, pyrene, anthracene, fluorene, and dibenzothiophene	Bezalel et al. 1996; Bogan et al. 1999; Cerniglia and Sutherland 2010
Scopulariopsis brevicaulis	Phenanthrene, benzopyrene	Mao and Guan 2016
Trametes versicolor	Anthracene, benzopyrene	Cerniglia and Sutherland 2010
Algae		
Chlamydomonas sp.	Lindane, naphthalene, phenol	Ardal 2014
Chlorella sp.	Lindane, chlordimeform	Ardal 2014
Dunaliella sp.	Naphthalene	Ardal 2014
Elkatothrix viridis	Anthracene	El-Sheekh et al. 2012
Lyngbya lagerlerimi	Phenol	El-Sheekh et al. 2012
Nitzschia sp. and *Skeletonema costatum*	Phenanthrene and fluoranthene	Hong et al. 2008
Nostoc linckia	Naphthalene	El-Sheekh et al. 2012

(continued)

Table 11.2 (continued)

Polyaromatic hydrocarbon degrading microorganisms		
Microorganism	Polyaromatic hydrocarbon (PAH)	Reference
Scenedesmus obliquus	Phenanthrene, naphthalene, Sulphonic acid	Safonova et al. 2005
Selenastrum capricornutum	Benzo[a]pyrene	Ardal 2014
Volvox aureus	2-methythie 3-phenyl quinazlin-4- 3H	El-Sheekh et al. 2012
Microbial consortium		
Burkholderia cepacia GS3C, *Pandoraea pnomenusa* GP3B *Pseudomonas* GP3A *Sphingomonas* GY2B,	Phenanthrene and Methylphenanthrenes	Gupta et al. 2015
Bacillus pumilus *Staphylococcus warneri*	Phenanthrene, Pyrene and Benzo[a]anthracene	Moscoso et al. 2012
Serratia marcescens L-11, *Streptomyces rochei* PAH-13 *Phanerochaete chrysosporium* VV-18	Fluorene, anthracene, phenanthrene and pyrene	Sharma et al. 2016
Rhodococcus sp. ASDC1 *Bacillus* sp. ASDC2 *Burkholderia* sp. ASDC3	Chrysene	Vaidya et al. 2018
Aeromonas hydrophila *Bacillus megaterium* *Raoultella ornithinolytica,* *Serratia marcescens*	Acenaphthene, fluorene	Alegbeleye et al. 2017
Aphanocapsa sp., *Chlorella minutissimma,* *Citrobacter* sp. SB9, *Pseudomonas aeruginosa* SA3, *Bacillus subtilis* SA7	PAH in crude oil effluents	Godsgift and Fagade 2016

may be DNA based or plasmid based. *Cycloclasticus* sp. are the most common and widely studied bacteria that have the potential to degrade multiple PAH compounds (Wang et al. 2018). Marine bacteria such as *Cycloclasticus spirillensus, Lutibacterium anuloederans and Neptunomonas naphthovorans* have been studied for their ability to degrade PAHs in the marine environment (Das and Dash 2014). Bacteria such as *Mycobacterium* sp., *Moraxella* sp., *Burkholderia cepacia, Pseudomonas fluorescens, Pseudomonas putida, Pseudomonas paucimobilis, Bacillus cereus, Rhodococcus* sp., *Streptomyces* sp., *Achromobacter denitrificans, Brevundimonas vesicularis, Comamonas testosteroni, Vibrio* sp., *Sphingomonas, Brevibacterium, Arthrobacter, Nocardioides* have exhibited their ability to degrade naphthalene and phenanthrene (Ghosal et al. 2016). *Sphingomonas paucimobilis* EPA505 has also shown an ability to grow on fluoranthene utilizing it as the sole

carbon source (Das and Dash 2014). Research studies have shown other bacteria such as *Sphingobacterium, Alteromonas, Streptomyces* and fungi *Irpex lacteus, Aspergillus fumigatus* can be used either individually or as a consortium with other PAH degrading microorganisms for bioremediation of PAH-contaminated environments (Bhatia et al. 2018). The degradation of the polyaromatic hydrocarbon, like in case of other substrates also depends upon the pH of the environment. The degradation of *Burkholderia cocovenenans* increases from 40% to 80% when the pH is changed from 5.5 to neutral (Mahjoubi et al. 2017).

The fungi *Pleurotus ostreatus, Phanerochaete chrysosporium, Phanerochaete laevis* HHB-1625*, Rigidoporus lignosus, Aspergillus terreus, Cunninghamella elegans, Fusarium* sp.*, Trametes versicolor, Phanerochaete sordida* have been studied for their ability to degrade various polyaromatic compounds (Bogan et al. 1996; Cerniglia 1982; Cerniglia and Sutherland 2010). Though degradation of PAHs by bacteria and fungi has been widely studied, much less is known about the degradation of these compounds by algae. *Scenedesmus obliquus*, a green alga has been reported to degrade phenanthrene by biotransformation (Safonova et al. 2005). *Nostoc linckia, Elkatothrix viridis* and *Volvox aureus* degraded naphthalene, anthracene and 2-methythie 3-phenyl quinazlin-4-3H, respectively. *Nitzschia* sp. and *Skeletonema costatum* biodegrade phenanthrene and fluoranthene by bioaccumulation of these compounds inside the cells (Hong et al. 2008). The algae *Prototheca zopfi* has also been reported to degrade polyaromatic hydrocarbons extensively.

Degradation of PAH has been found to be more effective on application of consortium of microorganisms to PAH-contaminated soils. Microbial communities from the rhizosphere have been reported to degrade PAHs in contaminated soils by synergistic action between the microorganisms (Bisht et al. 2015). Investigations using a consortium of *Staphylococcus warneri* and *Bacillus pumilus* in the degradation of Phenanthrene, Pyrene and Benzo[a]anthracene were found to yield results with the removal of about 80–90% of the aromatic compound in 3 days in a bioreactor (Moscoso et al. 2012). Bacterial consortium *Serratia marcescens* L-11, *Streptomyces rochei* PAH-13 and *Phanerochaete chrysosporium* VV-18 were found to be 85–100% effective against soil contaminated with fluorene, anthracene, phenanthrene and pyrene within a period of 30 days when the soil was amended with compost (Sharma et al. 2016). A bacterial algal consortium with *Chlorella minutissimma* and *Aphanocapsa* sp. as the algal counterparts and *Citrobacter* sp. SB9, *Pseudomonas aeruginosa* SA3, *Bacillus subtilis* SA7 as the bacterial inoculants was studied for its efficiency in degradation of PAHs from crude oil effluents. A combination of *Chlorella minutissimma* and the bacterial inoculants was found to be the most effective in comparison with all the algal and bacterial inoculants used together or when *Aphanocapsa* sp. was used along with the bacterial inoculants. Therefore, the success and efficiency of the consortium depends on the synergistic action between the inoculants (Godsgift and Fagade 2016).

11.7.2 Bioremediation of Crude Oil-Based Hydrocarbons by Microorganisms

Crude oil-based hydrocarbons pose a major threat to humans as well as to the terrestrial and marine ecosystems. Bioremediation approaches for the removal of these crude oil-based hydrocarbons have received much attention largely due to their efficacy in detoxifying the contaminants effectively. The interaction and biodegradation of hydrocarbon substrates depend essentially on the adhesion mechanisms of the bacterial cell that include the outer membrane proteins and lipids, fimbriae, pili and extracellular polymers and capsules. It has been reported that in *Acinetobacter* sp. RAG-1 (Table 11.3), the utilization of Alkane is dependent upon the presence of fimbriae. However, it is not just the bacteria with hydrophobic cell surface that degrade the pollutants. Bacteria with hydrophilic cell surface have also been demonstrated to metabolize hydrocarbon pollutants owing to modifications in their outer membranes. These hydrophilic hydrocarbon degrading bacteria possess more potential in degrading the hydrocarbon as it involves direct assimilation and action on the hydrocarbon substrate in comparison with the hydrophobic bacteria. This is due to the high cell surface hydrophobicity which promotes cell aggregation and biofilm formation (Prakash et al. 2014).

Bioremediation of hydrocarbon involves two approaches: Bioaugmentation and biostimulation. Bioaugmentation involves introduction of highly efficient hydrocarbon degrading bacteria to degrade the hydrocarbon (Mahjoubi et al. 2017), whereas biostimulation is the stimulation of the indigenous bacteria by modifying the environmental conditions. Though biodegradation of the hydrocarbons has been studied in bacteria yeast and fungi, bacteria are the major class of microorganisms involved in biodegradation of hydrocarbons. Hydrocarbon biodegradation by various marine strains that has been studied includes bacteria belonging to the genera *Acinetobacter, Achromobacter, Alcanivorax, Alkanindiges, Alteromonas, Arthrobacter, Burkholderia, Dietzia, Enterobacter, Kocuria, Micrococcus, Marinococcus, Methylobacterium, Marinobacter, Mycobacterium, Pseudomonas, Pandoraea, Nocardia, Planococcus, Rhodococcus, Staphylococcus, Streptococcus, Streptobacillus, Sphingomonas* and *Vibrio* (Tremblay et al. 2017). A wide number of pseudomanads are capable of degrading a wide variety of petroleum-based hydrocarbons (Varjani and Upasani 2012; Wu et al. 2018; Muriel-Millán et al. 2019).

Bioremediation of oil spills by novel bacterial isolates, capable of degrading crude oil has been reported which can utilize these hydrocarbons as a source of carbon and energy. *Vibrio* and *Acinetobacter* sp. reported by Kharangate-Lad and Bhosle (2014) were capable of growing on crude oil and produced EPS which were capable of bioemulsifying hydrocarbons. Surface sediment bacteria, *Halomonas* sp. MS1 isolated from the Kish Island in the Persian Gulf showed a significant ability to utilize crude oil as the sole source of carbon and energy and making it a potentially important bacteria in bioremediation of crude oil contaminated sites (Sadeghi et al. 2016). Interestingly bacteria such as A*lkanindiges* sp. which are rare in non-polluted sediments show a dominance in these sediments when polluted

with diesel. Similarly, bacteria belonging to the obligate hydrocarbonoclastic (OHCB) group such as *Alcanivorax, Marinobacter, Thallassolituus, Cycloclasticus, Oleispira* were undetectable or few in number before pollution. However, they were found to be abundant and dominating the site after pollution with petroleum oil. These rare-to-dominant phenomenon of hydrocarbon degrading bacteria play a crucial role in the biotransformation and bioremediation of the crude oil hydrocarbons. Though bacteria utilizing wide range of crude oil components like *Dietzia* sp. and *Achromobacter xylosoxidans* DN002 have been reported, no bacteria can degrade the entire spectrum of petroleum hydrocarbons (Xu et al. 2018). Therefore, efficient removal of crude oil requires combined action of multiple bacteria degrading various hydrocarbons.

Commercial consortiums have been developed for bioremediation of hydrocarbons with bacteria such as *Agreia, Marinobacter, Pseudoalteromonas, Pseudomonas, Psychrobacter* and *Shewanella*. This consortium has been reported to efficiently degrade crude oil and its components. Bacterial consortium developed using *Ochrobactrum* sp., *Stenotrophomonas maltophilia* and *Pseudomonas aeruginosa* could effectively degrade 3% of crude oil by 83%. Significantly, when exogenous *Bacillus subtilis* was applied with indigenous bacterial consortium, it effectively accelerated the degradation of crude oil (Xu et al. 2018). A bioaugmentation field study, on the treatment of diesel oil-contaminated soil demonstrated that with exogenous consortium containing *Aeromonas hydrophila, Alcaligenes xylosoxidans, Gordonia* sp., *Pseudomonas fluorescens, Pseudomonas putida, Rhodococcus equi, Stenotrophomonas maltophilia* and *Xanthomonas* sp. a high biodegradation efficiency of 89% was observed in 365 days. Other bacterial consortiums that effectively degrade hydrocarbon pollutants have been mentioned in Table 11.3. Bacterial-fungal consortiums have found to be very efficient in the degradation of both PAH and petroleum-based hydrocarbons (Tang et al. 2012).

Fungi such as *Amorphoteca, Graphium, Neosartorya, Talaromyces* and yeast like *Candida, Yarrowia* and *Pichia* have been isolated from petroleum contaminated soils and that exhibit hydrocarbon degradation. Other genera such as *Aspergillus, Cephalosporium, Penicillium, Rhizopus, Paecilomyces, Pleurotus, Alternaria, Mucor, Talaromyces, Gliocladium, Fusarium* and *Cladosporium* have also been reported to have potential to degrade crude oil hydrocarbons. The yeast species isolated from contaminated water, *Candida lipolytica, Geotrichum* sp., *Torulopsis, Rhodotorula mucilaginosa* and *Trichosporon mucoides* were also seen to degrade petroleum compounds (Das and Chandran 2011).

Algae such as *Prototheca zopfi* has been studied for its ability to utilize crude oil and mixed hydrocarbon substrates. It also was reported to extensively degrade *n*-alkanes and isoalkanes (Das and Chandran 2011).

11.8 Bioremediation of Plastic Polymers by Microorganisms

With growth in industrialization and population, synthetic plastic pollution poses a major problem to the environment. Among the global plastic usage, 80% are petrochemical plastics that include polyethylene (PE), polypropylene (PP),

Table 11.3 Microorganisms used in bioremediation of crude oil-based hydrocarbons

Crude oil and crude oil component degrading bacteria		
Microorganism	Pollutant	Reference
Bacteria		
Achromobacter xylosoxidans DN002	Mono and polyaromatic hydrocarbons	Xu et al. 2018
Alcanivorax sp.	*n*-alkanes	Xu et al. 2018
Brevibacillus laterosporus	Diesel	Amina and Chibani 2016
Dietzia sp.	*n*-alkanes (C6–C40)	Xu et al. 2018
Halomonas sp. MS1	Crude oil	Sadeghi et al. 2016
Pseudomonas aeruginosa	*n*-alkanes	Wu et al. 2018; Muriel-Millán et al. 2019
Fungi		
Aspergillus sp.	Petroleum hydrocarbon	Al-Nasrawi 2012; Al-Hawash et al. 2018b
Beauveria bassiana		Al-Nasrawi 2012
Cochliobolus lunatus	Crude oil	Al-Nasrawi 2012
Cunninghamella echinulate *Cunninghamella elegans*	Crude oil	Rudd et al. 1996
Fusarium solani	Crude oil	Al-Nasrawi 2012
Meyerozyma guilliermondii	Gasoline	Sangale et al. 2019
Mortierella sp.		Sangale et al. 2019
Penicillium sp. *Penicillium documbens*	Crude oil	Al-Nasrawi 2012; Govarthanan et al. 2017; Al-Hawash et al. 2018a
Scolecobasidium obovatum	Crude oil	Mahmoud and Bagy 2018
Yeast		
Candida lipolytica *Candida glabrata* *Candida krusei*	*n*-alkanes	Das and Chandran 2011; Burghal et al. 2016
Geotrichum sp.	Crude oil	Das and Chandran 2011
Rhodotorula mucilaginosa	Crude oil	Das and Chandran 2011
Trichosporon mucoides	Crude oil	Das and Chandran 2011
Saccharomyces cerevisiae	Crude oil	Burghal et al. 2016
Polysporus sp. S133	Crude oil	Burghal et al. 2016
Algae		
Prototheca zopfi	*n*-alkanes and isoalkanes	Das and Chandran 2011
Fucus vesiculosus	Petroleum waste	Aditi et al. 2015
Consortium		
Burkholderia cepacia GS3C, *Pandoraea pnomenusa* GP3B *Pseudomonas* GP3A *Sphingomonas* GY2B	Alkanes, alkylcycloalkanes, alkylbenzenes	Tang et al. 2012

(continued)

Table 11.3 (continued)

Crude oil and crude oil component degrading bacteria		
Microorganism	Pollutant	Reference
Ochrobactrum sp., *Pseudomonas aeruginosa* *Stenotrophomonas maltophilia*	Crude oil	Xu et al. 2018
Brachybacterium sp., *Cytophaga* sp., *Sphingomonas* sp., *Pseudomonas* sp.	Oil spills	Angelim et al. 2013
Micrococcus sp., *Bacillus* sp., *Corynebacterium* sp., *Flavobacterium* sp., *Pseudomonas* sp.	*n*-alkane	Rahman et al. 2003
Alteromonas putrefaciens, *Klebsiella pneumoniae, Pseudomonas fragi* *Moraxella saccharolytica*,	Diesel hydrocarbon	Sharma and Rehman 2009
Acinetobacter faecalis, *Staphylococcus* sp. *Neisseria elongate*	Crude petroleum oil	Mukred et al. 2008
Brachybacterium sp., *Cytophaga* sp., *Pseudomonas* sp. *Sphingomonas* sp.,	Oil spills	Angelim et al. 2013
Aeromonas hydrophila, *Alcaligenes xylosoxidans*, *Gordonia* sp. *Pseudomonas fluorescens*, *Pseudomonas putida*, *Rhodococcus equi*, *Stenotrophomonas maltophilia*, *Xanthomonas* sp.	Diesel	Xu et al. 2018

polystyrene (PS), polyethylene terephthalate (PET) and polyvinyl chloride (PVC) which pollute the soil and water environment.

Biodegradation of plastic polymers by microorganisms proceeds via four important steps, biodeterioration, biofragmentation, assimilation and mineralization (Fig. 11.6). Biodeterioration involves initial colonization by microorganisms by adhesion thereby affecting the physical, chemical and mechanical properties of the plastic. Abiotic factors play a synergistic role in initializing the degradation. Microorganisms colonize and produce biofilm or EPS that invade the polymeric pores resulting in grooves and cracks. Therefore, weakening the polymeric structure of the plastic and physically deteriorating the polymer. The release of corrosive compounds during metabolism such as sulphuric acid (*Thiobacillus* sp.), nitrous acid (*Nitrosomonas* sp.) or nitric acid (*Nitrobacter* sp.) by chemolithotrophic bacteria and production of organic acids such as citric, fumaric, oxalic, gluconic, glutaric, oxaloacetic and glyoxalic acids affects the microplastic matrix resulting in chemical deterioration of the polymer. In biofragmentation the polymeric plastic is cleaved

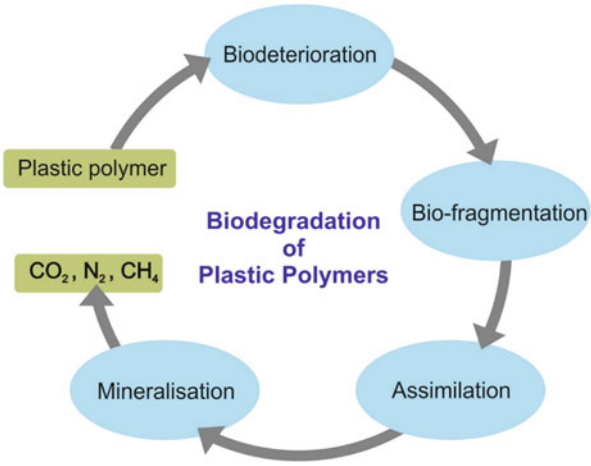


Fig. 11.6 The different steps in biodegradation of plastic polymers by microorganisms

into oligomers, dimers or monomers by the action exo-enzymes or free radicals produced by the microorganisms. Bacteria that degrade plastics usually contain the enzyme oxygenases that catalyses the addition of an oxygen molecule to the polymeric chain converting it to a less recalcitrant molecule such as an alcohol or peroxyl group. Assimilation involves the absorption of molecules across the cell cytoplasm for metabolic process to form cell biomass or cell structures. Mineralization is the complete degradation of the absorbed molecules into oxidized metabolites such as carbon dioxide, nitrogen, methane and water vapour (Dussud et al. 2018).

In studies involving biodegradation of plastic polymers, *Pseudomonas* and *Clostridium* are the most dominant bacteria that can metabolize plastics like polyethene, PVC, PHB (Table 11.4) (Ghosh et al. 2013). Studies on *Rhodococcus* sp. demonstrate the ability to degrade plastic by 8% of its dry weight in 30 days (Urbanek et al. 2018). Other bacteria known to degrade plastic polymers are *Acidovorax* sp., *Alcaligenes* sp., *Brevibacillus borstelensis, Comamonas acidovorans, Diplococcus* sp., *Moraxella* sp., *Pseudomonas* sp., *Streptococcus* sp., *Staphylococcus* sp. and *Micrococcus* sp., *Thermomonospora fusca, Schlegelella thermodepolymerans* and *Amycolatopsis* sp. (Ghosh et al. 2013; Kathiresan 2003). Bacteria degrading plastic polymers such as *Alcanivorax, Shewanella, Moritella, Psychrobacter*, *Pseudomonas* and *Tenacibaculum* that exhibited biodegradation ability against polyester PCL have been reported from the deep-sea sediments. The highest biodegradation capacity for PCL was observed in *Pseudomonas* and *Rhodococcus* (Urbanek et al. 2018).

Bacteria such as *Phormidium, Pseudophormidium, Bacteroides, Lewinella, Proteobacteria, Arcobacter and Colwellia* sp. isolated from the surface of PET bottles and microplastic polymers have been identified for their ability to degrade these polymers. Analysis of enzymatic profiles of most plastic degrading microorganisms suggests that the presence of the enzyme lipase plays a crucial role in the ability of these microorganisms to degrade plastic polymers as it catalyses

Table 11.4 Microorganisms used in bioremediation of plastic polymers

Plastic polymer degrading microorganisms		
Microorganism	Pollutant	Reference
Bacteria		
Alcanivorax	Monofilament fibres of PCL, PHB/V, PBS	Sekiguchi et al. 2011
Arcobacter sp., Colwellia sp.	LDPE	Urbanek et al. 2018
Bacillus brevis	Polycaprolactone	Urbanek et al. 2018
Ideonella sakaiensis	PET	Urbanek et al. 2018
Moritella sp.	PCL	Sekiguchi et al. 2011
Ochrobactrum sp.	PVC	Ghosh et al. 2013
Phormidium, Lewinella	PET	Urbanek et al. 2018
Proteobacteria, Bacteroides	Microplastics	Urbanek et al. 2018
Pseudomonas sp.	PCL, commercially available bag based on potato and corn starch monofilament fibres of PCL, PHB/V, PBS	Sekiguchi et al. 2011
Psychrobacter sp.	PCL	Sekiguchi et al. 2011
Rhodococcus sp.	PCL, commercially available bag based on potato and corn starch	Sekiguchi et al. 2011
Rivularia	PP, PE	Urbanek et al. 2018
Shewanella sp.	PCL	Sekiguchi et al. 2011
Stanieria, Pseudophormidium	PET	Urbanek et al. 2018
Streptomyces sp.	PHB, poly(3-hydoxybutyarate-co-3-hydroxyvalerate), and starch or polyester	Ghosh et al. 2013
Tenacibaculum sp.	Monofilament fibres of PCL, PHB/V, PBS	Urbanek et al. 2018
Zalerion maritimum	PE	Urbanek et al. 2018
Fungi		
Asp*ergillus versicolor, Aspergillus* sp. *Aspergillus sydowii*	LDPE PVC	Urbanek et al. 2018; Sangale et al. 2019
Clonostachys rosea, Trichoderma sp.	PCL, commercially available bag based on potato and corn starch	Urbanek et al. 2018
Ochrobactrum anthropi strain L1-W	di-2-ethylhexyl phthalate	Nshimiyimana et al. 2020
Pleurotus ostreatus	PE	Rodrigues da luz et al. 2019
Myceliophthora sp.	Polyethylene	Ibrahim 2013
Penicillium chrysogenum	Polythene	Sangale et al. 2019
Trichoderma viride	LDPE	Munir et al. 2018

(continued)

Table 11.4 (continued)

Plastic polymer degrading microorganisms		
Microorganism	Pollutant	Reference
Pestalotiopsis microspora	Polyurethane	Russell et al. 2011
Yeast		
Candida rugosa	Polyurethane	Russell et al. 2011
Pseudozyma sp.	Poly-butylene succinate or poly-butylene succinate-co-adipate	Kitamoto et al. 2011
Algae		
Anabaena spiroides	Polyethylene	Kumar et al. 2017
Scenedesmus dimorphus	Polyethylene	Kumar et al. 2017
Navicula pupula	Polyethylene	Kumar et al. 2017
Consortium		
Vibrio alginolyticus, Vibrio parahaemolyticus	PVA-LLDPE	Urbanek et al. 2018

the hydrolysis of ester bonds. Microbial lipases can efficiently hydrolyse polyesters of PCL. Therefore, lipase producing strains *Agreia, Cryobacterium*, *Polaromonas, Micrococcus, Subtercola, Leifsonia* and *Flavobacterium* from the marine environment have potential to degrade plastic polymers. Other microbial enzymes like cutinases, ureases, depolymerases (PHA-depolymerases, PHB-depolymerases PLA depolymerases, PCL depolymerases), esterases, proteinases (proteinase K against PLA) and dehydratases produced by microorganisms also aid in degradation of plastic polymers. Recent studies on the bacterium *Ideonella sakaiensis* have shown the presence of a novel enzyme PETase (Urbanek et al. 2018).

Fungi, *Clonostachys rosea* and *Trichoderma* sp. have been reported to degrade plastic polymers. *Aspergillus versicolor* and other *Aspergillus* sp. actively degrade LDPE plastic polymers. Saprophytic fungi capable of degrading polyurethane, *Agaricus bisporus*, *Marasmius oreades*, *Cladosporium cladosporioides, Xepiculopsis graminea* and *Penicillium griseofulvum* were isolated from floating plastic litter from the shorelines of Lake Zurich, Switzerland (Brunner et al. 2018). *Alternaria* sp., *Aspergillus niger, Geomyces pannorum, Nectria* sp., *Phoma* sp., *Paraphoma* sp., *Penicillium* sp., *Plectosphaerella* sp. and *Neonectria* sp. are fungi that utilized polyurethane as the sole source of carbon. Yeast *Candida rugosa* has been reported to have polyurethane degrading enzymes and *Pseudozyma* sp. exhibits ability to degrade poly-butylene succinate or poly-butylene succinate-co-adipate films (Kitamoto et al. 2011).

The microalgae *Anabaena spiroides* (blue-green alga), *Scenedesmus dimorphus* (Green microalga) and *Navicula pupula* (Diatom) are being considered as the novel solutions for degradation of polyethylene (Kumar et al. 2017). Microalgae promote efficient biodegradation of plastic polymers by using its enzymes and toxins (Bhuyar et al. 2018).

Microbial consortium using microorganisms with enzymatic profiles necessary for degradation of LDPE and polyethylene has been obtained from culture collection and tested for their potential application in degradation of these plastic polymers (Skariyachan et al. 2016). A consortium of marine bacteria *Vibrio alginolyticus* and *Vibrio parahaemolyticus* when incubated with polyethylene for 15 days showed disintegration of the polymer in the form of grooves and cracks. Studies on bacterial consortium are focused on biodegradation of plastic polymers using indigenous microbial population and biostimulation, by incorporating microbial strains that produce specific plastic degrading enzymes. Research on bacterial consortium also suggests that tailored consortia can thrive in the plastic mixtures and participate in their biodegradation (Syranidou et al. 2019).

11.9 Bioremediation of Recalcitrant Agro-Chemicals by Microorganisms

The rise in the global population has increased the demand for food supplies and therefore involves incessant use of fertilizers, pesticides, fungicides, insecticides and herbicides in farming. Pesticides and herbicides are chemicals that are used to control insects and unwanted weeds, respectively. It is necessary to use these in moderate amounts, only as required in order to control the pests and weeds. However unrestricted use of these pesticides has led to their accumulation in the soil as well as in the water bodies resulting in problems due to biomagnification. Landfilling and pyrolysis of these xenobiotic compounds lead to formation of toxic intermediates. Therefore, bioremediation of these compounds using microorganisms is a promising technique for the removal of these compounds from the soil and marine environment.

The bacteria involved in degradation of pesticides include *Alteromonas undina*, *Alteromonas haloplanktis, Bacillus diminuta, Flavobacterium* sp., *Arthrobacter* sp., *Azotobacter* sp., *Burkholderia* sp., *Pseudomonas* sp., *Raoultella* sp., and *Bacillus sphaericus.* These have been reported to degrade herbicidal and fungicidal compounds (Table 11.5) (Uqab et al. 2016). The biodegradation of these xenobiotic compounds involves complete oxidation of the compound to carbon dioxide and water with the release of energy for the microbes. Bacterial strains of *Pseudomonas fluorescens* and *Bacillus polymyxa* from the Kyrgyzstan pesticide dumping sites exhibited high rate of degradation of aldrin. These dumping sites also showed an abundance of bacteria belonging to the genera *Pseudomonas, Bacillus* and *Micrococcus*. Reports on biodegradation of endosulfan highlight the degradative abilities of *Klebsiella* sp., *Acinetobacter* sp., *Alcaligenes* sp., *Flavobacterium* sp. and *Bacillus* sp. in degradation of this compound. The microbial action on endolsulfan results in the production of intermediates (endosulfan diol, endosulfan ether, and endosulfan lactone) of lesser toxicity than the original compound. Bioremediation of pesticide and related compounds by using microorganisms is preferred due to the production of less toxic intermediates. However, in soils where the innate microbial population is unable to degrade these compounds, addition of external microflora

Table 11.5 Microorganisms used in bioremediation of recalcitrant agro-chemicals

Recalcitrant agro-chemical degrading microorganisms		
Microorganism	Pollutant	Reference
Bacteria		
Acidomonas sp.	Allethrin	Paingankar et al. 2005
Aminobacter sp. MSH1	2,6-dichlorobenzamide (BAM)	Ellegaard-Jensen et al. 2017
Bacillus amyloliquefaciens IN937a *Bacillus pumilus* SE34	Propamocarb and Propamocarb hydrochloride	Ardal 2014
Bacillus polymyxa	Aldrin	Uqab et al. 2016
Bacillus thuringiensis	Melathion	Javaid et al. 2016
Micrococcus	Aldrin	Uqab et al. 2016
Mycobacterium chlorophenolicum	PCB	
Ochrobactrum anthropi NC-1	Phenmedipham	Pujar et al. 2019
Ochrobactrum anthropi Strain SH14	Azoxystrobin	Feng et al. 2020
Pseudomonas sp.	Organophosphates, neonicotinoids, endosulfan, atrazine	Uqab et al. 2016; Doolotkeldieva et al. 2018
Rhizobium meliloti	Chlorinated phosphates	Javaid et al. 2016
Sphingobium japonicum	Hexachlorocyclohexane	Javaid et al. 2016
Stenotrophomonas maltophilia	Endosulfan, DDT	Javaid et al. 2016
Shewanella sp.	Methyl parathion	Javaid et al. 2016
Fungi		
Aspergillus sp.	Endosulfan, organophosphates	Frazar 2000
Fusarium proliferatum CF2	Allethrin	Bhatt et al. 2020
Mortierella sp. LEJ701	Diuron	
Mortierella sp. LEJ701, *Aminobacter* sp. MSH1	2,6-dichlorobenzamide (BAM)	Ellegaard-Jensen et al. 2017
Phanerochaete	Aldrin, DDT, etc.	Uqab et al. 2016
Pleurotus ostreatus	Aldrin, DDT, etc.	Uqab et al. 2016
Pleurotus sp.	Endosulfan, chlorothalonil paraquat	Camacho-Morales and Sánchez 2016
Variovorax sp. SRS16 *Arthrobacter globiformis* D47 *Mortierella* sp. LEJ702	Diuron	Ellegaard-Jensen et al. 2017
Algae		
Chlorella sp..	Mirex, chlordimeform	Ardal 2014
Chlamydomonas sp.	Toxaphene, methoxychlor	Ardal 2014
Chlorococcum sp.	Mirex	Ardal 2014
Cylindrotheca sp.	DDT	Ardal 2014
Dunaliella sp.	Mirex	Ardal 2014
Euglena gracilis	DDT, parathion	Ardal 2014
Scenedesmus obliquus	DDT, parathion	Ardal 2014

(continued)

Table 11.5 (continued)

Recalcitrant agro-chemical degrading microorganisms		
Microorganism	Pollutant	Reference
Selenastrum capricornutum	Benzene, toluene, chlorobenzene, 1,2-dichlorobenzene, nitrobenzene Naphthalene, 2,6-dinitrotoluene, phenanthrene, di-*n*-butylphthalate, Pyrene	Ardal 2014
Consortiums		
Bacillus sp. *and Chryseobacterium joostei*	Lindane, methyl parathion, and carbofuran	Javaid et al. 2016
Pseudomonas putida (NII 1117), Klebsiella sp.*, (NII 1118), Pseudomonas stutzeri (NII 1119), Pseudomonas aeruginosa (NII 1120)*	Chlorpyrifos	Sasikala et al. 2012

capable of degrading these compounds has been recommended. The biodegradation depends on enzymatic abilities of the microbes as well as the factors such as pH, temperature, nutrients, oxygen, etc. *Pseudomonas* sp. have been reported to degrade organophosphate compounds and neonicotinoids (Doolotkeldieva et al. 2018; Uqab et al. 2016). Immobilization of bacteria on alginate and other matrix have been used to achieve degradation of various pesticides under different flow rates and environmental conditions (Javaid et al. 2016).

In case of fungi, they make minor changes in the structure of these compounds during degradation, making them more accessible for degradation by other microbes. The fungal species *Flammulina velutipes, Stereum hirsutum, Coriolus versicolor, Dichomitus squalens, Hypholoma fasciculare, Auricularia auricula, Pleurotus ostreatus, Avatha discolor* and *Agrocybe semiorbicularis* have exhibited the ability to degrade pesticides such as chlorinated organophosphorus compounds triazine, dicarboximide and phenylurea (Uqab et al. 2016). Reports on white rot fungi especially *Phanerochaete* such as *Phanerochaete chrysosporium*, *Phanerochaete sordida*, *Pleurotus ostreatus*, *Phellinus weirii* and *Polyporus versicolor* have shown the ability to degrade aldrin, chlordane, mirex, gamma-hexachlorocyclohexane (g-HCH), heptachlor atrazine, terbuthylazine, lindane, metalaxyl, dieldrin, diuron, dichlorodiphenyltrichloroethane (DDT), etc. *Aspergillus* sp., *Fusarium oxysporum*, *Penicillium chrysogenum* and *Trichoderma* sp. have shown effective biodegradation of organophosphate pesticides (Frazar 2000; Uqab et al. 2016). *Aspergillus* sp. have also been reported to actively degrade endosulfan (Bhalerao and Puranik 2007). Oliveira et al. (2015) reported the fungal species *Penicillium citrinum*, *Aspergillus fumigatus, Aspergillus terreus* and *Trichoderma harzianum* that could tolerate and degrade chlorfenvinphos.

A fungal-bacterial consortium of *Mortierella* sp. LEJ701 and *Aminobacter* sp. MSH1 was used for the degradation of 2,6-dichlorobenzamide (BAM) and it was

observed that the mineralization of the compound proceeded faster than when these strains were used individually. Degradation of agro-chemicals has been found to be most effective on using the bacterial and fungal consortiums than using the microorganisms individually. Biosorption by *Aspergillus niger* and *Mycobacterium chlorophenolicum* has been studied for the removal of polychlorinated phenols (PCP) from aqueous solutions and was found to be pH dependent.

Algal cells such as *Chlamydomonas* sp., *Chlorella* sp., *Chlorococcum* sp., *Cylindrotheca* sp., *Dunaliella* sp., *Euglena gracilis, Scenedesmus obliquus, Selenastrum capricornutum* have been reported to degrade agro-chemicals (Table 11.5) (Ardal 2014).

The algae either metabolize these toxic pollutants using them as energy source or utilize cytochrome P450, a specialized family of monooxygenase enzymes to oxidize herbicides and pesticides. Biotransformation of these agro-chemicals has been reported in *Chlorella* sp. using the cytochrome P450. The presence of P450 has also been demonstrated in the presence of herbicide Metflurazon in the algae *Chlorella fusca* and *Chlorella sorokiniana.* Research on green algae degrading phenol, lindane, DDT, chlordimeform has also been reported (Priyadarshani et al. 2011).

Bacterial consortiums have been preferred for bioremediation of soils contaminated with mixed pesticides. *Bacillus* sp. and *Chryseobacterium joostei* have been used together to treat soils contaminated with lindane, methyl parathion and carbofuran. Abraham and others (Abraham et al. 2014) reported the use of a ten strain bacterial consortium containing *Alcaligenes* sp. JAS1, *Ochrobactrum* sp. JAS2, *Sphingobacterium* sp. JAS3 isolated from chlorpyrifos contaminated soil; *Enterobacter ludwigii* JAS17, *Pseudomonas moraviensis* JAS18 and *Serratia marcescens* JAS16 isolated from monocrotophos containing soil and *Klebsiella pneumoniae* JAS8, *Enterobacter cloacae* JAS7, halophilic bacterial strain JAS4, *Enterobacter asburiae* JAS5 isolated from endosulfan contaminated soil in the biodegradation of organophosphorus and organochlorine pesticides. Similar studies using a consortium isolated from chlorpyrifos contaminated soil containing the bacteria *Pseudomonas putida* (NII 1117), *Klebsiella* sp., (NII 1118), *Pseudomonas stutzeri* (NII 1119), *Pseudomonas aeruginosa* (NII 1120) in biodegradation of chlorpyrifos have been reported (Sasikala et al. 2012). The bacterial consortium using *Acinetobacter* sp., *Bacillus* sp., *Citrobacter freundii, Flavobacterium* sp., Pseudomonads (*Pseudomonas putida, Pseudomonas aeruginosa* and *other Pseudomonas sp*). *Stenotrophomonas* sp., *Proteus* sp., *Proteus vulgaris* and *Klebsiella* sp. was seen to be effective in degradation of methyl parathion and p-nitrophenol (Pino et al. 2011).

11.10 Microorganisms Used in Bioremediation of Dye Compounds

Rapid urbanization and industrialization have led to an increase in the use of fast dyes in industries such as textiles, plastic, food, etc. About 50% of the dye used is released in the industrial effluent. Azo dyes are a potential hazard to the environment due to their bio-recalcitrant, toxic, carcinogenic and mutagenic effects on living organisms. Commonly applied techniques for the removal of the dye involve physical, chemical and decolourization processes which pose a cost issue. Green technologies using microorganisms such as bacterial and fungal biomass provide a low-cost solution.

Various bacteria capable of degrading dyes have been reported. These include lactic acid bacteria, *Pseudomonas, Staphylococcus arlettae, Micrococcus luteus, Listeria denitrificans* and *Nocardia atlantica, Bacillus megaterium*. Basidiomycetous fungi such as *Trametes pubescens* and *Pleurotus ostreatus* and other fungal species such as *Aspergillus tamarii, Aspergillus ochraceus, Aspergillus niger, Fusarium oxysporum, Penicillium purpurogenum* and *Trichoderma lignorum* have also been identified for their role in biodegradation of dyes (Table 11.6) (Patel and Gupte 2016; Rani et al. 2014).

Significant findings have also been reported using consortium of bacteria containing two aerobic strains of bacteria and *Pseudomonas putida* (MTCC1194) in degradation of a mixture of azo dyes from textile effluents (Senan and Abraham 2004). Bacterial consortium of *Neisseria* sp., *Vibrio* sp., *Bacillus* sp., *Bacillus* sp. and *Aeromonas* sp. reportedly showed a degradation of the dyes that ranged from 65% to 90% with decolourization of the dye. This was significantly more than when the monocultures were used proving that bacterial consortium is more efficient in treating dye effluents (Karim et al. 2018).

11.11 Bioremediation of Toxic Pollutants Using Genetically Modified Microorganisms

Xenobiotic compounds cannot be easily degraded by the naturally occurring autochthonous population of microorganisms. These toxic pollutants persist in nature owing to their hydrophobic nature which makes it difficult for the microorganisms to take it up as they lack the uptake transport pathways for such compounds. Recombinant DNA technology involves introducing the desired gene by gene manipulation and plasmid DNA resulting in the development of strains of genetically modified microbes that are efficient in bioremediation. Many genetically modified strains have been used in bioremediation of various complex and toxic anthropogenic compounds especially from the genera *Pseudomonas* and *E. coli* (Table 11.7). This is due to the simple nature of *E. coli* and easy ability to manipulate its genome. While *Pseudomonas* sp. have a natural ability to degrade complex compounds, the genome can be further modified to yield more efficient strains. Marine bacteria have been efficiently transformed by inserting gene coding for

Table 11.6 Microorganisms used in bioremediation of dye compounds

Dye compound degrading microorganisms		
Microorganism	Compound	Reference
Bacteria		
Acinetobacter baumannii	Azo dyes effluents	Kumar et al. 2016a
Bacillus firmus	Vat dyes, textile effluents	Adebajo et al. 2016
Bacillus macerans	Vat dyes, textile effluents	Adebajo et al. 2016
Bacillus pumilus HKG212	Textile dye (Remazol black B), Sulphonated di-azo dye reactive red HE8B, RNB dye	Das et al. 2015
Bacillus sp. ETL-2012	Textile dye (Remazol black B), Sulphonated di-azo dye reactive red HE8B, RNB dye	Shah 2013
Bacillus subtilis strain NAP1, NAP2, NAP4	Oil-based based paints	Phulpoto et al. 2016
Bacillus cereus	Azo dyes effluents	Kumar et al. 2016a
Exiguobacterium indicum	Azo dyes effluents	Kumar et al. 2016a
Exiguobacterium aurantiacum	Azo dyes effluents	Kumar et al. 2016a
Pseudomonas aeruginosa	Textile dye (Remazol black B), Sulphonated di-azo dye reactive red HE8B, RNB dye	Das et al. 2015
Klebsiella oxytoca	Vat dyes, textile effluents	Adebajo et al. 2016
Listeria denitrificans	Textile azo dyes	Hassan et al. 2013
Micrococcus luteus	Textile azo dyes	Hassan et al. 2013
Nocardia atlantica	Textile azo dyes	Hassan et al. 2013
Staphylococcus aureus	Vat dyes, textile effluents	Adebajo et al. 2016
Fungi		
Myrothecium roridum IM 6482	Industrial dyes	Jasinska et al. 2015
Pycnoporus sanguineous	Industrial dyes	Yan et al. 2014
Phanerochaete chrysosporium	Industrial dyes	Yan et al. 2014
Penicillium ochrochloron	Industrial dyes	Shedbalkar and Jadhav 2011
Trametes trogii	Industrial dyes	Yan et al. 2014

Table 11.7 Genetically modified microorganisms used in bioremediation processes

Genetically modified bacteria used for bioremediation		
Microorganism	Pollutant	Reference
Bacteria		
Corynebacterium glutamicum	As	De et al. 2008
Deinococcus geothermalis	Mercury (II), Fe (III)-nitrilotriacetic acid, Uranium (VI), and Chromium (VI).	Brim et al. 2003
Deinococcus radiodurans	Toluene, ionic Mercury	Brim et al. 2003
Deinococcus radiodurans DR1-bf +	Uranium and heavy metals	Manobala et al. 2019
E. coli	*cis*-1,2-dichloroethylene	Kumar et al. 2013
E. coli JM109	Cd	Deng et al. 2007
Escherichia coli ArsR -ELP153AR	As	De et al. 2008
Escherichia coli	Polychlorinated benzene (PCB), benzene and toluene	Kumamaru et al. 1998
Escherichia coli FM5/pKY287	Trichloroethylene (TCE) and toluene	Winter et al. 1989
Nocardia sp.	Crude oil	Balba et al. 1998
Pseudoalteromonas haloplanktis TAC125	Aromatic compounds	Papa et al. 2009
Pseudomonas aeruginosa PA142 *P. aeruginosa* JB	2-chlorobenzoate	Kumar et al. 2013
Pseudomonas putida DLL-1	Methyl parathion	Kumar et al. 2013
Sphingomonas sp. CDS-1	Methyl parathion	Kumar et al. 2013
Sphingomonas sp. *CDS-1*	Organophosphate and carbamate-degrading	Kumar et al. 2013
Sulphate-reducing bacteria (SRB)	Chromate	Das and Dash 2014
Synechococcus sp.	Heavy metals	Das and Dash 2014
Thalassospira lucentensis	Hydrocarbons	Das and Dash 2014
Fungi		
Fusarium solani	DDT	Kumar et al. 2013
Gliocladium virens	Paraoxon and diisopropylfluorophosphate	Kumar et al. 2013
Pichia pastoris	Azo dyes, anthraquinone dyes	Kumar et al. 2013
Trichoderma atroviride	Dichlorvos pesticide	Kumar et al. 2013
Yeast		
Saccharomyces cerevisiae CP2 HP3	Cd, Zn	De et al. 2008

(continued)

Table 11.7 (continued)

Genetically modified bacteria used for bioremediation		
Microorganism	Pollutant	Reference
Algae		
Chlamydomonas reinhardtii	Cd	De et al. 2008; Kumar et al. 2013; Igiri et al. 2018
Chlorella sorokiniana ANA9	Heavy metals	Kumar et al. 2013
Laminaria japonica	Pb	Kumar et al. 2013
Nitella pseudoflabellata	Chromium (VI)	Kumar et al. 2013
Phaeodactylum tricornutum	PET	Moog et al. 2019

metallothionein. This has been successfully used in bioremediation of metal contaminated environments. Genetically modified marine Antarctic bacterium, *Pseudoalteromonas haloplanktis* TAC125 has reportedly shown promise in bioremediation of aromatic compounds (Table 11.7). A genetically modified strain of *Pseudomonas putida* ENV2030 was obtained by mutation and was reported to degrade an organophosphorus compound paraoxon by utilizing it as a sole source of carbon and nitrogen. The strain from *Acinetobacter* sp. YAA was mutated by several rounds of mutagenesis to increase the activity of aniline dioxygenase against aniline, 2,4-dimethylaniline and 2-isopropylaniline. *Burkholderia cepacia* strain V350F and V350M are mutants that produce the enzyme 2,4-dinitrotoluene dioxygenase that is reported to have significant activity against m-nitrophenol, o-nitrophenol, o-methoxyphenol and o-cresol. The bacteria *Agrobacterium radiobacter* AD1 was reported to efficiently degrade TCA at contaminated sites. Genomic shuffling has increased the degradation potential of *Sphingobium chlorophenolicum* ATCC 39723 for the pesticide pentachlorophenol. The most significant application for bioremediation involves protein engineering for large subunit of the hybrid enzyme of biphenyl dioxygenase from *Pseudomonas pseudoalcaligenes* KF707 and *Burkholderia cepacia* LB400 that results in enhanced degradation of polychlorobiphenyls (Kumamaru et al. 1998; Kumar et al. 2013). Toxic mercury-degrading gene from terrestrial bacteria has been used to transform marine bacteria for their applications in field for bioremediation of mercury contaminated environments (Das and Dash 2014). *Deinococcus radiodurans* is genetically modified bacteria and the most radiation resistant bacteria that has been designed to digest toluene and ionic mercury from nuclear wastes (Brim et al. 2003). The plasmid from *Deinococcus radiodurans* has been reportedly used to transform *Deinococcus geothermalis,* another radiation resistant bacterium that can reduce Mercury (II), Fe (III)-nitrilotriacetic acid, Uranium (VI) and Chromium (VI). A recombinant strain of *Deinococcus radiodurans* DR1-bf + has gained importance as a potential bacterium for the bioremediation of uranium and heavy metals due to its ability to form biofilms (Manobala et al. 2019). Genes for metallothioneins and phytochelatins from fungi and plants have been cloned in *Escherichia coli* which

demonstrates an enhanced binding of heavy metals. Genetically engineered bacteria such as *E. coli* JM109, *Mesorhizobium huakuii, Pseudomonas putida* and *Caulobacter crescentus* that bioaccumulate Cd^{+2} by presence of phytochelatins and metal-binding proteins have been reported. Other bacteria that have been engineered and are being studied for bioremediation have been mentioned in Table 11.7. Modifications in the active sites of enzymes of microorganisms such as *Pseudomonas putida*, *Bacillus megaterium*, *Burkholderia cepacia* strain LB400, *Comamonas testosteroni* B-365 and *Rhodococcus globerulus* P6 by genetic manipulation has resulted in increased efficiency of these enzymes in degrading the target pollutant. *Halobacteriaceae* family protein MBSP1that had biosurfactant activity when used to transform *E. coli Rosetta* ™ (DE3) demonstrated significant increase in hydrocarbon degradation (Araújo et al. 2020).

Saccharomyces cerevisiae has been genetically modified to express P450 cytochrome complexes to express genes to degrade dioxins. Another yeast, *Hansenula polymorpha* has been genetically modified for bioremediation of chromate. The fungi *Fusarium solani* has been genetically modified to improve production of dehalogenase enzyme that is crucial in degradation of DDT. Other fungi that have been genetically modified for the degradation of target pollutants are included in Table 11.7.

A brown algae *Laminaria japonica* from the marine ecosystem was chemically modified for the removal of lead from the wastewaters. The green algae, *Chlorella sorokiniana* ANA9 was used in removal of heavy metals from soil. It was reported to play a crucial role in preventing the diffusion of toxic Cd^{+2} in the soil. The toxicity of chromium (VI) in contaminated waters can be reduced by using *Nitella pseudoflabellata.* To enhance ability of *Chlamydomonas* to bind metals, a foreign metallothionein gene was expressed in *Chlamydomonas reinhardtii.* This enhanced the ability of the strain to absorb Cd by two-fold in comparison to the wild strain in damp soils and aquatic ecosystems (Kumar et al. 2013). Marine microalgae, *Phaeodactylum tricornutum*, has been modified to carry polyethylene terephthalate, PETase gene from *Ideonella sakaiensis* is an eco-friendly method for recycling strategies (Moog et al. 2019).

11.12 Bioremediation of Toxic Pollutants Using Microbial Biosurfactants and Bioemulsifiers

Bioemulsifiers and biosurfactants are surface active compounds which are amphiphilic in nature and promote emulsification of two immiscible phases. These biomolecules are produced by microorganisms such as yeast, bacteria and fungi. They find potential applications in environmental bioremediation, industrial processes and food processing industries.

Although the terms biosurfactants and bioemulsifiers have been used interchangeably with each other, they differ based on their physicochemical properties of interaction and the physiological role they play in bringing the miscibility of the two phases. Bioemulsifiers and biosurfactants both by virtue of being amphiphilic

biomolecules possess hydrophilic and hydrophobic structural moieties which allow them to dissolve in polar and non-polar solvents.

Biosurfactants can be either glycolipids which includes rhamnolipids, sophorolipids or trehalose lipids, wherein the sugars are linked to β-hydroxy fatty acids. Lipopeptides biosurfactants such as iturin and fungicin contain cycloheptapeptides with amino acids linked to fatty acids of different chain lengths. Other biosurfactants include polymeric and particulate surfactants. The surface activity of biosurfactants is due to their ability to lower the surface and interfacial tension between the two phases (liquid- air), (liquid- liquid), (liquid- solid). This is carried out by adsorption onto the different surfaces stimulating more interaction and mixing of the immiscible phases. Biosurfactants possess critical micelle concentration (CMC) that form stable emulsions. CMC is the minimum concentration of biosurfactant that is needed to reduce the surface tension to a minimum level and forms micelles. Biosurfactants have low toxicity, high biodegradability and exhibit diversity. Thus, they find potential applications as wetting, foaming and solubilizing agents in industrial processes (Uzoigwe et al. 2015).

A marine strain of *Pseudomonas aeruginosa* isolated from oil-contaminated sea water was found to produce biosurfactant that was effective in degrading hydrocarbons such as 2-methylnaphthalene, tetradecane, hexadecane, octadecane, heptadecane and nonadecane. Hydrocarbonoclastic bacteria that are ubiquitous in the marine environment have the ability to degrade aliphatic and aromatic fractions of crude oil. A mixture of biosurfactants produced by these bacteria stimulate the degradation of these hydrocarbons. Biosurfactant producing strains *Acinetobacter haemolyticus* and *Pseudomonas* ML2 showed a significant reduction in hydrocarbons up to 75%. A lipopolypeptide from *Bacillus subtilis* was found to be stable at varying temperatures, pH and salt concentrations and therefore exhibited potential in applications for bioremediation of hydrocarbons in the marine environment. Biosurfactants such as surfactin, lichenysin and rhamnolipids are found to be effective in hydrocarbon degradation. The biosurfactants produced by *Acinetobacter venetianus* ATCC 31012 exhibited removal of 89% of the crude oil by emulsification (Uzoigwe et al. 2015).

The biosurfactants from *Candida sphaerica* exhibited a bioremediation efficiency of 95% for iron, 90% for zinc and 79% for lead. The surfactant interacted with the heavy metal ion resulting in their detachment from the soil. *Candida* sp. could bioaccumulate nickel and copper by producing biosurfactants (Luna et al. 2016). Heavy metal removal was found to be productive when biosurfactants like surfactin, rhamnolipid, sophorolipids were used for bioremediation of copper and zinc. *Rhodotorula mucilaginosa* was studied for the removal of metal with an efficiency up to 95% due to its ability to form biofilms. The production of biofilm plays a crucial role in bioremediation as biofilms are a direct result of EPS formation which contains molecules that possess surfactant or emulsifying properties (Grujić et al. 2017; El-Masry et al. 2004). The biosurfactant EPS isolated from *Vibrio* sp. emulsified the hydrocarbon hexadecane and xylene by reducing the surface tension between the two immiscible phases (Kharangate-Lad and Bhosle 2014).

In microbial cells, apart from special components produced by cells, many EPS produced by yeast, bacteria and fungi are bioemulsifiers in nature. *Halobacillus trueperi* has been reported to produce an EPS that possesses bioemulsifying properties with the hydrocarbon hexadecane (Kharangate-Lad and Bhosle 2015). This EPS bioemulsifier on characterization was found to be glycopeptide in nature. Bioemulsifiers efficiently emulsify two immiscible liquids and form stable emulsions at low concentration. Significantly, it is important to understand that though all biosurfactants bioemulsify all bioemulsifiers do not reduce surface tension. Therefore, it can be suggested that though all biosurfactants are bioemulsifiers, all bioemulsifiers are not biosurfactants.

Research has shown that efficient stabilization property of bioemulsifiers is a function of their chemical composition. It has been reported that in *Acinetobacter* sp. RAG-1 (Table 11.8), the utilization of alkane is dependent upon the presence of fimbriae. Microorganisms producing biosurfactants and bioemulsifiers that have potential applications in the field of bioremediation have been listed in Table 11.8. An alanine-containing bioemulsifier has been reported in *A. radioresistens* KA53. Alasan is a complex of alanine in association with polysaccharides and proteins. It is a secreted by the cell and remains cell bound and has the ability to emulsify a wide range of hydrocarbons such as long chains alkanes and aromatics, solubilization of polyaromatic hydrocarbons (PAHs) and paraffins and crude oils (Uzoigwe et al. 2015). *Acinetobacter* sp. also exhibited a bioemulsifier that was composed of 53% protein, 42% polysaccharide and only 2% lipid. Owing to the significant ability of this bioemulsifier to emulsify hydrocarbons and solvents, it showed potential for bioremediation studies. *Stenotrophomonas maltophilia* UCP 1601 showed production of bioemulsifier that had excellent dispersion capacity and formed stable oil in water emulsions. The EPS produced by *Halomonas eurihalina*, which was rich in uronic acid and was composed of smaller fractions of carbohydrates and protein components had significant ability to bioemulsify and detoxify hydrocarbons. Similar bioemulsifiers produced by *Klebsiella* sp. were seen to exhibit bioremediation potential.

Relatively a smaller number of filamentous fungi have been identified for the production of biosurfactants. These fungi include *Aspergillus niger, Cunninghamella echinulate, Fusarium* sp., *Penicillium chrysogenum* SNP5, *Rhizopus arrhizus* and *Trichoderma* sp. (Silva et al. 2018). Filamentous fungi are less extensively used in bioremediation due to their slow growth. However, they are excellent producers of biosurfactants and bioemulsifiers and promote dispersion of hydrophobic compounds that aids in bioavailability and biodegradation of these compounds (Table 11.8).

Mannoproteins are glycoproteins that are produced by the yeast in their cell walls. Mannoproteins of *Kluyveromyces marxianus, Saccharomyces cerevisiae* exhibit significant emulsifying properties. These mannoproteins could form stable emulsions with hydrocarbons, solvents and waste oil suggesting potential application in bioremediation. Other yeasts which have been reported for the production of biosurfactants are *Rhodotorula glutinis*, *Candida* sp., *Yarrowia lipolytica*,

Table 11.8 Biosurfactant and bioemulsifier producing microorganisms used in bioremediation processes

Microorganisms producing biosurfactants and bioemulsifiers used in bioremediation			
Microorganism	Biosurfactant/ bioemulsifiers	Pollutant	Reference
Bacteria			
Acinetobacter calcoaceticus BD4 13	Emulsan (polysaccharide-protein bioemulsifier)	Oil in water emulsion stabilization	Uzoigwe et al. 2015
Acinetobacter radioresistens KA53	Alanine (alanine-based glycoprotein bioemulsifier)	Oil in water emulsion stabilization	Uzoigwe et al. 2015
Acinetobacter sp. ATCC 31012 (RAG-1)	Emulsan (Glycolipopeptide bioemulsifier)	Insoluble toxic pollutants, heavy metals, hydrocarbon emulsification	Ron and Rosenberg 2001
Arthrobacter sp.	Trehalose, corynemycolates	*n*-alkane	Uzoigwe et al. 2015
Bacillus licheniformis	Lichenysin	Oil recovery	Uzoigwe et al. 2015
Bacillus subtilis K1	Lipoprotein Subtilisin	Oil recovery	Pathak and Keharia 2014
Halomonas eurihalina	Uronic acid rich glycopeptides	Emulsification and detoxification of hydrocarbons	Martínez-Checa et al. 2002
Klebsiella sp.	Uronic acid rich glycopeptides	Emulsification and detoxification of hydrocarbons	Uzoigwe et al. 2015
Nocardia farcinica BN26	Trehalose	Toxic pollutants	Uzoigwe et al. 2015
Pseudomonas aeruginosa DS10-129	Rhamnolipid	Toxic pollutants	Uzoigwe et al. 2015
Rhodococcus erythropolis	Trehalose	Dissolution of hydrocarbons (*n*-alkanes)	Uzoigwe et al. 2015
Rhodococcus sp.	Mycolates, corynemycolates	Oil recovery	Uzoigwe et al. 2015
Rhodococcus wratislaviensis BN38	Trehalose	Toxic pollutants	Tuleva et al. 2008
Fungi			
Aspergillus niger	Glycolipid	Hydrocarbon degradation	Silva et al. 2018
Aspergillus ustus	Glycolipoprotein	Hydrocarbon degradation	Silva et al. 2018
Cunninghamella echinulate	Carbohydrate-protein-lipid complex	Hydrocarbon degradation	Silva et al. 2018
Fusarium sp.	Trehalose	Hydrocarbon degradation	Silva et al. 2018

(continued)

Table 11.8 (continued)

Microorganisms producing biosurfactants and bioemulsifiers used in bioremediation			
Microorganism	Biosurfactant/ bioemulsifiers	Pollutant	Reference
Penicillium chrysogenum SNP5	Lipopeptide	Hydrocarbon degradation	Silva et al. 2018
Ustilago maydis	Glycolipid	Hydrocarbon degradation	Bhardwaj et al. 2013
Yeast			
Candida lipolytica	Lipopolysaccharide	*n*-alkane dissolution	Uzoigwe et al. 2015
Kluyveromyces marxianus	Mannoproteins	Hydrocarbon emulsification	Uzoigwe et al. 2015
Saccharomyces cerevisiae	Mannoproteins	Hydrocarbon emulsification	Uzoigwe et al. 2015
Torulopsis sp	Sophorolipids	Hydrocarbon emulsification	Uzoigwe et al. 2015
Algae			
Cyanobacteria	Trehalose dicorynomycolate, lipid based bioemulsifier	Hydrocarbon biodegradation	Alizadeh-Sani et al. 2018
Diatoms	Lipid based bioemulsifier	Hydrocarbon biodegradation	Alizadeh-Sani et al. 2018
Phormidium sp.	Lipid-protein-carbohydrate bioemulsifiers	Hydrocarbon biodegradation	Alizadeh-Sani et al. 2018

Pseudozyma rugosa, Trichosporon asahii, *Wickerhamomyces anomalus* and *Kurtzmanomyces* sp. (Bhardwaj et al. 2013; Silva et al. 2018).

A variety cyanobacteria belonging to *Oscillatoriales* produce bioemulsifiers. *Phormidium* sp. ATCC 39161 have been successfully used to yield hydrocarbon and oil emulsions in water. The bioemulsifier showed fractions of lipid, proteins and carbohydrates and showed significant stability of oil in water emulsions (Alizadeh-Sani et al. 2018). Marine algae and diatoms are increasingly being explored for their potential to produce bioemulsifiers. These bioemulsifiers are EPS based lipid bioemulsifiers that have potential application in bioremediation and industries.

11.13 Conclusion

Microbial bioremediation, although a cost effective and eco-friendly technique for biodegradation of recalcitrant toxic compounds, faces issues due to the biotic and abiotic factors affecting biodegradation. In the natural environment, constant fluctuations in oxygen, nutrient, pH and temperature occur that hinders and reduces

the efficiency of microbial bioremediation. Despite these limitations the advantages outweigh the disadvantages and bioremediation using microbes and their components have been successfully implemented in cleanup of many toxic contaminants. Naturally occurring microbes and genetically designed microbes are important tools for successful cleanup of contaminated sites using green technology. However, considering the lacunae in the efficiency of microbial cell mediated bioremediation, integrated approaches involving microorganisms, nanoparticles and physical methods are now being explored.

Acknowledgement The authors wish to thank Pankaj Lad for graphic designing of the diagrams and the valuable inputs in the chapter.

References

Abatenh E, Gizaw B, Tsegaye Z, Wassie M (2017) The role of microorganisms in bioremediation- a review. Open J Environ Biol 2(1):38–46. https://doi.org/10.17352/ojeb.000007

Abdelatey LM, Khalil WKB, Ali TH, Mahrous KF (2011) Heavy metal resistance and gene expression analysis of metal resistance genes in gram-positive and gram-negative bacteria present in Egyptian soils. J Appl Sci Environ Sanit 6:201–211

Abd-Elnaby H, Abou-Elela GM, El-Sersy NA (2011) Cadmium resisting bacteria in Alexandria Eastern Harbor (Egypt) and optimization of cadmium bioaccumulation by *Vibrio harveyi*. Afr J Biotechnol 10(17):3412–3423. https://doi.org/10.5897/AJB10.1933

Abou-Shanab RI, Delorme TA, Angle JS et al (2003) Phenotypic characterization of microbes in the rhizosphere of *Alyssum murale*. Int J Phytoremediation 5:367–380. https://doi.org/10.1080/15226510309359043

Abraham J, Silambarasan S, Logeswari P (2014) Simultaneous degradation of organophosphorus and organochlorine pesticides by bacterial consortium. J Taiwan Inst Chem Eng 45 (5):2590–2596. https://doi.org/10.1016/j.jtice.2014.06.014

Achal V, Kumari D, Pan X (2011) Bioremediation of chromium contaminated soil by a brown-rot fungus, G*loeophyllum sepiarium*. Res J Microbiol 6(2):166–171. https://doi.org/10.3923/jm.2011.166-171

Achal V, Pan X, Fu Q, Zhang D (2012) Biomineralization based remediation of as (III) contaminated soil by *Sporosarcina ginsengisoli*. J Hazard Mater 201:178–184. https://doi.org/10.1016/j.jhazmat.2011.11.067

Acosta-Rodríguez I, Cárdenas-González JF, Juárez VMM, Pérez AR, Zarate MGM, Castillo NCP (2017) Biosorption of heavy metals by *Candida albicans*. In: Shiomi N (ed) Advances in bioremediation and phytoremediation. Intech Open, London. https://doi.org/10.5772/intechopen.72454

Acosta-Rodríguez I, Cárdenas-González JF, Pérez AR, Oviedo JT, Juárez VMM (2018) Bioremoval of different heavy metals by the resistant fungal strain *Asp.ergillus niger*. Bioinorg Chem Appl 2018:3457196. https://doi.org/10.1155/2018/3457196

Adebajo SO, Balogun SA, Akintokun AK (2016) Decolourization of vat dyes by bacterial isolates recovered from local textile Mills in southwest, Nigeria. Microbiol Res J Int 18(1):1–8. https://doi.org/10.9734/MRJI/2017/29656

Aditi G, Kumar PG, Suneetha V (2015) The role of algae in degradation of petroleum wastes - a study. J Chem Pharm 7(1):499–503

Agrawal N, Verma P, Shahi SK (2018) Degradation of polycyclic aromatic hydrocarbons (phenanthrene and pyrene) by the ligninolytic fungi *Ganoderma lucidum* isolated from the hardwood stump. Bioresour Bioprocess 5:11. https://doi.org/10.1186/s40643-018-0197-5

Aguilar-Barajas E, Paluscio E, Cervantes C, Rensing C (2008) Expression of chromate resistance genes from *Shewanella* sp. strain ANA-3 in Escherichia coli. FEMS Microbiol Lett 285:97–100. https://doi.org/10.1111/j.1574-6968.2008.01220.x

Alegbeleye OO, Opeolu BO, Jackson V (2017) Bioremediation of polycyclic aromatic hydrocarbon (PAH) compounds: (acenaphthene and fluorene) in water using indigenous bacterial species isolated from the Diep and Plankenburg rivers, Western cape, South Africa. Braz J Microbiol 48 (2):314–325. https://doi.org/10.1016/j.bjm.2016.07.027

Al-Hawash AB, Alkooranee JT, Abbood HA, Zhang J, Sun J, Zhang X, Ma F (2018a) Isolation and characterization of two crude oil-degrading fungi strains from Rumaila oil field, Iraq. Biotechnol Rep 17:104–109. https://doi.org/10.1016/j.btre.2017.12.006

Al-Hawash AB, Zhang X, Ma F (2018b) Removal and biodegradation of different petroleum hydrocarbons using the filamentous fungus *Aspergillus* sp. RFC-1. Microbiol Open 8(1): e00619. https://doi.org/10.1002/mbo3.619

Al-Homaidan AA, Alabdullatif JA, Al-Hazzani AA, Al-Ghanayem AA, Alabbad AF (2015) Adsorptive removal of cadmium ions by *Spirulina platensis* dry biomass. Saudi J Biol Sci 22 (6):795–800. https://doi.org/10.1016/j.sjbs.2015.06.010

Alizadeh-Sani M, Hamishehkar H, Khezerlou A, Azizi-Lalabadi M, Azadi Y, Nattagh-Eshtivani E, Fasihi M, Ghavami A, Aynehchi A, Ehsani A (2018) Bioemulsifiers derived from microorganisms: applications in the drug and food industry. Adv Pharm Bull 8(2):191–199. https://doi.org/10.15171/apb.2018.023

Al-Nasrawi H (2012) Biodegradation of crude oil by Fungi isolated from Gulf of Mexico. J Bioremed Biodegr 3(4):1–6. https://doi.org/10.4172/2155-6199.1000147

Amina B, Chibani A (2016) Biodegradation of diesel and isomerate by *Pseudomonas aeruginosa* and *Brevibacillus laterosporus* isolated from hydrocarbons contaminated soil. Adv Environ Biol 10(7):208–215

Angelim A, Costa S, Farias B, Aquino L, Melo V (2013) An innovative bioremediation strategy using a bacterial consortium entrapped in chitosan beads. J Environ Manag 127:10–17. https://doi.org/10.1016/j.jenvman.2013.04.014

Araújo SCS, Silva-Portela RCB, de Lima DC et al (2020) MBSP1: a biosurfactant protein derived from a metagenomic library with activity in oil degradation. Sci Rep 10:1340. https://doi.org/10.1038/s41598-020-58330-x

Ardal E (2014) Phycoremediation of pesticides using microalgae. Dissertation, Swedish University of Agricultural Sciences, Sweden

Bahafid W, Joutey NT, Asri M, Sayel H, Tirry N, El Ghachtouli N (2017) Yeast biomass: an alternative for bioremediation of heavy metals. In: Morata A, Loira I (eds) Yeast industrial applications. Intech Open, London. https://doi.org/10.5772/intechopen.70559

Balamurugan D, Udayasooriyan C, Kamaladevi B (2014) Chromium (VI) reduction by *Pseudomonas putida* and *Bacillus subtilis* isolated from contaminated soils. Int J Environ Sci 5 (3):522–529

Balba MT, Al-Awadhi R, Al-Daher R (1998) Bioremediation of oil contaminated soil: microbiological methods for feasibility and field evaluation. J Microbiol Methods 32 (2):155–164. https://doi.org/10.1016/S0167-7012(98)00020-7

Bezalel L, Hadar Y, Fu PP, Freeman JP, Cerniglia CE (1996) Initial oxidation products in the metabolism of pyrene, anthracene, fluorene, and dibenzothiophene by the white rot fungus *Pleurotus ostreatus*. Appl Environ Microbiol 62(7):2554–2559

Bhalerao T, Puranik P (2007) Biodegradation of organochlorine pesticide, endosulfan, by a fungal soil isolate, *Aspergillus niger*. Int Biodeterior Biodegrad 59:315–321. https://doi.org/10.1016/j.ibiod.2006.09.002

Bhardwaj G, Cameotra SS, Chopra HK (2013) Biosurfactants from Fungi: a review. J Pet Environ Biotechnol 4:160. https://doi.org/10.4172/2157-7463.1000160

Bhatia S, Kalia M, Singh B (2018) Bioremediation of Polyaromatic hydrocarbons: current status and recent advances. In: Kumar V, Kumar M, Prasad R (eds) Phytobiont and ecosystem restitution. Springer, Singapore, pp 275–293. https://doi.org/10.1007/978-981-13-1187-1_15

Bhatt P, Zhang W, Lin Z, Pang S, Huang Y, Chen S (2020) Biodegradation of Allethrin by a novel fungus *Fusarium proliferatum* strain CF2, isolated from contaminated soils. Microorganisms 8 (4):593. https://doi.org/10.3390/microorganisms8040593

Bhuyar P, Sudhakar M, Natanamurugaraj G (2018) Green revolution to protect environment – an identification of potential micro algae for the biodegradation of plastic waste in Malaysia. In: World congress on biopolymers and Bioplastics & Recycling, expert Opin environ biol, vol 7. SciTechnol, London. https://doi.org/10.4172/2325-9655-C5-033

Bisht S, Pandey P, Bhargava B, Sharma S, Kumar V, Sharma KD (2015) Bioremediation of polyaromatic hydrocarbons (PAHs) using rhizosphere technology. Braz J Microbiol 46 (1):7–21. https://doi.org/10.1590/S1517-838246120131354

Bogan BW, Lamar RT, Hammel KE (1996) Fluorene oxidation in vivo by *Phanerochaete chrysos*p. *orium* and in vitro during manganese peroxidase-dependent lipid peroxidation. Appl Environ Microbiol 62:1788–1792

Bogan BW, Lamar RT, Burgos WD, Tien M (1999) Extent of humification of anthracene, fluoranthene, and benzo[*a*]pyrene by *Pleurotus ostreatus* during growth in PAH-contaminated soils. Lett Appl Microbiol 28(4):250–254. https://doi.org/10.1046/j.1365-2672.1999.00537.x

Brim H, Venkateswaran A, Kostandarithes HM, Fredrickson JK, Daly MJ (2003) Engineering *Deinococcus geothermalis* for bioremediation of high-temperature radioactive waste environments. Appl Environ Microbiol 69(8):4575–4582. https://doi.org/10.1128/AEM.69.8.4575-4582.2003

Brunner I, Fischer M, Rüthi J, Stierli B, Frey B (2018) Ability of fungi isolated from plastic debris floating in the shoreline of a lake to degrade plastics. PLoS One 13(8):e0202047. https://doi.org/10.1371/journal.pone.0202047

Burdin KS (1985) The basis of biological monitoring. MSU, Moscow

Burghal A, Ali N, Al-Tamimi W (2016) Mycodegradation of crude oil by fungal species isolated from petroleum contaminated soil. Int J Innov Res Sci Eng Technol 5:1517–1524. https://doi.org/10.15680/IJIRSET.2016.0502068

Cajthaml T, Erbanová P, Kollmann A, Novotný C, Šašek V, Mougin C (2008) Degradation of PAHs by Ligninolytic enzymes of *Irpex lacteus*. Folia Microbiol 53(4):289–294. https://doi.org/10.1007/s12223-008-0045-7

Camacho-Morales RL, Sánchez JE (2016) Chapter 12 - biotechnological use of Fungi for the degradation of recalcitrant agro-pesticides. Mushroom Biotechnol 2016:203–214. https://doi.org/10.1016/B978-0-12-802794-3.00012-6

Capotorti G, Digianvincenzo P, Cesti P, Bernardi A, Guglielmetti G (2004) Pyrene and benzo[*a*] pyrene metabolism by an *Aspergillus terreus* strain isolated from a polycylic aromatic hydrocarbons polluted soil. Biodegradation 15(2):79–85. https://doi.org/10.1023/B:BIOD.0000015612

Capotorti G, Cesti P, Lombardi A, Guglielmetti G (2005) Formation of sulfate conjugates metabolites in the degradation of phenanthrene, anthracene, pyrene and benzo[*a*]pyrene by the ascomycete *Aspergillus terreus*. Polycycl Aromat Compd 25(3):197–213. https://doi.org/10.1080/10406630590950273

Cerniglia CE (1982) Initial reactions in the oxidation of anthracene by *Cunninghamella elegans*. J Gen Microbiol 128:2055–2061

Cerniglia CE, Sutherland JB (2010) Degradation of polycyclic aromatic hydrocarbons by Fungi. In: Timmis KN (ed) Handbook of hydrocarbon and lipid microbiology. Springer, Berlin, Heidelberg, pp 2079–2110. https://doi.org/10.1007/978-3-540-77587-4_151

Chatterjee S, Chatterjee CN, Dutta S (2012) Bioreduction of chromium (VI) to chromium (III) by a novel yeast strain *Rhodotorula mucilaginosa* (MTCC9315) African. J Biotechnol 11 (83):14920–14929

Chibuike G, Obiora S (2014) Heavy metal polluted soils: effect on plants and bioremediation methods. Appl Environ Soil Sci 2014:752708. https://doi.org/10.1155/2014/752708

Chung WK, King GM (2001) Isolation, characterization, and polyaromatic hydrocarbon degradation potential of aerobic bacteria from marine macrofaunal burrow sediments and description *of*

Lutibacterium anuloederans gen. Nov., sp. nov., and *Cycloclasticus spirillensus* sp. nov. Appl Environ Microbiol 67(12):5585–5592. https://doi.org/10.1128/AEM.67.12.5585-5592.2001

Coelho LM, Rezende HC, Coelho LM, de Sousa PA, Melo DF, Coelho NM (2015) Bioremediation of polluted waters using microorganisms. In: Shiomi N (ed) Advances in bioremediation of wastewater and polluted soil. InTech Open, London. https://doi.org/10.5772/60770

Das N, Chandran P (2011) Microbial degradation of petroleum hydrocarbon contaminants: an overview. Biotechnol Res Int 2011:941810. https://doi.org/10.4061/2011/941810

Das S, Dash HR (2014) Microbial bioremediation: a potential tool for restoration of contaminated areas. In: Das S (ed) Microbial degradation and bioremediation. Elsevier, London, pp 1–21. https://doi.org/10.1016/B978-0-12-800021-2.00001-7

Das A, Mishra S, Verma VK (2015) Enhanced biodecolorization of textile dye remazol navy blue using an isolated bacterial strain *Bacillus pumilus* HKG212 under improved culture conditions. J Biochem Technol 6(3):962–969

Davis TA, Volesky B, Mucci A (2003) A review of the biochemistry of heavy metal biosorption by brown algae. Water Res 37(18):4311–4330. https://doi.org/10.1016/S0043-1354(03)00293-8

De J, Ramaiah N, Vardanyan I (2008) Detoxification of toxic heavy metals by marine bacteria highly resistant to mercury. Mar Biotechnol 10(4):471–477. https://doi.org/10.1007/s10126-008-9083-z

Deng X, Yi XE, Liu G (2007) Cadmium removal from aqueous solution by gene-modified *Escherichia coli* JM109. J Hazard Mater 139:340–344. https://doi.org/10.1016/j.jhazmat.2006.06.043

Dong G, Wang Y, Gong L et al (2013) Formation of soluble Cr (III) end-products and nanoparticles during Cr (VI) reduction by *Bacillus cereus* strain XMCr-6. Biochem Eng J 70:166–172. https://doi.org/10.1016/j.bej.2012.11.002

Doolotkeldieva T, Konurbaeva M, Bobusheva S (2018) Microbial communities in pesticide-contaminated soils in Kyrgyzstan and bioremediation possibilities. Environ Sci Pollut Res 25:31848–31862. https://doi.org/10.1007/s11356-017-0048-5

Dussud C, Hudec C, George M et al (2018) Colonization of non-biodegradable and biodegradable plastics by marine microorganisms. Front Microbiol 9:1571. https://doi.org/10.3389/fmicb.2018.01571

Ellegaard-Jensen L, Horemans B, Raes B, Aamand J, Hansen L (2017) Groundwater contamination with 2,6-dichlorobenzamide (BAM) and perspectives for its microbial removal. Appl Microbiol Biotechnol 101:5235–5245. https://doi.org/10.1007/s00253-017-8362-x

El-Masry MH, El-Bestawy E, El-Adl NI (2004) Bioremediation of vegetable oil and grease from polluted wastewater using a sand biofilm system. World J Microbiol Biotechnol 20(6):551–557. https://doi.org/10.1023/B:WIBI.0000043162.17813.17

El-Sheekh MM, Ghareib MM, Abou-EL-Souod GW (2012) Biodegradation of phenolic and polycyclic aromatic compounds by some algae and cyanobacteria. J Bioremed Biodegr 3 (1):1000133

Farhan SN, Khadom A (2015) Biosorption of heavy metals from aqueous solutions by saccharomyces cerevisiae. Int J Ind Chem 6:119–130. https://doi.org/10.1007/s40090-015-0038-8

Feng Y, Zhang W, Pang S et al (2020) Kinetics and new mechanism of azoxystrobin biodegradation by an *Ochrobactrum anthropi* strain SH14. Microorganisms 8(5):E625. https://doi.org/10.3390/microorganisms8050625

Frazar C (2000) The bioremediation and phytoremediation of pesticide-contaminated sites. U.S. Environmental Protection Agency, Washington, DC

Fulke AB, Kotian A, Giripunje MD (2020) Marine microbial response to heavy metals: mechanism, implications and future prospect. Bull Environ Contam Toxicol 105:182–197. https://doi.org/10.1007/s00128-020-02923-9

Ghosal D, Ghosh S, Dutta TK, Ahn Y (2016) Current state of knowledge in microbial degradation of polycyclic aromatic hydrocarbons (PAHs): a review. Front Microbiol 7:1369. https://doi.org/10.3389/fmicb.2016.01369

Ghosh SK, Pal S, Ray S (2013) Study of microbes having potentiality for biodegradation of plastics. Environ Sci Pollut Res 20:4339–4355. https://doi.org/10.1007/s11356-013-1706-x

Godsgift OE, Fagade OE (2016) Microalgal-bacterial consortium in Polyaromatic hydrocarbon degradation of petroleum – based effluent. J Bioremed Biodegr 7:359. https://doi.org/10.4172/2155-6199.1000359

Govarthanan M, Fuzisawa S, Hosogai T, Chang Y (2017) Biodegradation of aliphatic and aromatic hydrocarbons using the filamentous fungus *Penicillium* sp. CHY-2 and characterization of its manganese peroxidase activity. RSC Adv 7(34):20716–20723. https://doi.org/10.1039/C6RA28687A

Grujić S, Vasić S, Radojević I, Čomić L, Ostojić A (2017) Comparison of the *Rhodotorula mucilaginosa* biofilm and planktonic culture on heavy metal susceptibility and removal potential. Water Air Soil Pollut 228(2):73. https://doi.org/10.1007/s11270-017-3259-y

Gupta P, Diwan B (2016) Bacterial exopolysaccharide mediated heavy metal removal: a review on biosynthesis, mechanism and remediation strategies. Biotechnol Rep 13:58–71. https://doi.org/10.1016/j.btre.2016.12.006

Gupta SK, Shriwastav A, Kumari S et al (2015) Phycoremediation of emerging contaminants. In: Singh B, Bauddh K, Bux F (eds) Algae and environmental sustainability. Springer, New Delhi, pp 129–146. https://doi.org/10.1007/978-81-322-2641-3_11

Hassan MM, Alam MZ, Anwar MN (2013) Biodegradation of textile azo dyes by Bacteria isolated from dyeing industry effluent. Int Res J Biol Sci 2(8):27–31

Hedlund BP, Geiselbrecht AD, Bair TJ, Staley JT (1999) Polycyclic aromatic hydrocarbon degradation by a new marine bacterium, *Neptunomonas naphthovorans* gen. Nov., sp. nov. Appl Environ Microbiol 65(1):251–259

Hong Y, Dong-Xing Y, Qing-Mei L, Ting-Lin Y (2008) Accumulation and biodegradation of phenanthrene and fluoranthene by the algae enriched from a mangrove aquatic ecosystem. Mar Pollut Bull 56:1400–1405. https://doi.org/10.1016/j.marpolbul.2008.05.003

Ibrahim M (2013) Biodegradation of polymers by Fungi isolated from plastic garbage and assay for optimum condition for growth. J Raf Env 1:33–43

Igiri BE, Okoduwa S, Idoko GO, Akabuogu EP, Adeyi AO, Ejiogu IK (2018) Toxicity and bioremediation of heavy metals contaminated ecosystem from tannery wastewater: a review. J Toxicol 2018:2568038. https://doi.org/10.1155/2018/2568038

Iyer A, Mody K, Jha B (2005) Biosorption of heavy metals by a marine bacterium. Mar Pollut Bull 50(3):340–343. https://doi.org/10.1016/j.marpolbul.2004.11.012

Jasinska A, Paraszkiewicz K, Sip A, Długonski J (2015) Malachite green decolorization by the filamentous fungus *Myrothecium roridum* – mechanistic study and process optimization. Bioresour Technol 194:43–48. https://doi.org/10.1016/j.biortech.2015.07.008

Javaid MK, Ashiq M, Tahir M (2016) Potential of biological agents in decontamination of agricultural soil. Scientifica 2016:1598325. https://doi.org/10.1155/2016/1598325

Kang CH, Kwon YJ, So JS (2016) Bioremediation of heavy metals by using bacterial mixtures. Ecol Eng 89:64–69. https://doi.org/10.1016/j.ecoleng.2016.01.023

Kanmani P, Aravind J, Preston D (2012) Remediation of chromium contaminants using bacteria. Int J Environ Sci Technol 9:183–193. https://doi.org/10.1007/s13762-011-0013-7

Karim ME, Dhar K, Hossaina MT (2018) Decolorization of textile reactive dyes by bacterial monoculture and consortium screened from textile dyeing effluent. J Genet Eng Biotechnol 16(2):375–380. https://doi.org/10.1016/j.jgeb.2018.02.005

Kathiresan K (2003) Polythene and plastic degrading microbes from the mangrove soil. Rev Biol Trop 51:629–634

Kharangate-Lad A, Bhosle S (2014) Studies on bioemulsifier production by a bacterial isolate. J Sci Ind Res 73(10):674–679

Kharangate-Lad A, Bhosle S (2015) Studies on the effects of zerovalent iron nanoparticles on bacteria from the mangrove ecosystem. Environ Sci Pollut Res 23:927–931. https://doi.org/10.1007/s11356-015-5588-y

Kitamoto HK, Shinozaki Y, Cao X et al (2011) Phyllosphere yeasts rapidly break down biodegradable plastics. AMB Express 1:44. https://doi.org/10.1186/2191-0855-1-44

Ksheminska H, Fedorovych D, Honchar T, Ivash M, Gonchar M (2008) Yeast tolerance to chromium depends on extracellular chromate reduction and Cr (III) chelation. Food Technol Biotechnol 46(4):419–426

Kumamaru T, Suenaga H, Mitsuoka M, Watanabe T, Furukawa K (1998) Enhanced degradation of polychlorinated biphenyls by directed evolution of biphenyl dioxygenase. Nat Biotechnol 16:663–666. https://doi.org/10.1038/nbt0798-663

Kumar Ramasamy R, Congeevaram S, Thamaraiselvi K (2011) Evaluation of isolated fungal strain from e-waste recycling facility for effective sorption of toxic heavy metal Pb (II) ions and fungal protein molecular characterization—a mycoremediation approach. Asian J Exp Biol Sci 2:342–347

Kumar S, Dagar VK, Khalsa YP, Kuhad RC (2013) Genetically modified organisms (GMO's) for bioremediation. In: Kuhad RC, Singh A (eds) Biotechnology for environmental management and resource recovery. Springer, New Delhi, pp 191–218. https://doi.org/10.1007/978-81-322-0876-1_11

Kumar S, Chaurasia P, Kumar A (2016a) Isolation and characterization of microbial strains from textile industry effluents of Bhilwara, India: analysis with bioremediation. J Chem Pharm Res 8:143–150

Kumar M, Kumar V, Varma A, Prasad R, Sharma A, Pal A, Arshi A, Singh J (2016b) An efficient approach towards the bioremediation of copper, cobalt and nickel contaminated field samples. J Soils Sediments 17(4):2118. https://doi.org/10.1007/s11368-016-1398-1

Kumar RV, Kanna GR, Elumalai S (2017) Biodegradation of polyethylene by green photosynthetic microalgae. J Bioremed Biodegr 8:381. https://doi.org/10.4172/2155-6199.1000381

Kumar V, Shahi SK, Singh S (2018a) Bioremediation: an eco-sustainable approach for restoration of contaminated sites. In: Singh J, Sharma D, Kumar G, Sharma N (eds) Microbial bioprospecting for sustainable development. Springer, Singapore, pp 115–136. https://doi.org/10.1007/978-981-13-0053-0_6

Kumar V, Kumar M, Sharma S, Prasad R (2018b) Microbial action on hydrocarbons. Springer, Singapore

Lee YC, Chang SP (2011) The biosorption of heavy metals from aqueous solution by Sp*irogyra* and *Cladophora* filamentous macroalgae. Bioresour Technol 102(9):5297–5304. https://doi.org/10.1016/biortech.2010.12.103

Luna JM, Santos Filho AS, Rufino RD, Sarubbo LA (2016) Production of biosurfactant from *Candida bombicola* URM 3718 for environmental applications. Chem Eng Trans 49:583–588. https://doi.org/10.3303/CET1649098

Mahjoubi M, Cappello S, Souissi Y, Jaouani A, Cherif A (2017) Microbial bioremediation of petroleum hydrocarbon–contaminated marine environments. Intech Open 2(19):1–16. https://doi.org/10.5772/intechopen.72207

Mahmoud GAE, Bagy MMK (2018) Microbial degradation of petroleum hydrocarbons. In: Kumar V, Kumar M, Prasad R (eds) Microbial action on hydrocarbons. Springer Nature, Singapore, pp 299–320. https://doi.org/10.1007/978-981-13-1840-5

Mane P, Bhosle A (2012) Bioremoval of some metals by living algae *Spirogyra* sp. and *Spirullina* sp. from aqueous solution. Int J Environ Res 6(2):571–576

Manobala T, Shukla SK, Subba Rao T et al (2019) A new uranium bioremediation approach using radio-tolerant *Deinococcus radiodurans* biofilm. J Biosci 44:122. https://doi.org/10.1007/s12038-019-9942-y

Mao J, Guan W (2016) Fungal degradation of polycyclic aromatic hydrocarbons (PAHs) by *Scopulariopsis brevicaulis* and its application in bioremediation of PAH-contaminated soil. Acta Agriculturae Scandinavica section B-soil. Plant Sci 66(5):1–7. https://doi.org/10.1080/09064710.2015.1137629

Martínez-Checa F, Toledo FL, Vilchez R, Quesada E, Calvo C (2002) Yield production, chemical composition, and functional properties of emulsifier H28 synthesized by *Halomonas eurihalina*

strain H-28 in media containing various hydrocarbons. Appl Microbiol Biotechnol 58 (3):358–363. https://doi.org/10.1007/s00253-001-0903-6

Mire CE, Tourjee JA, O'Brien WF, Ramanujachary KV, Hecht GB (2004) Lead precipitation by *Vibrio harveyi*: evidence for novel quorum-sensing interactions. Appl Environ Microbiol 70 (2):855–864. https://doi.org/10.1128/AEM.70.2.855-864.2004

Moog D, Schmitt J, Senger J, Zarzycki J et al (2019) Using a marine microalga as a chassis for polyethylene terephthalate (PET) degradation. Microb Cell Factories 18(1):171. https://doi.org/10.1186/s12934-019-1269-8

Moscoso F, Teijiz I, Deive FJ, Sanromán MA (2012) Efficient PAHs biodegradation by a bacterial consortium at flask and bioreactor scale. Bioresour Technol 119:270–276. https://doi.org/10.1016/j.biortech,2012.05.095

Mukred A, Hamid A, Hamzah A, Yusoff W (2008) Development of three Bacteria consortium for the bioremediation of crude Petroleum-oil in Contaminated Water. J Biol Sci 8:73–79. https://doi.org/10.3844/ojbsci.2008.73.79

Munir E, Harefa RSM, Priyani N, Suryanto D (2018) Plastic degrading fungi *Trichoderma viride* and *Aspergillus nomius* isolated from local landfill soil in Medan. IOP Conf Ser Earth Environ Sci 126(1):012145

Muriel-Millán LF, Rodríguez-Mejía JL, Godoy-Lozano EE et al (2019) Functional and genomic characterization of a *Pseudomonas aeruginosa* strain isolated from the southwestern Gulf of Mexico reveals an enhanced adaptation for long-chain alkane degradation. Front Mar Sci 6:572. https://doi.org/10.3389/fmars.2019.00572

Mustapha MU, Halimoon N (2015) Microorganisms and biosorption of heavy metals in the environment: a review paper. J Microb Biochem Technol 7:253–256. https://doi.org/10.4172/1948-5948.1000219

Nshimiyimana JB, Khadka S, Zou P et al (2020) Study on biodegradation kinetics of di-2-ethylhexyl phthalate by newly isolated halotolerant *Ochrobactrum anthropi* strain L1-W. BMC Res Notes 13(1):252. https://doi.org/10.1186/s13104-020-05096-0

Ojuederie OB, Babalola OO (2017) Microbial and plant-assisted bioremediation of heavy metal polluted environments: a review. Int J Environ Res Public Health 14(12):1504. https://doi.org/10.3390/ijerph14121504

Oliveira BR, Penetra A, Cardoso VV et al (2015) Biodegradation of pesticides using fungi species found in the aquatic environment. Environ Sci Pollut Res Int 22(15):11781–11791. https://doi.org/10.1007/s11356-015-4472-0

Paingankar M, Jain M, Deobagkar D (2005) Biodegradation of allethrin, a pyrethroid insecticide, by an acidomonas sp. Biotechnol Lett 27(23–24):1909–1913. https://doi.org/10.1007/s10529-005-3902-3

Panwichian S, Kantachote D, Wittayaweerasak B, Mallavarapu M (2011) Removal of heavy metals by exopolymeric substances produced by resistant purple nonsulfur bacteria isolated from contaminated shrimp ponds. Electron J Biotechnol 14(4):2. https://doi.org/10.2225/vol14-issue4-fulltext-2

Papa R, Parrilli E, Sannia G (2009) Engineered marine Antarctic bacterium *Pseudoalteromonas haloplanktis* TAC125: a promising micro-organism for the bioremediation of aromatic compounds. J Appl Microbiol 106(1):49–56. https://doi.org/10.1111/j.1365-2672.2008.03971.x

Patel Y, Gupte A (2016) Evaluation of bioremediation potential of isolated bacterial culture YPAG-9 (*Pseudomonas aeruginosa*) for Decolorization of sulfonated di-azodye reactive red HE8B under optimized culture conditions. Int J Curr Microbiol App Sci 5:258–272. https://doi.org/10.20546/ijcmas.2016.508.027

Pathak KV, Keharia H (2014) Application of extracellular lipopeptide biosurfactant produced by endophytic Bacillus subtilis K1 isolated from aerial roots of banyan (*Ficus benghalensis*) in microbially enhanced oil recovery (MEOR). 3 Biotech 4(1):41–48. https://doi.org/10.1007/s13205-013-0119-3

Phulpoto H, Qazi MA, Mangi S, Ahmed S, Kanhar NA (2016) Biodegradation of oil-based paint by *Bacillus* species monocultures isolated from the paint warehouses. Int J Environ Sci Technol 13:125–134. https://doi.org/10.1007/s13762-015-0851-9

Pino NJ, Domínguez MC, Peñuela GA (2011) Isolation of a selected microbial consortium capable of degrading methyl parathion and *p*-nitrophenol from a contaminated soil site. J Environ Sci Heal Part B 46(2):173–180. https://doi.org/10.1080/03601234.2011.539142

Prakash A, Bisht S, Singh J, Teotia P, Kela R, Kumar V (2014) Biodegradation potential of petroleum hydrocarbons (PHCs) by bacteria and mixed bacterial consortium isolated from contaminated sites. Turkish J Eng Environ Sci 38(1):31–40

Priyadarshani I, Sahu D, Rath B (2011) Microalgal bioremediation: current practices and perspectives. J Biochem Technol 3(3):299–304

Pujar NK, Laad S, Premakshi HG, Pattar SV, Mirjankar M, Kamanavalli CM (2019) Biodegradation of phenmedipham by novel *Ochrobactrum anthropi* NC-1. 3 Biotech 9(2):52. https://doi.org/10.1007/s13205-019-1589-8

Rahman KSM, Rahman TJ, Kourkoutas Y, Petsas I, Marchant R, Banat IM (2003) Enhanced bioremediation of n-alkane in petroleum sludge using bacterial consortium amended with rhamnolipid and micronutrients. Bioresour Technol 90:159–168. https://doi.org/10.1016/S0960-8524(03)00114-7

Rahman A, Nahar N, Nawani NN et al (2015) Bioremediation of hexavalent chromium (VI) by a soil-borne bacterium, *Enterobacter cloacae* B2-DHA. J Environ Sci Health A 50 (11):1136–1147. https://doi.org/10.1080/10934529.2015.1047670

Rani B, Kumar V, Singh J et al (2014) Bioremediation of dyes by fungi isolated from contaminated dye effluent sites for bio-usability. Braz J Microbiol 45(3):1055–1063. https://doi.org/10.1590/s1517-83822014000300039

Rehan M, Alsohim AS (2019) Bioremediation of heavy metals. In: Saldarriaga-Norena H, Murillo-Tovar MA, Farooq R, Dongre R, Riaz S (eds) Environmental chemistry and recent pollution control approaches. Intech Open, London. https://doi.org/10.5772/intechopen.88339

Rodrigues da Luz JMR, Soares da Silva MC, Ferreira dos Santos L, Kasuya MCM (2019) Plastics polymers degradation by Fungi. In: Microorganisms. Intech Open, London. https://doi.org/10.5772/intechopen.88608

Ron EZ, Rosenberg E (2001) Natural roles of biosurfactants. Environ Microbiol 3:229–236

Rudd L, Perry J, Houk V, Williams R, Claxton L (1996) Changes in mutagenicity during crude oil degradation by fungi. Biodegradation 7:335–343. https://doi.org/10.1007/BF00115747

Russell JR, Huang H, Anand P, Kucera K et al (2011) Biodegradation of polyester polyurethane by endophytic Fungi. Appl Environ Microbiol 77(17):6076–6084. https://doi.org/10.1128/AEM.00521-11

Sadeghi HZM, Ebrahimipour G, Shahriari MM, Fakhari J, Abdoli T (2016) Bioremediation of crude oil using bacterium from the coastal sediments of Kish Island, Iran. Iran J Public Health 45 (5):670–679

Safonova E, Kvitko K, Kuschk P, Möder M, Reisser W (2005) Biodegradation of Phenanthrene by the green alga *Scenedesmus obliquus* ES-55. Eng Life Sci 5(3):234–239. https://doi.org/10.1002/elsc.200520077

Sangale MK, Shahnawaz M, Ade AB (2019) Potential of fungi isolated from the dumping sites mangrove rhizosphere soil to degrade polythene. Sci Rep 9:5390. https://doi.org/10.1038/s41598-019-41448-y

Sasikala C, Jiwal S, Rout P, Ramya M (2012) Biodegradation of chlorpyrifos by bacterial consortium isolated from agriculture soil. World J Microbiol Biotechnol 28(3):1301–1308. https://doi.org/10.1007/s11274-011-0879-z

Sekiguchi T, Sato T, Enoki M et al (2011) Isolation and characterization of biodegradable plastic degrading bacteria from deep-sea environments. JAMSTEC Rep Res Dev 11:33–41

Selvaratnam S, Schoedel BA, Mcfarland BL, Kulpa CF (1997) Application of the polymerase chain reaction (PCR) and reverse transcriptase PCR for determining the fate of phenol-degrading

Pseudomonas putida ATCC11172 in a bio augmented sequencing batch reactor. Appl Microbiol Biotechnol 47:236–240

Senan RC, Abraham TE (2004) Bioremediation of textile azo dyes by aerobic bacterial consortium aerobic degradation of selected azo dyes by bacterial consortium. Biodegradation 15:275–280. https://doi.org/10.1023/B:BIOD.0000043000.18427.0a

Shah MP (2013) Microbial degradation of textile dye (Remazol black B) by *Bacillus* spp. ETL-2012. J Appl Environ Microbiol 1(1):6–11. https://doi.org/10.12691/jaem-1-1-2

Sharma A, Rehman M (2009) Laboratory scale bioremediation of diesel hydrocarbon in soil by indigenous bacterial consortium. Indian J Exp Biol 47:766–769

Sharma A, Singh S, Sharma R, Chaudhary P, Pandey A, Ansari R, Vasudevan V, Arora A, Singh S, Saha S, Nain L (2016) Enhanced biodegradation of PAHs by microbial consortium with different amendment and their fate in in-situ condition. J Environ Manag 181:728–736. https://doi.org/10.1016/j.jenvman.2016.08.024

Shedbalkar U, Jadhav J (2011) Detoxification of malachite green and textile industrial effluent by *Penicillium ochrochloron*. Biotechnol Bioprocess Eng 16(1):196–204. https://doi.org/10.1007/s12257-010-0069-0

Silva ACS, Santos PN, Silva TAL, Andrade RFS, Campos-Takaki GM (2018) Biosurfactant production by fungi as a sustainable alternative. Arq Inst Biol 85:e0502017. https://doi.org/10.1590/1808-1657000502017

Skariyachan S, Manjunatha V, Sultana S et al (2016) Novel bacterial consortia isolated from plastic garbage processing areas demonstrated enhanced degradation for low density polyethylene. Environ Sci Pollut Res 23(18):18305–18319. https://doi.org/10.1007/s11356-016-7000-y

Srivastava S, Dwivedi AK (2015) Biological wastes the tool for biosorption of arsenic. J Bioremed Biodegr 7(2):323. https://doi.org/10.4172/2155-6199.1000323

Sukumar M (2010) Reduction of hexavalent chromium by *Rhizopus oryzae*. Afr J Environ Sci Technol 4(7):412–418

Sutar H, Kumar D (2012) A review on: bioremediation. Int J Res Chem Environ 2:13–21

Syranidou E, Karkanorachakia K, Amorottiaf F, Avgeropoulos A et al (2019) Biodegradation of mixture of plastic films by tailored marine consortia. J Hazard Mater 375:33–42. https://doi.org/10.1016/j.jhazmat.2019.04.078

Tang J, Lu X, Sun Q, Zhu W (2012) Aging effect of petroleum hydrocarbons in soil under different attenuation conditions. Agric Ecosyst Environ 149:109–117. https://doi.org/10.1016/j.agee.2011.12.020

Tastan BE, Ertugrul S, Dönmez G (2010) Effective bioremoval of reactive dye and heavy metals by *Aspergillus versicolor*. Bioresour Technol 101(3):870–876. https://doi.org/10.1016/j.biortech.2009.08.099

Travieso L, Cañizares RO, Borja R, Benítez F, Domínguez AR, Dupeyrón R, Valiente V (1999) Heavy metal removal by microalgae. Bull Environ Contam Toxicol 2(2):144–151

Tremblay J, Yergeau E, Fortin N et al (2017) Chemical dispersants enhance the activity of oil-and gas condensate-degrading marine bacteria. ISME J 11:2793–2808. https://doi.org/10.1038/ismej.2017.129

Tuleva B, Christova N, Cohen R, Stoev G, Stoineva I (2008) Production and structural elucidation of trehalose tetraesters (biosurfactants) from a novel alkanothrophic Rhodococcus wratislaviensis strain. J Appl Microbiol 104:1703–1710. https://doi.org/10.1111/j.1365-2672.2007.03680.x

Uqab B, Mudasir S, Nazir R (2016) Review on bioremediation of pesticides. J Bioremed Biodegr 7:343. https://doi.org/10.4172/2155-6199.1000343

Urbanek AK, Rymowicz W, Mirończuk AM (2018) Degradation of plastics and plastic-degrading bacteria in cold marine habitats. Appl Microbiol Biotechnol 102:7669–7678. https://doi.org/10.1007/s00253-018-9195-y

Uzoigwe C, Burgess JG, Ennis CJ, Rahman PK (2015) Bioemulsifiers are not biosurfactants and require different screening approaches. Front Microbiol 6:245–251. https://doi.org/10.3389/fmicb.2015.00245

Vaidya S, Devpura N, Jain K, Madamwar D (2018) Degradation of chrysene by enriched bacterial consortium. Front Microbiol 9:1333. https://doi.org/10.3389/fmicb.2018.01333

Varjani SJ, Upasani VN (2012) Characterization of hydrocarbon utilizing *Pseudomonas* strains from crude oil contaminated samples. Int J Sci Comput 6:120–124

Vullo DL, Ceretti HM, Daniel MA, Ramírez SA, Zalts A (2008) Cadmium, zinc and copper biosorption mediated by *Pseudomonas veronii* 2E. Bioresour Technol 99(13):5574–5581. https://doi.org/10.1016/j.biortech.2007.10.060

Wang W, Wang L, Zongze Shao Z (2018) Polycyclic aromatic hydrocarbon (PAH) degradation pathways of the obligate marine PAH degrader *Cycloclasticus* sp. Strain P1. Appl Environ Microbiol 84(21):e012618. https://doi.org/10.1128/AEM.01261-18

Wifak B, Nezha TJ, Meryem A et al (2017) Yeast biomass: an alternative for bioremediation of heavy metals. In: Antonio M, Iris L (eds) Yeast - industrial applications. IntechOpen, London. https://doi.org/10.5772/intechopen.70559

Winter R, Yen K, Ensley B (1989) Efficient degradation of trichloroethylene by a recombinant *Escherichia Coli*. Nat Biotechnol 7:282–285. https://doi.org/10.1038/nbt0389-282

Wu T, Xu J, Xie W, Yao Z, Yang H, Sun C, Li X (2018) *Pseudomonas aeruginosa* L10: a hydrocarbon-degrading, biosurfactant-producing, and plant-growth-promoting endophytic bacterium isolated from a reed (*Phragmites australis*). Front Microbiol 9:1087. https://doi.org/10.3389/fmicb.2018.01087

Xu X, Liu W, Tian S et al (2018) Petroleum hydrocarbon-degrading Bacteria for the remediation of oil pollution under aerobic conditions: a perspective analysis. Front Microbiol 9:2885. https://doi.org/10.3389/fmicb.2018.02885

Yan G, Viraraghavan T (2003) Heavy metal removal from aqueous solution by fungus *Mucor rouxii*. Water Res 37:4486–4496. https://doi.org/10.1016/S0043-1354(03)00409-3

Yan J, Niu J, Chen D, Chen Y, Irbis C (2014) Screening of *Trametes* strains for efficient decolorization of malachite green at high temperatures and ionic concentrations. Int Biodeterior Biodegrad 87:109–115. https://doi.org/10.1016/j.ibiod.2013.11.009

Microbial Scavenging of Heavy Metals Using Bioremediation Strategies

12

Ghada Abd-Elmonsef Mahmoud

Abstract

In the last years, increasing the population growth followed by an acceleration of the industrial process costs the quality of our ecosystem. Large waste quantities of industrial activities deposit risk concentrations of toxic materials like heavy metals. Heavy metal pollution has been distinguished as serious contaminants with worldwide risk since the industrial modern revolution. Environment depositions of these contaminants intimidate all the biological life forms for its high toxic characteristics. Chemical, physical, and mechanical strategies proved its low efficiency for its high energy needs, high costs, and even leave other secondary wastes to pass through the environment that raising another contaminant issue. Bioremediation through biological scavenging of heavy metals by microorganisms offers simple, low costs, low energy, and eco-friendly strategy for heavy metal elimination. Microorganisms developed extracellular (adsorption) and intracellular (accumulation) ways to bind metal ions through its viable or dead cells in a magnificent biosorption strategy. These strategies prop up as natural cell self-defense mechanisms for the elimination of the toxic effect of these hazardous materials. The whole bioremediation practicability affected by diverse factors such as microbial strain sensitivity, biomass concentricity, pH, surrounded temperature, and many else agents controls the metal ion bioavailability and the fast speed of the biosorption process.

Keywords

Bioremediation · Biodegradation · Heavy metals · Pollutants · Microbes

G. A.-E. Mahmoud (✉)
Botany and Microbiology Department, Faculty of Science, Assiut University, Assiut, Egypt
e-mail: ghadamoukabel@aun.edu.eg

© The Author(s), under exclusive licence to Springer Nature Singapore Pte Ltd. 2021

V. Kumar et al. (eds.), *Rhizobiont in Bioremediation of Hazardous Waste*,
https://doi.org/10.1007/978-981-16-0602-1_12

12.1 Introduction

Metals stand as a significant constituent of our ecological system with concentrations and availability related to its cycling, through various ecosystems geological and biological processes (Ehrlich 2002). Heavy metals (HM) distinguished as metallic trait elements with 420 atomic number that exist through industrialization activities and urbanization with critical or toxic environment levels (Jing et al. 2007). It is present naturally as an intrinsic micronutrient for plentiful organisms involving plants, fungi, algae, yeast, bacteria, and animals unless its concentration exceeds specific level, these metals generate biochemical, physiological, and genotoxic thirties through all living forms (Emamverdian et al. 2015; Mahmoud et al. 2020a; Ibrahim and Mahmoud 2020).

Industrial revolution generates large quantities of contaminants which enter through the environment by accidents or even misusing the elimination protocols (Mahmoud and Bagy 2019). Throughout the last century, electroplating, smelting, tanneries, pesticides, fertilizer, electronic, paper, and petroleum manufactures exonerate large amounts of HM through our natural ecosystem each year, which disrupted the biological systems and its physiological functions (Arivalagan et al. 2014; Mahmoud et al. 2015a, 2015b; Taiwo et al. 2016). It impulse multiple health troubles that injury the human pancreas, lung, liver, kidney, causing also multiple functional disorders. These heavy metals could cause critical issues that reach to DNA damage (Kumar et al. 2017). Heavy metal contamination also occurs naturally by leaching it through atmospheric deposition, metal corrosion, groundwater, sediment, and water resources metal evaporation (Weerasundara et al. 2017; Francová et al. 2017). In soil they could precipitate through the layers and staying for many years, (Manafi et al. 2012), however in water environments they could settle in the bottom and accumulate in the deposits (Kang and So 2016).

Environmental common hazardous HM includes Lead (Pb), Aluminum (Al), Copper (Cu), Chromium (Cr), Nickel (Ni), Mercury (Hg), Arsenic (As), Zinc (Zn), and Cadmium (Cd) representing key pollutants in anthropogenic regions causing serious issues to various organisms and even humans (Islam et al. 2007; Dhanarani et al. 2016; Karthik et al. 2017). It enters the environment system via natural and/or anthropogenic practicability and deposited in water, soils, or even transmitted and present in the surrounded air (Chen et al. 2015; Kuppusamy et al. 2017). It can mobile through the aquatic ecosystems generating toxic effects to higher and smaller life forms, which prioritized them as major inorganic environmental contaminants (Khan et al. 2008). The sources of HM through human activities include the discharging of toxic level wastes from electroplating, mining, refining, metallurgical, and chemical industries, while HM releases by biological processes related to the geological weathering (Basta et al. 2004; Monteiro et al. 2009; Kumar et al. 2015b). Several physicochemical methods were established for HM abstraction as chemical reactions for precipitation, solvent extraction, ion exchange reactions, and oxidation reactions, however, all these frameworks required large operational charges, high levels of energy input, and spaced capital investment (Gupta and Rastogi 2008; Singh et al. 2018).

High concentrations of HM effects on the microbiota societies through two lines, metabolic function deactivation and genetic materials modulation (Yuan et al. 2015). Heavy metals caused distribution of the viable membranes of the cells (Karthik et al. 2016), ordinary cell division (Banfalvi 2011), cell enzyme activity (Khan et al. 2009), protein deformations (Banfalvi 2011), genetic material damaging (Sobol and Schiestl 2012) and even could deactivate all the transcription active process (Gundacker et al. 2010). Bioremediation processes could name as biosorption, biological biotransformation, biomineralization, and microbial bioaccumulation that carries through the microorganisms, however, phytoremediation is established by multiple plants in a metal-polluted environment (Arivalagan et al. 2014).

Bioremediation technology introduced affordable, applicable, economic, and low energy consuming ways for heavy metal remediation. Living and even non-living bacteria, algae, fungi, and yeast have proven high metals uptake and binding reflecting its potentiality for remediation of heavy metal pollutants from various ecosystem types (Shanab et al. 2012; Abdel-Ghani and El-Chaghaby 2014). Heavy metal affects on the biological life forms through inhibiting its enzyme activity, changing its protein conformations and even its nucleic acid. However, microorganisms developed various intracellular defense mechanisms assist them to reduce or cancel the heavy metal toxic effect (Haferburg and Kothe 2007), also established extracellular detoxify systems that prevents the entrance of heavy metals into the viable cells, while the intracellular system mechanisms protect only the intracell system from the chock of excess highly toxic metals entrance (Bellion et al. 2006).

Metal uptake included two stages, adsorption and cell bioaccumulation process by viable or dead microorganisms defined as biosorption process. First, metal ions adsorbed on the viable or non-viable cell surface for little time may be seconds or even minutes; then start to enter the cells slowly through its cell membrane and finally accumulated within the cell. Microbiota cell wall is responsible for the metal-binding through specific binding groups (Siddiquee et al. 2015). Adsorption process promoted by binding special groups like OH^-, PO_4^{3-}, SH^-, COO^-, NO_3^-, RO^-, etc. (PeralesVela et al. 2006). Bioaccumulation process restricted to the living cells, including metal ion transport through the cell membrane and binds to the cytoplasmic polysaccharides or proteins, or polyphosphate bodies, or cellular organs like vacuoles (Micheletti et al. 2008; De Philippis et al. 2011; Markou et al. 2015). The microbial responses towards HM through the bioremediation practicability rise from normal cell self-defense strategies in it which includes changes in the cell surface and cause cells agglomeration to eliminate the toxic impact of the heavy metals (Jacob et al. 2018).

12.2 Bioremediation Strategies of Heavy Metal Pollutants

Microorganisms assist in the mineralization of harmful elements completely into carbon dioxide (CO_2) and water (H_2O) or partially into less toxic compounds that could be utilized by other organisms until complete degradation. Bioremediation

could perform also by the transformation of available toxic heavy metal into unavailable form which is known as metal detoxification (Ma et al. 2016). Different reactions of heavy metal bio-removing were conducted including immobilization, oxidation, binding, transformation, and even volatilizing the heavy metals (Verma and Kuila 2019). All these reactions depend on the existence or absence of oxygen (O_2); in aerobic biodegradation oxygen contributory as electron acceptor and the organic toxic pollutants oxidized by the reduction of the electron acceptors, however in anaerobic biodegradation microorganisms could utilize other organic compounds like ferrous (Fe^{+3}) or manganese (Mn^{+4}) as electron acceptor (e^{-}) (Lovley and Phillips 1988). Availability of alternative electron acceptors is critical for the anaerobic declination of pollutants (Spormann and Widdel 2000).

There are various techniques applied for HM bio-removal process. Bioremediation utilizes adsorption: this type concentrated on the extracellular substances associated with the microbial cell wall that will affects directly on the metal element adsorption process (Guine et al. 2006). These polymeric substances have high metal and binding capabilities towards heavy metals using the proton exchange in the microorganism's cell walls (Fang et al. 2010).

12.2.1 Bioremediation Using Bioaugmentation

Addition of specialized microorganisms (exogenous or indigenous insertion) in the site of pollution to eat the contaminant is called bioaugmentation. To upgrade the microbial growth good nutrients, air (for aerobic degradation), electron acceptors, and convenient organic substrates are required. This bioremediation method considered as effective, affordable, and highly fast remediation process treated the problem in its location and highly applicable in site managers (EPA 2006).

12.2.2 Bioremediation Using Biosorption

Biosorption means the adsorption of metal contaminant to a biological matrix by chemical interactions like ions and protons displacement, physical interactions with electrostatic forces, complexation, and chelation especially at neutral pH that the microbial surface will contain the anionic moieties which will work as binding sites for the cationic heavy metals (Fomina and Gadd 2014). Using biosorption practicability in heavy metal abstraction lean basically on the balanced between a biosorbent (microorganism) and sorbate (metal ions) (Das et al. 2008). Various natural microbial species and also engineered species were used in the biosorption process (Ueda 2016). The kinetics of the sorption practicability, utmost sorption capability, regeneration, bound metals elimination needed to analyze for estimation of the utilized microorganism stability as a biosorbent (Verma and Kuila 2019). Selected biosorbent should prepare by low costs, reusable, easy to separate from the pollutant solution (in the aquatic environment), and it must be fast removal (Bae et al. 2003). Aquatic heavy metal biosorption strategies include exo-polysaccharides production,

using dead biomass for the cleaning or living cultures as biosorbent (Verma and Kuila 2019).

Despite all the previous advantages; biosorbtion encounters many challenges like pH dependence, ionic strength, and biosorbent that has specific lifespans especially with dead biomass which will degrade by the time with unavailable binding sites (Fomina and Gadd 2014). Contrast, the bioaccumulation way is a pushing metabolic operation that the microorganisms enter the heavy metals into membrane intracellular space with a translocation lane via the lipid bilayer. After that, the HM sequestered using various peptide and protein ligands (Mishra and Malik 2013; Diep et al. 2018).

Microorganisms could grow speedily giving high biomass yield which is very adequate to the remediation process of HM polluted areas (Aryal and Liakopoulou-Kyriakides 2015). For achieving high HM remediation high adsorption capacity is needed. This could be obtained naturally in the microbial biomass without pretreated; however, acid or alkali pretreatment raises the adsorption capacity. Throughout acid medication, the microbial growth is protonated with positive (+) charge density improving resulting in much more binding sites with high electrostatic force amidst microorganisms and HM with negatively charged (Yin et al. 2019). The addition of polyacrylic acid to *Corynebacterium glutamicum* raised cadmium Cd(II) removing by 3.2 times (Mao et al. 2013). Alkali treatment using sodium, ammonium and calcium hydroxides, and carbonates treatments also increases the negative charge microorganisms surface and augments the electrostatic force for positive (+) heavy metal. Khalil et al. (2016) reported that alkali medication raised the uranium (U) biosorption by mycotic mycelia than untreated samples. Yan and Viraraghavan (2000) reported that alkali treatment of *Mucor rouxii* biomass improved its adsorption efficient.

12.3 Bioremediation of Heavy Metals by Bacteria

Bacteria characterized by particular genetic mechanisms play roles in the mitigation of the environmental hazardous (Jacob et al. 2018). The functional binding sites of bacteria include carboxyl, sulfonate, hydroxyl, phosphonate, and amide groups that involved strictly to the metals uptake process (Huang and Liu 2013). Microbial responses to heavy metal as biosorbent materials generated as natural self-defense mechanism of the cell that includes changes through the cell morphology and physiology, for example, the wall of bacterial cells in Cr(VI) contaminated media appeared irregular to form clump/adherence while in normal medium appeared as smooth surface elongated cell wall (Jacob et al. 2018).

There are two mechanisms through bacterial cells by which the hazards of heavy metal pass to the bacterial cell; non-specific technique that works on energetic transport without ATP dependent that produces fast transportation HM directly through the bacterial growth. Latest mechanism is ATP-subordinate by the bacterial cells which made it the slower speed and highly substrate-dependent (Ahemad 2012). In bacteria, heavy metals accumulated in the cell wall chemical groups,

peptidoglycan layer determines the bacterial metal-binding capability, Gram (+ve) positive bacteria found to aggregate higher HM concentrations on their walls than Gram (−ve) negative bacteria (Rani and Goel 2009). Extracellular polysaccharides participated in heavy metals accumulation depending on the bacterial species (Yee and Fein 2001).

Bacterial biomass proved its potentiality for the heavy metals uptake from various polluted sites or media (Table 12.1) especially *Streptomyces*, *Citrobacter*, *Pseudomonas*, and *Bacillus* species that utilize heavy metal by biosorption strategies and transfer these metals to their biomass matrix (Dhanarani et al. 2016). *Pseudomonas* and *Bacillus* sp. have been utilized widely in heavy removal from soils and wastewater sites for their richly metal ions attaching alliance (Ullah et al. 2015). Bacterial cell wall is taking charge of the metal-attaching process, for its anionic nature that enables it to attach the cations throughout the electrostatic energy (Siddiquee et al. 2015). Gram (+ve) positive contains rustic cell walls that contain teichoic, peptidoglycan biomolecules, and teichuronic acids, while Gram (−ve) negative bacteria contain thin peptidoglycan layer which assumed that other positive bacterial type are much dynamic in metal ions trapping technique (Karthik et al. 2017; Jacob et al. 2018).

Escherichia coli and *Bacillus idriensis* were utilized in arsenic (Ar) bioremediation (Singh et al. 2008; Liu et al. 2011). *Achromobacter* species, *Acidithiobacillus ferrooxidans*, *Arthrobacter viscosus*, *Bacillus cereus*, *Deinococcus radiodurans*, *Pseudomonas aeruginosa*, and *Staphylococcus epidermidis* used in mercury (Hg) bioremediation (Brim et al. 2000; Sasaki et al. 2005; Kiyono et al. 2009; Ng et al. 2009; Sinha et al. 2012; Yin et al. 2016; Hlihor et al. 2017; Quiton et al. 2018).

Bacillus coagulans, *Bacillus licheniformis*, *Bacillus megaterium*, *Desulfovibrio desulfuricans*, *Kocuria rhizophila*, and *Pantoea agglomerans*, utilized in chromium (Cr) bioremediation (Srinath et al. 2002; Zouboulis et al. 2004; Sikander et al. 2012; Kim et al. 2015; Haq et al. 2016). *Bacillus firmus*, *Desulfovibrio desulfuricans*, *Lactobacillus* sp., and *Micrococcus luteus* utilized in copper (Cu) bioremediation (Salehizadeh and Shojaosadati 2003; Schut et al. 2011; Puyen et al. 2012; Kim et al. 2015).

Alcaligenes sp., *Bacillus firmus*, *Bacillus subtilis*, *Enterobacter cloacae*, *Geobacillus thermocatenulatus*, *Pseudomonas fluorescens*, *Micrococcus luteus*, and *Staphylococcus saprophyticus* utilized in lead (Pb) bioremediation (Huang et al. 2001; Salehizadeh and Shojaosadati 2003; Bondarenko et al. 2008; Jencarova and Luptakova 2012; Samarth et al. 2012; Puyen et al. 2012; Kang et al. 2015; Jin et al. 2017).

Bacillus firmus, *Brevibacterium* sp., *Rhodobacter capsulatus*, *Pseudomonas putida*, *Streptomyces rimosus*, and *Thiobacillus ferrooxidans* utilized in zinc (Zn) bioremediation (Mameri et al. 1999; Taniguchi et al. 2000; Salehizadeh and Shojaosadati 2003; Chen et al. 2005; Nagashetti et al. 2013; Magnin et al. 2014). *Escherichia coli*, *Desulfovibrio desulfuricans*, *and Pseudomonas* sp. used in nickel (Ni) bioremediation (Liu et al. 2004; Sulaymon et al. 2012; Kim et al. 2015).

Table 12.1 Common bacteria utilized as heavy metal scavengers in bioremediation process

Biosorbent	Metals	References	Biosorbent	Metals	References
Escherichia coli	Arsenic (Ar)	Singh et al. (2008)	*Bacillus firmus*	Copper (Cu)	Salehizadeh and Shojaosadati (2003)
Bacillus idriensis	Arsenic (Ar)	Liu et al. (2011)	*Desulfovibrio desulfuricans*	Copper (Cu)	Kim et al. (2015)
Achromobacter sp.	Mercury (Hg)	Ng et al. (2009)	*Micrococcus luteus*	Copper (Cu)	Puyen et al. (2012)
Acidithiobacillus ferrooxidans	Mercury (Hg)	Sasaki et al. (2005)	*Lactobacillus* species	Copper	Schut et al. (2011)
Bacillus cereus	Mercury (Hg)	Sinha et al. (2012)	*Bacillus firmus*	Lead	Salehizadeh and Shojaosadati (2003)
Deinococcus radiodurans	Mercury (Hg)	Brim et al. (2000)	*Enterobacter cloacae*	Lead (Pb)	Kang et al. (2015)
Pseudomonas aeruginosa	Mercury (Hg)	Yin et al. (2016)	*Bacillus subtilis*	Lead (Pb)	Huang et al. (2001)
Pseudomonas sp.	Mercury (Hg)	Kiyono et al. (2009)	*Pseudomonas fluorescens*	Lead (Pb)	Bondarenko et al. (2008)
Arthrobacter viscosus	Mercury (Hg)	Hlihor et al. (2017)	*Geobacillus thermocatenulatus*	Lead (Pb)	Samarth et al. (2012)
Staphylococcus epidermidis	Mercury (Hg)	Quiton et al. (2018)	*Staphylococcus saprophyticus*	Lead (Pb)	Jencarova and Luptakova (2012)
Pantoea agglomerans	Chromium (Cr)	Sikander et al. (2012)	*Micrococcus luteus*	Lead (Pb)	Puyen et al. (2012)
Bacillus coagulans	Chromium (Cr)	Srinath et al. (2002)	*Alcaligenes* species	Lead	Jin et al. (2017)
Bacillus licheniformis	Chromium (Cr)	Zouboulis et al. (2004)	*Bacillus firmus*	Zinc	Salehizadeh and Shojaosadati (2003)
Desulfovibrio desulfuricans	Chromium (Cr)	Kim et al. (2015)	*Brevibacterium* sp.	Zinc (Zn)	Taniguchi et al. (2000)

(continued)

Table 12.1 (continued)

Biosorbent	Metals	References	Biosorbent	Metals	References
Kocuria rhizophila	Chromium (Cr)	Haq et al. (2016)	*Rhodobacter capsulatus*	Zinc (Zn)	Magnin et al. (2014)
Bacillus megaterium	Chromium (Cr)	Srinath et al. (2002)	*Pseudomonas putida*	Zinc	Chen et al. (2005)
Salmonella typhi	Cadmium (Cd)	Basha and Rajaganesh (2014)	*Thiobacillus ferrooxidans*	Zinc (Zn)	Nagashetti et al. (2013)
Bacillus cereus	Cadmium (Cd)	Huang et al. (2013)	*Streptomyces rimosus*	Zinc (Zn)	Mameri et al. (1999)
Ochrobactrum sp.	Cadmium (Cd)	Khadivinia et al. (2014)	*Desulfovibrio desulfuricans*	Nickel (Ni)	Kim et al. (2015)
Bacillus licheniformis	Cadmium (Cd)	Zouboulis et al. 2004	*Pseudomonas* sp.	Nickel (Ni)	Liu et al. (2004)
Pseudomonas putida	Cadmium (Cd)	Wu et al. (2006)	*Escherichia coli*	Nickel (Ni)	Sulaymon et al. (2012)
Enterobacter species	Cadmium	Lu et al. (2005)	*Pseudomonas* sp.	Cobalt (Co)	Nanda et al. (2011)
Kocuria rhizophila	Cadmium (Cd)	Haq et al. (2016)	*Bacillus licheniformis*	Ferrous (Fe)	Karakagh et al. (2012)
Mesorhizobium species	Cadmium	Sriprang et al. (2003)	*Pseudomonas* sp.	Arsenic (Ar)	Nanda et al. (2011)

Genetically modified bacterial strains upgraded their catabolic properties and used highly throughout the bioaugmentation practicability (Mrozik et al. 2011). Emenike et al. (2017) utilized bacteria consortium like *Lysinibacillus* species, *Bacillus* species, and *Rhodococcus* species in the bioaugmentation and concluded that reduced the HM concentrations with 88% in copper, 41% in cadmium, and 71% in lead. Fauziah et al. (2017) stated that the microbial consortium of *L. sphaericus*, *B. thuringiensis*, *and R. wratislaviensis* reduced nickel contamination with >50%. However bacterial biostimulation utilizes bacterial strains with providing suitable conditions to increase the bacterial resistant potentiality against toxic metals and ultimately enhance overall the bioremediation process (Atagana 2008), like addition nitrogen, phosphorus, oxygen, and carbon as nutrients to enhance the bacterial growth (Bundy et al. 2012).

12.4 Bioremediation of Heavy Metals by Fungi

Fungi are remarkable by their ability to live under elevated concentrations of toxic heavy metals pollutants that made it utilize as HM scaviours. Fungi used as heavy metal scavengers owing to their unique cell wall structure with high cell/surface ratio, which gives them a high tendency to contact these metals (Jacob et al. 2018). It detoxified heavy metal effects through transformation, precipitations, and uptake process (Thatoi et al. 2014). Chitin, polysaccharides, glucuronic acid, and phosphate in mycological cells performed critical part throughout bioremediation process of HM including ion exchange process (Purchase et al. 2009) also the working groups of carboxyl (COO^-), hydroxyl (OH^-), amine (NH_2), and phosphate (PO_4) action on the mycological removing capability of fungi to the heavy metals.

The acidic surface of *Termitomyces clypeatus* cells utilize chromium metals with the active groups assist of carboxyl (COO^-), phosphate (PO_4), imidazole ($C_3H_4N_2$), and hydroxyl (OH^-) (Ramrakhiani et al. 2011). The high content of carboxyl throughout the mycotic cell wall polysaccharides augments highly the HM biosorption operation (Raja et al. 2015). Owing to the lineal interaction by the cell wall and toxic HM; fungal morphology deformations observed in several fungal species (Mahmoud et al. 2020a). However, these heavy metals in very small concentrations could utilize as antifungal agents (Abdelhamid et al. 2020). Many fungal species used to remove various types of heavy metals included in Table 12.2.

Pleurotus platypus used in silver (Ag) bioremediation (Das et al. 2010); *Pleurotus sapidus* and *Rhizopus arrhizus* used in mercury (Hg) bioremediation (Tobin et al. 1984; Yalcinkaya et al. 2002); *Aspergillus niger*, *Aspergillus fumigatus*, *Ganoderma lucidum*, *Penicillium chrysogenum*, *Rhizopus arrhizus*, *Rhizopus nigricans*, and *Termitomyces clypeatus* utilized in chromium (Cr) bioremediation (Merrin et al. 1998; Sudha Bai and Abraham 2001; Muter et al. 2002; Dursun et al. 2003; Tan and Cheng 2003; Ramrakhiani et al. 2011; Mondal et al. 2017; Dhal and Pandey 2018). *Aspergillus niger*, *Aspergillus oryzae*, *Mucor rouxii*, *Pleurotus sapidus*, *and Trichoderma* sp. utilized in cadmium (Cd) bioremediation (Huang

Table 12.2 Common fungi and yeast utilized as heavy metal scavengers in bioremediation process

Biosorbent	Metals	References	Biosorbent	Metals	References
Pleurotus platypus	Silver (Ag)	Das et al. (2010)	*Aspergillus niger*	Copper (Cu)	Gunasekaran et al. (2003)
Pleurotus sapidus	Mercury (Hg)	Yalcinkaya et al. (2002)	*Rhizopus oryzae*	Copper (Cu)	Fu et al. (2012)
Rhizopus arrhizus	Mercury (Hg)	Tobin et al. (1984)	*Ganoderma lucidum*	Copper (Cu)	Muter et al. (2002)
Ganoderma lucidum	Chromium (Cr)	Muter et al. (2002)	*Lepiota hystrix*	Copper (Cu)	Kariuki et al. (2017)
Penicillium chrysogenum	Chromium (Cr)	Tan and Cheng (2003)	*Saccharomyces cerevisiae*	Copper (Cu)	Amirnia et al. (2015)
Aspergillus niger	Chromium (Cr)	Dursun et al. (2003), Mondal et al. (2017)	*Rhizopus arrhizus*	Copper (Cu)	Tobin et al. (1984)
Aspergillus fumigatus	Chromium (Cr)	Dhal and Pandey (2018)	*Penicillium citrinum*	Copper	Verma et al. (2013)
Rhizopus arrhizus	Chromium (Cr)	Merrin et al. (1998)	*Penicillium spinulosum*	Copper (Cu)	Townsley et al. (1986)
Rhizopus nigricans	Chromium (Cr)	Sudha Bai and Abraham (2001)	*Aspergillus niger*	Zinc (Zn)	Gunasekaran et al. (2003)
Termitomyces clypeatus	Chromium (Cr)	Ramrakhiani et al. (2011)	*Penicillium chrysogenum*	Zinc (Zn)	Fourest et al. (1994)
Pleurotus sapidus	Cadmium (Cd)	Yalcinkaya et al. (2002)	*Rhizopus arrhizus*	Zinc (Zn)	Tobin et al. (1984)
Trichoderma sp.	Cadmium (Cd)	Bazrafshan et al. (2016)	*Rhizopus nigricans*	Lead (Pb)	Volesky and Holan (1995)
Aspergillus niger	Cadmium (Cd)	Tsekova et al. (2010)	*Mucor rouxii*	Lead	Yan and Viraraghavan (2001)
Aspergillus oryzae	Cadmium (Cd)	Huang et al. (1988)	*Penicillium chrysogenum*	Lead (Pb)	Niu et al. (1993)

M. rouxii	Cadmium	Yan and Viraraghavan (2001)	*P. chrysogenum*	Nickel	Tan and Cheng (2003)
Ganoderma lucidum	Lead (Pb)	Muter et al. (2002)	*M. rouxii*	Nickel	Magyarosy et al. (2002)
A. niger	Lead	Dursun et al. (2003)	*M. rouxii*	Nickel	Yan and Viraraghavan (2001)
Lepiota hystrix	Lead (Pb)	Kariuki et al. (2017)	*Saccharomyces cerevisiae*	Manganese	Fadel et al. (2017)
Penicillium simplicissimum	Lead	Fan et al. (2008)	*Rhizopus arrhizus*	Manganese (Mn)	Tobin et al. (1984)

et al. 1988; Yan & Viraraghavan 2001; Yalcinkaya et al. 2002; Tsekova et al. 2010; Bazrafshan et al. 2016).

Aspergillus niger, *Ganoderma lucidum*, *Lepiota hystrix*, *Rhizopus nigricans*, *Mucor rouxii*, *Penicillium chrysogenum*, and *Penicillium simplicissimum* used in lead (Pb) bioremediation (Niu et al. 1993; Volesky and Holan 1995; Yan & Viraraghavan 2001; Muter et al. 2002; Dursun et al. 2003; Fan et al. 2008; Kariuki et al. 2017). *Aspergillus niger*, *Ganoderma lucidum*, *Lepiota hystrix*, *Rhizopus oryzae*, *Rhizopus arrhizus*, *Saccharomyces cerevisiae*, *Penicillium citrinum*, and *Penicillium spinulosum* utilized in copper (Cu) bioremediation (Tobin et al. 1984; Townsley et al. 1986; Muter et al. 2002; Gunasekaran et al. 2003; Fu et al. 2012; Verma et al. 2013; Amirnia et al. 2015; Kariuki et al. 2017). *Aspergillus niger*, *Penicillium chrysogenum*, and *Rhizopus arrhizus* used in zinc (Zn) bioremediation (Tobin et al. 1984; Fourest et al. 1994; Gunasekaran et al. 2003). *Mucor rouxii* and *Penicillium chrysogenum* used in nickel (Ni) bioremediation (Yan & Viraraghavan 2001; Magyarosy et al. 2002; Tan and Cheng 2003). *Saccharomyces cerevisiae* and *Rhizopus arrhizus* used in manganese (Mn) bioremediation (Tobin et al. 1984; Fadel et al. 2017).

Metal ion uptake using living fungal cells depends on the cell age, absorption time, pH level, temperature, etc. Biosorption of Cu, Cd, Zn, and Pb using living cells of *Penicillium*, *Aspergillus*, and *Rhizopus* takes from 1 to 4 h depending on all the previous conditions (Mullen et al. 1992). This process kinetics represented by a rapid initial phase that contributes up to 90% biosorption and takes about 10 min then the second slower phase lasts to about 4 h depending on the used fungal strain. Volesky and May (1995) stated that twelve hour old *Saccharomyces cerevisiae* was able to absorb heavy metals 2.6 times more than 24 h yeast cells.

12.5 Bioremediation of Heavy Metals by Algae

Algae are photosynthetic microorganisms found in various water types like freshwater, saltwater, and special water environments. Algae used in polluted water HM bioremediation and stated the capability of algae for HM utilization. Algae used various peptides as cell defense against heavy metal toxicity to protect the algae (Bilal et al. 2018). *Fucus vesiculosus* and *Cladophora fascicularis* were found as lead biosorbents (Deng et al. 2007; Demey et al. 2018). *Cystoseira crinitophylla* and *Sargassum* have been reported as copper Cu (II) biosorbent from water solutions (Christoforidis et al. 2015; Barquilha et al. 2017). *Desmodesmus* sp., *Sargassum fusiforme*, and *Saccharina japonica* utilized as copper (Cu^{+2}), cadmium (Cd^{+2}), nickel (Ni^{+2}), and zinc (Zn^{+2}) biosorbents (Rugnini et al. 2018; Poo et al. 2018).

12.6 Agents Affecting on HM Bioremediation

Bioremediation process represents a complex biological process affects by many control factors (biotic - abiotic) that impacts on the microbial expansion and the metabolic process. Microorganisms could decrease HM bioavailability through acids production, oxidation, reduction, and complexing agent's productions (Gadd 2010).

12.6.1 Biotic Factors

Biotic factors affect mainly the microbial growth, cell size, and the metabolite formations. Using the right biomass quantity represents one of the critical successful points of the biosorption processes. Biomass concentration affects significantly on the heavy metal removal, increasing the biomass quantities enhanced the metal ions absorption for the high availability of metal-binding sites, however very high concentrations have a reverse effect with lower heavy metal removal capacity due to the aggregation of biomass that leads to lower metal-binding sites availability (Monteiro et al. 2012). Biomass concentration represents an important biological factor; low biomass have high intercellular space and higher metal removal efficiency (Park and Choi 2002).

Romera et al. (2007) stated that the ultimate biosorption potentiality is established by the lowest microbial mass quantities. Many researchers stated that low biomass inoculums give high removal efficiency in *Saccharomyces cerevisiae*, *Pseudomonas aeruginosa*, and *Bacillus subtilis* (Fadel et al. 2017). Higher biomass concentrations restrict the interaction process to only the microbial superficial binding sites and generate the shell effect on the microbial cell surface (Romera et al. 2007; Abbas et al. 2014).

Higher biomass also diminishes the inside cell spaces bring in efficiently decreasing of metal hazard elimination (Fadel et al. 2017). Gong et al. (2005) reported decreasing in metal uptakes in high biomass concentration (20-40 g/l). However, at equilibrium levels, heavy metals adsorbed efficiently and also could enter the cells by the metal concentration gradient (Vasudevan et al. 2002).

12.6.2 Abiotic Factors

Abiotic factors related to the climatic conditions like temperature, humidity, wind speed, and physicochemical parameters like pH, oxygen, metal concentration, nutrient availability, and water content.

12.6.2.1 Temperature

Temperature affects on almost all rates of the chemical reaction, a higher temperature much favors for the high metal ions solubility which decreased the metal ions microbial sorption process (Lau et al. 1999). Optimum temperature for the microbial

biosorption varies by the kind of metal ion and the microbial biosorbent species (Gupta et al. 2010). Temperature higher than optimum levels decreased the bioremediation process by inducing modifications in the protein synthesis however lower temperatures decreased the membrane fluidity and the transport systems (de Groot and Ventura 2006).

In algae as biosorbent, Gupta and Rastogi (2008) stated that cadmium adsorption through *Oedogonium* sp. was decreased at elevated temperatures. In bacteria as biosorbent, *Acinetobacter* species (Panda and Sarkar 2012), *E. aerogenes* (Fu et al. 2012), *B. cereus* (Naik et al. 2012), and *Rhizobium* species (Karthik et al. 2016) revealed maximum heavy metal bioremediation efficiency in mesophilic conditions. In fungi as biosorbent, *A. niger* (Gu et al. 2015) and *R. oryzae* (Fu et al. 2012) showed high remediation of heavy metal also in mesophilic conditions.

12.6.2.2 pH

Many studies revealed that the biosorption of HM ions is correlated to the surrounding pH that affects on metal solubility and toxicity especially in water environment (Brinza et al. 2007). pH has the potency to vary the microbial biomass, metal chemistry complexation, enzyme effectiveness, and manner of functional groups in the cell outer surface (Gupta and Rastogi 2008). pH affects the toxicity availability degree of these metals through the water ecosystem affecting in the chemistry of water and the water microbial ecosystem (Brinza et al. 2007).

Acidic pH alters the characteristics of surface functional groups and their interaction with metal ions (Jacob et al. 2018). Alkaline pH conditions generated hydroxo-metal complexes and increase the microbial logarithmic phase which reduces the bioremediation process (Govarthanan et al. 2016). In bacteria as biosorbent, like *Bacillus* species (Naik et al. 2012), *Escherichia coli* (Samuel et al. 2012), *M. luteus* (Puyen et al. 2012), and *P. aeruginosa* (Oves et al. 2013) the bioremediation efficiently was the highest in neutral pH range.

Fungi like *Pleurotus* species (Das et al. 2010) and *Trichoderma* species (Mohsenzadeh and Shahrokhi 2014) prefer a neutral pH range. For algae as microbial sorbent, since the preponderance of metal ion attaching sites is acidic (especially carboxyl) the biosorbent process regarded as pH-dependent (Han et al. 2006). Optimal pH for Cesium, Cu, Cr, and Cd biosorption by *Durvillaea potatorum*, *Padina* sp., *Sargassum* sp., *Padina australis* was pH 2 and even lower (Yu et al. 2000; Jalali et al. 2004). For uranium accumulation by *C. vulgaris* was pH 3–6 (Gunther et al. 2008), Cr accumulation by *C. miniata* was pH 3–4.5 (Han et al. 2006).

12.6.2.3 Metal Ion Concentration

Lower levels of heavy metals could involve directly in various metabolic processes of the microorganisms, however, by elevated the levels it starts to affect on the growth and physiological process of the microorganisms even with biosorption ability (Singh et al. 2010). Metal ion concentration affects on the biosorbent microorganisms highly as each microorganism has specific bioremediation rate. *Aspergillus niger* eliminates copper 15.6 mg/g after 1 h (Dursun et al. (2003),

however, *Micrococcus luteus* eliminates 408 mg/g by 12 h (Puyen et al. 2012), and *Desulfovibrio desulfuricans* eliminates only 98.2 mg/g by 168 h (Kim et al. 2015).

Fusarium chlamydosporum, *Fusarium solani*, *and Aspergillus niger* were highly affected by copper present in the medium than *Alternaria alternata* and *Trichoderma harzianum* (Ibrahim and Mahmoud 2019). Also, by increasing cadmium concentration to high levels growth inhibition and morphological disturbances cleared in *Cladosporium cladosporioides*, *Fusarium oxysporum* and *F. solani* (Ibrahim et al. 2020). High heavy metal toxicity induced various physiological changes in microorganisms, e.g. biomass reduction, cellular functions disturbance, and microbial enzyme inhibition (Oves et al. 2016). Much heavy metal intensity react via microbial viable membrane resulting irreversible unstoppable membrane destruction, enter the cytoplasm, and disrupt the enzymes and could cause genetic modifications (Fashola et al. 2016).

12.6.2.4 Nutrients and Oxygen Availability

Nutrients or oxygen availability related directly to the bioremediation site and the microbial bioremediation requirements. Good microbial growth needs carbon, nitrogen, and phosphorus that are directly involved through the microbial metabolism and reflected on the growth for both fungi and bacteria. The previous three components involved in organic compounds, protein, ATP, and nucleic acid biosynthesis (Xu et al. 2015; Mohamed and Mahmoud 2018) and found in almost all growth media of bacteria, yeast, and fungi (Mahmoud et al. 2019; Abdel-Hakeem et al. 2019). Optimum carbon and nitrogen sources will affect straightly through the whole microbial growth (Nafady et al. 2015; Mahmoud et al. 2020b) which will reflect on the metal removal efficiency (Venil et al. 2011). Preponderance of microbial scavengers needs oxygen for the bioremediation process as they grow aerobically and it is used in energy yielding (Jacob et al. 2018).

12.7 Harmful Effect of Heavy Metals

Heavy metals have different effects on various life forms related to its concentration in the environment. Heavy metals even in low concentrations affect badly in human health and lead to serious disease that could end by human death. Heavy metal toxicity could lessing the human rational, nervous actions, and harmful the lungs, skin, liver, pancreatic, and kidneys (Vardhan et al. 2019). Plants uptake necessary minerals from soil using the expanded root; these minerals classified as essential nutrients and non-essential nutrients, also the essential nutrients classified as macronutrients as nitrogen, potassium, phosphorus, silicon, calcium, sulfur, magnesium and micronutrients needed in tiny amounts as sodium, nickel, chlorine, molybdenum, manganese, boron, zinc, copper, and iron (Xun et al. 2018). Micronutrients as Ni, Zn, and Cu required to plant metabolism only with very small amounts, however, other micronutrients even in low concentrations are toxic to plants, e.g. mercury, chromium, cadmium, lead, and silver (Muszynska et al. 2018). High HM concentrations incorporated with plant chlorosis, leaf rolling, senescence, low

biomass, shriveling, and low seeds quantities (Shahid et al. 2017; Shi et al. 2018). Higher lead concentration throughout the soil generated plants with irregular morphology (Kushwaha et al. 2018). Higher nickel concentration results in nutrient imbalances and cell membrane scatters of its capacities (Mendez et al. 2014). Chromium affects on the plants photosynthesis process and enzyme activities resulting of putrefaction and shrinking of leaves (Kumar et al. 2015a; Kumari et al. 2018). The effects of heavy metals on microorganisms depend on the microorganism sensitivity and the metal concentration. According to Ibrahim et al. (2020) and Mahmoud et al. (2020a) elevated concentration of cadmium caused microbial growth inhibition with various degrees depending on the microbial strain and morphological deformation in mycelia, phialid, conidia and also cause speeding in chlamydospores formation which reflect the huge stress of cadmium heavy metal on the microbial cells. Copper also showed inhibition effects on several phytopathogenic fungi especially in high concentrations with cellulase enzyme inhibition (Ibrahim and Mahmoud 2019).

12.8 Conclusion

Heavy metal violation turns out as one of the prime pollution affair that threatens human, biological and animal lives. This problem arises from industrial speeding with low safety procedures for wastes disposal. Many heavy metal remediation techniques have been used, however, bioremediation listed as the low cost and safest remediation strategy. Microbial scavenging of heavy metals is characterized as low energy, low cost, speedy, and eco-friendly technique having potential for application in large contaminated sites. Microbial scavenge requires efficient microbiome as bacteria, yeast, cyanobacteria, fungi, and algae with efficient biomass and powerful activity to degrade, or absorb, or adsorb, or convert heavy metal from hazard toxic forms into almost un-harmful forms. Success of these technique focuses mainly on picking the right scavenger microbe as per the contaminated site chemicals, the prevailing environmental conditions. Providing the required optimum growth conditions for microorganisms in the contaminated sites will increase HM degradation process with less harmful effects on the environment.

References

Abbas SH, Ismail IM, Mostafa TM, Sulaymon AH (2014) Biosorption of heavy metals: a review. J Chem Sci Technol 3:74–102

Abdel-Ghani NT, El-Chaghaby GA (2014) Biosorption for metal ions removal from aqueous solutions: a review of recent studies. Int J Latest Res Sci Technol 3:24–42

Abdel-Hakeem SS, Mahmoud GA-E, Abdel-Hafeez HH (2019) Evaluation and microanalysis of parasitic and bacterial agents of Egyptian fresh sushi, *Salmo salar*. Microsc Microanal 25 (6):1498–1508. https://doi.org/10.1017/S143192761901506X

Abdelhamid HN, Mahmoud GA-E, Sharmouk W (2020) A cerium-based MOFzyme with multi-enzyme-like activity for the disruption and inhibition of fungal recolonization. J Mater Chem B 8:7548–7556

Ahemad M (2012) Implications of bacterial resistance against heavy metals in bioremediation. A review. IIOABJ 3:39–46

Amirnia S, Ray MB, Margaritis A (2015) Heavy metals removal from aqueous solutions using Saccharomyces cerevisiae in a novel continuous bioreactor–biosorption system. Chem Eng J 264:863–872

Arivalagan P, Singaraj D, Haridass V, Kaliannan T (2014) Removal of cadmium from aqueous solution by batch studies using *Bacillus cereus*. Ecol Eng 71:728–735

Aryal M, Liakopoulou-Kyriakides M (2015) Bioremoval of heavy metals by bacterial biomass. Environ Monit Assess 187:41–73

Atagana HI (2008) Compost bioremediation of hydrocarbon-contaminated soil inoculated with organic manure. Afr J Biotechnol 7(10):1516–1525

Bae W, Wu CH, Kostal J, Mulchandani A, Chen W (2003) Enhanced mercury biosorption by bacterial cells with surface-displayed MerR. Appl Environ Microbiol 69:3176–3180

Banfalvi G (2011) Cellular effects of heavy metals. Springer, New York

Barquilha C, Cossich E, Tavares C, Silva E (2017) Biosorption of nickel (II) and copper (II) ions in batch and fixed-bed columns by free and immobilized marine algae *Sargassum* sp. J Clean Prod 150:58–64

Basha SA, Rajaganesh K (2014) Microbial bioremediation of heavy metals from textile industry dye effluents using isolated bacterial strains. Int J Curr Microbiol App Sci 3:785–794

Basta NT, Ryan JA, Chaney RL (2004) Trace element chemistry in residual-treated soil key concepts and metal bioavailability. J Environ Qual 34:49–63

Bazrafshan E, Zarei AA, Mostafapour FK (2016) Biosorption of cadmium from aqueous solutions by *Trichoderma* fungus: kinetic, thermodynamic, and equilibrium study, Desalin. Desalin Water Treat 57:14598–14608

Bellion M, Courbot M, Jacob C, Blaudez D, Chalot M (2006) Extracellular and cellular mechanisms are sustaining metal tolerance in ectomycorrhizal fungi. FEMS Microbiol Lett 254:173–181

Bilal M, Rasheed T, Sosa-Hernandez JE, Raza A, Nabeel F, Iqbal H (2018) Biosorption: an interplay between marine algae and potentially toxic elements-a review. Mar Drugs 16:65

Bondarenko O, Rolova T, Kahru A, Ivask A (2008) Bioavailability of Cd, Zn and Hg in soil to nine recombinant luminescent metal sensor bacteria. Sensors 8:6899–6923

Brim H, McFarlan SC, Fredrickson JK, Minton KW, Zhai M, Wackett LP, Daly MJ (2000) Engineering *Deinococcus radiodurans* for metal remediation in radioactive mixed waste environments. Nat Biotechnol 18:85–90

Brinza L, Dring MJ, Gavrilescu M (2007) Marine micro and macroalgal species as bioscience for heavy metals. Environ Eng Manag J 6:237–251

Bundy JG, Paton G, Campbell CD (2012) Microbial communities in different soils types do not converge after diesel contamination. J Appl Microbiol 92:276–288

Chen XC, Wang YP, Lin Q, Shi JY, Wu WX, Chen YX (2005) Biosorption of copper (II) and zinc (II) from aqueous solution by *Pseudomonas putida* CZ1. Colloids Surf B Biointerfaces 46:101–107

Chen M, Xu P, Zeng G, Yang C, Huang D, Zhang J (2015) Bioremediation of soils contaminated with polycyclic aromatic hydrocarbons, petroleum, pesticides, chlorophenols and heavy metals by composting: applications, microbes and future research needs. Biotechnol Adv 33:745–755

Christoforidis A, Orfanidis S, Papageorgiou S, Lazaridou A, Favvas E (2015) Mitropoulos, study of Cu (II) removal by *Cystoseira crinitophylla* biomass in batch and continuous flow biosorption. Chem Eng J 277:334–340

Das N, Vimala R, Karthika P (2008) Biosorption of heavy metals—an overview. Indian J Biotechnol 7:159–169

Das D, Das N, Mathew L (2010) Kinetics, equilibrium and thermodynamic studies on biosorption of Ag(I) from aqueous solution by macrofungus *Pleurotus platypus*. J Hazard Mater 184:765–774

de Groot NS, Ventura S (2006) Effect of temperature on protein quality in bacterial inclusion bodies. FEBS Lett 580:6471–6476

De Philippis R, Colica G, Micheletti E (2011) Exopolysaccharide producing cyanobacteria in heavy metal removal from water: molecular basis and practical applicability of the biosorption process. Appl Microbiol Biotechnol 92:697–708

Demey H, Vincent T, Guibal E (2018) A novel algal-based sorbent for heavy metal removal. Chem Eng J 332:582–595

Deng L, Su Y, Su H, Wang X, Zhu X (2007) Sorption and desorption of lead (II) from wastewater by green algae *Cladophora fascicularis*. J Hazard Mater 14:220–225

Dhal B, Pandey BD (2018) Mechanism elucidation and adsorbent characterization for removal of Cr (VI) by native fungal adsorbent. Sustainable Environ Res 28:289–297

Dhanarani S, Viswanathan E, Piruthiviraj P, Arivalagan P, Kaliannan T (2016) Comparative study on the biosorption of aluminum by free and immobilized cells of *Bacillus safensis* KTSMBNL 26 isolated from explosive contaminated soil. J Taiwan Inst Chem Eng 69:61–67

Diep P, Mahadevan R, Yakunin AF (2018) Heavy metal removal by bioaccumulation using genetically engineered microorganisms. Front Bioeng Biotechnol 6:157. https://doi.org/10.3389/fbioe.2018.00157

Dursun AY, Uslu G, Cuci Y, Aksu Z (2003) Bioaccumulation of copper(II), lead(II) and chromium (VI) by growing *Aspergillus niger*. Process Biochem 38:1647–1651

Ehrlich HL (2002) Geomicrobiology, 4th edn. Marcel Dekker Publisher, New York

Emamverdian A, Ding Y, Mokhberdoran F, Xie Y (2015) Heavy metal stress and some mechanisms of plant defense response. Sci World J 2015:e756120

Emenike CU, Agamuthu P, Fauziah S (2017) Sustainable remediation of heavy metal polluted soil: a biotechnical interaction with selected bacteria species. J Geochem Explor 182:275–278

EPA (2006) Engineering issue: in situ and ex situ biodegradation technologies for remediation of contaminated sites, vol 62. EPA, Washington, DC, pp 6–15

Fadel M, Hassanein NM, Elshafei MM, Mostafa AH, Ahmed MA, Khater HM (2017) Biosorption of manganese from groundwater by biomass of *Saccharomyces cerevisiae*. HBRC J 13:106–113

Fan T, Liu Y, Feng B, Zeng G, Yang C, Zhou M, Zhou H, Tan Z, Wang X (2008) Biosorption of cadmium (II), zinc(II) and lead(II) by *Penicillium simplicissimum*: isotherms, kinetics and thermodynamics. J Hazard Mater 160:655–661

Fang LC, Huang QY, Wei X, Liang W, Rong XM, Chen WL, Cai P (2010) Microcalorimetric and potentiometric titration studies on the adsorption of copper by extracellular polymeric substances (EPS) minerals and their composites. Bioresour Technol 101:5774–5779

Fashola MO, Ngole-Jeme VM, Babalola OO (2016) Heavy metal pollution from gold mines: environmental effects and bacterial strategies for resistance. Int J Environ Res Public Health 13:1047

Fauziah SH, Agamuthu P, Hashim R, Izyani AK, Emenike CU (2017) Assessing the bioaugmentation potentials of individual isolates from landfill on metal-polluted soil. Environ Earth Sci 76:401

Fomina M, Gadd GM (2014) Biosorption: current perspectives on concept, definition and application. Bioresour Technol 160:3–14. https://doi.org/10.1016/j.biortech.2013.12.102

Fourest E, Canal C, Roux J (1994) Improvement of heavy metal biosorption by mycelial dead biomass (*Rhizopus arrhizus*, *Mucor miehei*, *Penicillium chrysogenum*): pH control and cationic activation. FEMS Microbiol Rev 14:325–332

Francová A, Chrastný V, Sillerov H, Vítkov M, Kocourkov J, Komarek M (2017) Evaluating the suitability of different environmental samples for tracing atmospheric pollution in industrial areas. Environ Pollut 220:286–297

Fu YQ, Li S, Zhu HY, Jiang R, Yin LF (2012) Biosorption of copper (II) from aqueous solution by mycelial pellets of *Rhizopus oryzae*. Afr J Biotechnol 11:1403–1411

Gadd GM (2010) Metals, minerals and microbes: geomicrobiology and bioremediation. Microbiol. Reading Engl 156:609–643

Gong R, Ding Y, Liu H, Chen Q, Liu Z (2005) Lead biosorption and desorption in intact and procreated *Spirulina maxima* biomass. Chemosphere 58:125–130

Govarthanan M, Mythili R, Selvankumar T, Kamala-Kannan S, Rajasekar A, Chang Y-C (2016) Bioremediation of heavy metals using an endophytic bacterium Paenibacillus sp. RM isolated from the roots of *Tridax procumbens*. 3 Biotech 6:242

Gu Y, Xu W, Liu Y, Zeng G, Huang J, Tan X, Jian H, Hu X, Li F, Wang D (2015) Mechanism of Cr (VI) reduction by *Aspergillus niger*: enzymatic characteristic, oxidative stress response, and reduction product. Environ Sci Pollut Res Int 22:6271–6279

Guine V, Spadini L, Sarret G, Muris M, Delolme C, Gaudet JP, Martins JM (2006) Zinc sorption to three gram-negative bacteria: Combined titration, modeling and EXAFS study. Environ Sci Technol 40:1806–1813

Gunasekaran P, Muthukrishnan J, Rajendran P (2003) Microbes in heavy metal remediation. Indian J Exp Biol 41:935–944

Gundacker C, Gencik M, Hengstschlager M (2010) The relevance of the individual genetic background for the toxicokinetics of two significant neuro developmental toxicants: mercury and lead. Mutat Res Rev Mutat Res 705:130–140

Gunther A, Raff J, Geipel G, Bernhard G (2008) Spectroscopic investigations of U(VI) species sorbed by the green algae Chlorella vulgaris. Biometals 21:333–341

Gupta VK, Rastogi A (2008) Equilibrium and kinetic modeling of cadmium(II) biosorption by non-living algal biomass *Oedogonium* sp. from the aqueous phase. J Hazard Mater 153:759–766

Gupta VK, Rastogi A, Nayak A (2010) Biosorption of nickel onto treated alga (*Oedogonium hatei*): application of isotherm and kinetic models. J Colloid Interface Sci 342:533–539

Haferburg G, Kothe E (2007) Microbes and metals: interactions in the environment. J Basic Microbiol 47:453–467

Han X, Wong YS, Tam NF (2006) Surface complexation mechanism and modeling in Cr(III) biosorption by a microsomal isolate, *Chlorella miniata*. J Colloid Interface Sci 303:365–371

Haq F, Butt M, Ali H, Chaudhary HJ (2016) Biosorption of cadmium and chromium from water by endophytic *Kocuria rhizophila*: equilibrium and kinetic studies. Desalin Water Treat 57:19946–19958

Hlihor RM, Figueiredo H, Tavares T, Gavrilescu M (2017) Biosorption potential of dead and living Arthrobacter viscosus biomass in the removal of Cr (VI): batch and column studies. Process Saf Environ Prot 108:44–56

Huang W, Liu Z (2013) Biosorption of Cd(II)/Pb(II) from aqueous solution by biosurfactant-producing bacteria: isotherm kinetic characteristic and mechanism studies. Colloids Surf B Biointerfaces 105:113–119

Huang CP, Westman D, Quirk K, Huang JP, Morehart AL (1988) Removal of cadmium (11) from dilute solutions by fungal biomass. Part Sci Technol 6:405–419

Huang M, Pan J, Zheng L (2001) Removal of heavy metals from aqueous solutions using bacteria. J Shanghai Univ 5(3):253–259

Huang F, Dang Z, Guo CL, Lu CN, Gu RR, Liu H, Zhang H (2013) Biosorption of Cd (II) by live and dead cells of *Bacillus cereus* RC-1 isolated from cadmium contaminated soil. Colloids Surf B: Biointerfaces 107:11–18

Ibrahim ABM, Mahmoud GA-E (2019) Nonstoichiometric mesoporous Cu 1.90 S nanoparticles hydrothermally prepared from a copper anthranilato complex inhibit cellulases of phytopathogenic fungi. J Inorg Organomet Polym Mater 29(4):1280–1287

Ibrahim ABM, Mahmoud GA-E (2020) Chemical- vs sonochemical-assisted synthesis of ZnO nanoparticles from a new zinc complex for improvement of carotene biosynthesis from *Rhodotorula toruloides* MH023518. Appl Organomet Chem 2020:e6086

Ibrahim ABM, Zidan ASA, Aly AAM, Mosbah HK, Mahmoud GA-E (2020) Mesoporous cadmium sulfide nanoparticles derived from a new cadmium anthranilato complex: characterization

and induction of morphological abnormalities in pathogenic fungi. Appl Organomet Chem 2019:e5391
Islam E, Yang XE, He ZL, Mahmood Q (2007) Assessing potential dietary toxicity of heavy metals in selected vegetables and food crops. J Zhejiang Univ Sci B 8:1–13
Jacob JM, Karthik C, Saratale RG, Kumar SS, Prabakar D, Kadirvelu K, Pugazhendhi A (2018) Biological approaches to tackle heavy metal pollution: a survey of literature. J Environ Manag 217:56–70
Jalali RR, Ghalocerian H, Asef Y, Dalir ST, Sahafipour MH, Gharanjik BM (2004) Biosorption of cesium by native and chemically modified biomass of marine algae: introduce the new biologist for biotechnology application. J Hazard Mater 116:125–134
Jencarova J, Luptakova A (2012) The elimination of heavy metal ions from waters by biogenic iron sulphides. Chem Eng Res Des 28:205–210
Jin Y, Yu S, Teng C, Song T, Dong L, Liang J, Bai X, Xu X, Qu J (2017) Biosorption characteristic of Alcaligenes sp. BAPb.1 for removal of lead(II) from aqueous solution. 3 Biotech 7:123
Jing Y, He Z, Yang X (2007) Role of soil rhizobacteria in phytoremediation of heavy metal contaminated soils. J Zhejiang Univ Sci 8:192–207
Kang CH, So JS (2016) Heavy metal and antibiotic resistance of ureolytic bacteria and their immobilization of heavy metals. Ecol Eng 97:304–312
Kang CH, Oh SJ, Shin Y, Han SH, Nam IH, So JS (2015) Bioremediation of lead by ureolytic bacteria isolated from soil at abandoned metal mines in South Korea. Ecol Eng 74:402–407
Karakagh RM, Chorom M, Motamedi H, Yuse Kalkhajeh YK, Oustan S (2012) Biosorption of Cd and Ni by inactivated bacteria isolated from agricultural soil treated with sewage sludge. Ecohydrol Hydrobiol 12(3):191–198
Kariuki Z, Kiptoo J, Onyancha D (2017) Biosorption studies of lead and copper using rogers mushroom biomass "*Lepiota hystrix*". J Chem Eng 23:62–70
Karthik C, Oves M, Thangabalu R, Sharma R, Santhosh SB, Indra Arulselvi P (2016) *Cellulosimicrobium funkei*-like enhances the growth of *Phaseolus vulgaris* by modulating oxidative damage under Chromium(VI) toxicity. J Adv Res 7:839–850
Karthik C, Barathi S, Pugazhendhi A, Ramkumar VS, Thi NBD, Arulselvi PI (2017) Evaluation of Cr(VI) reduction mechanism and removal by *Cellulosimicrobium funkei* strain AR8, a novel haloalkaliphilic bacterium. J Hazard Mater 333:42–53
Khadivinia E, Sharafi H, Hadi F, Zahiri HS, Modiri S, Tohidi A, Mousavi A, Salmanian AH, Noghabi KA (2014) Cadmium biosorption by a glyphosate-degrading bacterium, a novel biosorbent isolated from pesticide-contaminated agricultural soils. J Ind Eng Chem 20:4304–4310
Khalil MM, Abou-Shanab RA, Salem ANM, Omer AM, Aboelazm TA (2016) Biosorption of trivalent chromium using Ca-alginate immobilized and alkalitreated biomass. J Chem Sci Technol. https://doi.org/10.5963/JCST0501001
Khan MA, Rao RAK, Ajmal M (2008) Heavy metal pollution and its control through non-conventional adsorbents (1998-2007): a review. J Int Environ Appl Sci 3:101–141
Khan MS, Zaidi A, Wani PA, Oves M (2009) Role of plant growth promoting rhizobacteria in the remediation of metal contaminated soils. Environ Chem Lett 7:1–19
Kim IH, Choi JH, Joo JO, Kim YK, Choi JW, Oh BK (2015) Development of a microbe-zeolite carrier for the effective elimination of heavy metals from seawater. J Microbiol Biotechnol 25:1542–1546
Kiyono M, Sone Y, Nakamura R, Pan-Hou H, Sakabe K (2009) The Mer E protein encoded by transposon Tn21 is a broad mercury transporter in Escherichia coli. FEBS Lett 583:1127–1131
Kumar KS, Dahms HU, Won EJ, Lee JS, Shin KH (2015a) Microalgae-a promising tool for heavy metal remediation. Ecol Environ Saf 113:329–352
Kumar S, Dubey RS, Tripathi RD, Chakrabarty D, Trivedi PK (2015b) Omics and biotechnology of arsenic stress and detoxification in plants: current updates and prospective. Environ Int 74:221–230

Kumar P, Kim KH, Bansal V, Lazarides T, Kumar N (2017) Progress in the sensing techniques for heavy metal ions using nanomaterials. J Ind Eng Chem 54:30–43

Kumari P, Rastogi A, Shukla A, Srivastava S, Yadav S (2018) Prospects of genetic engineering utilizing potential genes for regulating arsenic accumulation in plants. Chemosphere 211:397–406

Kuppusamy S, Thavamani P, Venkateswarlu K, Lee YB, Naidu R, Megharaj M (2017) Remediation approaches for polycyclic aromatic hydrocarbons (PAHs) contaminated soils: technological constraints, emerging trends and future directions. Chemosphere 168:944–968

Kushwaha A, Hans N, Kumar S, Rani R (2018) A critical review on speciation, mobilization and toxicity of lead in soil-microbe-plant system and bioremediation strategies. Ecotoxicol Environ Saf 147:1035–1045

Lau PS, Lee HY, Tsang CCK, Tam NFY, Wong YS (1999) Effect of metal interference, pH and temperature on Cu and Ni biosorption by Chlorella vulgaris and Chlorella miniata. Environ Technol 20:953–961

Liu HL, Chen BY, Lan YW, Chen YC (2004) Biosorption of Zn (II) and Cu (II) by the indigenous *Thiobacillus thiooxidans*. Chem Eng J 97:195–201

Liu S, Zhang F, Chen J, Sun GX (2011) Arsenic removal from contaminated soil via biovolatilization by genetically engineered bacteria under laboratory conditions. J Environ Sci 23:1544–1550

Lovley DR, Phillips EJP (1988) Novel mode of microbial energy metabolism: organic carbon oxidation to dissimilatory reduction of iron or manganese. Appl Environ Microbiol 54:1472–1480

Lu WB, Shi JJ, Wand CH, Chang JS (2005) Biosorption of lead, copper and cadmium by an indigenous isolate *Enterobacter* sp. J1 processing high heavy metal resistance. J Hazard Mater 134:80–86

Ma Y, Oliveira RS, Freitas H, Zhang C (2016) Biochemical and molecular mechanisms of plant-microbe-metal interactions: relevance for phytoremediation. Front Plant Sci 7:918

Magnin JP, Gondrexon N, Willison JC (2014) Zinc biosorption by the purple nonsulfur bacterium *Rhodobacter capsulatus*. Can J Microbiol 60:829–837

Magyarosy A, Laidlaw RD, Kilaas R, Echer C, Clark DS, Keasling JD (2002) Nickel accumulation and nickel oxalate precipitation by *Aspergillus niger*. Appl Microbiol Biotechnol 59:382–388

Mahmoud GA-E, Bagy MMK (2019) Microbial degradation of petroleum hydrocarbons. Microbial action on hydrocarbons. Springer, Singapore

Mahmoud GA-E, Koutb MMM, Morsy FM, Bagy MMK (2015a) Mycoflora isolated from mazot and solar polluted soils in upper Egypt. Egypt J Soil Sci 55(1):15–30

Mahmoud GA-E, Koutb MMM, Morsy FM, Bagy MMK (2015b) Characterization of lipase enzyme produced by hydrocarbons utilizing fungus Aspergillus terreus. Eur J Biol Res 5 (3):70–77

Mahmoud GA-E, Zidan ASA, Aly AAM, Mosbah HK, Ibrahim ABM (2019) Calcium and strontium anthranilato complexes as effective *Fusarium moniliforme* controlling agents. Appl Organomet Chem 33(2):e4740

Mahmoud GA-E, Ibrahim ABM, Mayer P (2020a) Zn(II) and Cd(II) thiosemicarbazones for stimulation/inhibition of kojic acid biosynthesis from *Aspergillus flavus* and the fungal defense behavior against the metal complexes' excesses. JBIC 25:797–809

Mahmoud GA-E, Soltan HAH, Abdel-Aleem WM, Osman SAM (2020b) Safe natural bio-pigment production by *Monascus purpureus* using mixed carbon sources with cytotoxicity evaluation on root tips of *Allium cepa* L. J Food Sci Technol 2020:1–12

Mameri N, Boudries N, Addour L, Belhocine D, Lounici H, Grib H (1999) Batch zinc biosorption by a bacterial nonliving *Streptomyces rimosus* biomass. Water Res 33:1347–1354

Manafi Z, Abdollahi H, Majd MZ, Golbang N, Emtiazi G, Olson GJ (2012) Isolation and identification of microorganisms causing microbial degradation of organic phase of the solvent extraction unit in the copper industries. Int J Miner Process 112:43–48

Mao J, Won SW, Yun YS (2013) Development of poly (acrylic acid)-modified bacterial biomass as a high-performance biosorbent for removal of Cd (II) from aqueous solution. Ind Eng Chem Res 52:6446–6452

Markou G, Mitrogiannis D, Celekli A, Bozkurt H, Georgakakis D, Chrysikopoulos CV (2015) Biosorption of Cu2+ and Ni2+ on *Arthrospira platensis* with different biochemical compositions. Chem Eng J 259:806–813

Mendez A, Paz-Ferreiro J, AraujoF GG (2014) Biochar from pyrolysis of deinking paper sludge and its use in the treatment of a nickel polluted soil. J Anal Appl Pyrolysis 107:46–52

Merrin JS, Sheela R, Saswathi N, Prakasham RS, Ramakrishna SV (1998) Biosorption of chromium (VI) using *Rhizopus arrhizus*. Indian J Exp Biol 36:1052–1055

Micheletti E, Colica G, Viti C, Tamagini P, De Philippis R (2008) Selectivity in the heavy metal removal by exopolysaccharide producing cyanobacteria. J Appl Microbiol 105:88–94

Mishra A, Malik A (2013) Recent advances in microbial metal bioaccumulation. Crit Rev Environ Sci Technol 43:1162–1222

Mohamed MH, Mahmoud GA-E (2018) Microbial gibberellins impact of on *Zea mays* (L.) plants under different levels of water salinity. Egypt J Soil Sci 58(3):373–382

Mohsenzadeh F, Shahrokhi F (2014) Biological removing of Cadmium from contaminated media by fungal biomass of *Trichoderma* species. J Environ Health Sci Eng 12:102

Mondal NK, Samanta A, Dutta S, Chattoraj S (2017) Optimization of Cr(VI) biosorption onto *Aspergillus niger* using 3-level Box-Behnken design: equilibrium, kinetic, thermodynamic and regeneration studies. J Genet Eng Biotechnol 15:151–160

Monteiro CM, Castro PML, Malcata FX (2009) Use of the macroglia *Scenedesmus obliquus* to remove cadmium cations from aqueous solutions. World J Microbiol Biotechnol 25:1573–1578

Monteiro CM, Castro PML, Malcata FX (2012) Metal uptake by microcode: underlying mechanisms and practical applications. Biotechnol Prog 28:299–311

Mrozik A, Miga S, Piotrowska-Seget Z (2011) Enhancement of phenol degradation by soil bioaugmentation with *Pseudomonas* sp. JS150. J Appl Microbiol 111:1357–1370

Mullen MD, Wolf DC, Beveridge TJ, Balley GW (1992) Sorption of heavy metals by the soil fungi *Aspergillus niger* and *Mucor rouxii*. Soil Biol Biochem 24:129–135

Muszynska E, Labudda M, Rozanska E, Hanus-Fajerska E, Znojek E (2018) Heavy metal tolerance in contrasting ecotypes of Alyssum montanum. Ecotoxicol Environ Saf 161:305–317

Muter O, Lubinya I, Millers D, Grigorjeva L, Ventinya E, Rapoport A (2002) Cr(VI) sorption by intact and dehydrated Candida utilis cells in the presence of other metals. Process Biochem 38:123–131

Nafady NA, Bagy MMK, Abd-Alla MH, Morsy FM, Mahmoud GA-E (2015) Improvement of medium components for high riboflavin production by *Aspergillus terreus* using response surface methodology. Rendiconti Lincei 26(3):335–344

Nagashetti V, Mahadeva Raju GK, Muralidhar TS, Javed A, Trivedi D, Bhusal KP (2013) Biosorption of heavy metals from soil by Pseudomonas aeruginosa. Int J Innov Technol Exp Eng 2(6):9–17

Naik UC, Srivastava S, Thakur IS (2012) Isolation and characterization of *Bacillus cereus* IST105 from electroplating effluent for detoxification of hexavalent chromium. Environ Sci Pollut Res 19:3005–3014

Nanda M, Sharma D, Kumar A (2011) Isolation and characterisation of bacteria resistant to heavy metals cadmium (Cd), arsenic (As), mercury (Hg) from industrial effluent. Glob J Appl Environ Sci 2:127–132

Ng SP, Davis B, Polombo EA, Bhave M (2009) Tn 5051 like mer containing transposon identified in a heavy metal tolerant strain *Achromobacter* sp. AO22. BMC Res Notes 7:2–38

Niu H, Xu SX, Wang JH, Volesky B (1993) Removal of lead from aqueous solutions by *Penicillium biomass*. Biotechnol Bioeng 42:785–797

Oves M, Khan MS, Zaidi A (2013) Chromium reducing and plant growth promoting novel strain *Pseudomonas aeruginosa* OSG41 enhance chickpea growth in chromium amended soils. Eur J Soil Biol 56:72–83

Oves M, Saghir Khan M, Huda Qari A, Nadeen Felemban M, Almeelbi T (2016) Heavy metals: biological importance and detoxification strategies. J Bioremed Biodegr 7:334

Panda J, Sarkar P (2012) Bioremediation of chromium by novel strains *Enterobacter aerogenes* T2 and *Acinetobacter* sp. PD 12 S2. Environ Sci Pollut Res 19:1809–1817

Park JK, Choi SB (2002) Metal recovery using immobilized cell suspension from a brewery. Korean J Chem Eng 19:68–74

PeralesVela HV, Pena Castro JM, Canizares Villanueva RO (2006) Heavy metal detoxification in eukaryotic microcode. Chemosphere 64:1–10

Poo KM, Son EB, Chang JS, Ren X, Choi Y, Chae K (2018) Biochars derived from wasted marine macro-algae (*Saccharina japonica* and *Sargassum fusiforme*) and their potential for heavy metal removal in aqueous solution. J Environ Manag 206:364–372

Purchase D, Scholes LN, Revitt DM, Shutes RBE (2009) Effects of temperature on metal tolerance and the accumulation of Zn and Pb by metal-tolerant fungi isolated from urban runoff treatment wetlands. J Appl Microbiol 106:1163–1174

Puyen ZM, Villagrasa E, Maldonado J, Diestra E, Esteve I, Sole A (2012) Biosorption of lead and copper by heavy-metal tolerant *Micrococcus luteus* DE2008. Bioresour Technol 126:233–237

Quiton KG, Doma B, Futalan CM, Wan M (2018) Removal of chromium (VI) and zinc (II) from aqueous solution using kaolin-supported bacterial biofilms of Gram-negative E. coli and Gram-positive Staphylococcus epidermidis. Environ Res 28:206–213

Raja CP, Jacob JM, Balakrishnan RM (2015) Selenium biosorption and recovery by marine *Aspergillus terreus* in an upflow bioreactor. J Environ Eng 142:C4015008

Ramrakhiani L, Majumder R, Khowala S (2011) Removal of hexavalent chromium by heat inactivated fungal biomass of *Termitomyces clypeatus*: surface characterization and mechanism of biosorption. Chem Eng J 171:1060–1068

Rani A, Goel R (2009) Strategies for crop improvement in contaminated soils using metal-tolerant bioinoculants. In: Khan MS, Zaidi A, Musarrat J (eds) Microbial strategies for crop improvement. Springer, Berlin, pp 105–132

Romera E, Gonzalez F, Ballester A, Blazquez ML, Munoz JA (2007) Comparative study of biosorption of heavy metals using different types of algae. Bioresour Technol 98:3344–3353

Rugnini L, Costa G, Congestri R, Antonaroli S, di Toppi LS, Bruno L (2018) Phosphorus and metal removal combined with lipid production by the green microalga *Desmodesmus* sp.: an integrated approach. Plant Physiol Biochem 125:45–51

Salehizadeh H, Shojaosadati SA (2003) Removal of metal ions from aqueous solution by polysaccharide produced from *Bacillus firmus*. Water Res 37:4231–4235

Samarth DP, Chandekar CJ, Bhadekar RK (2012) Biosorption of heavy metals from aqueous solution using *Bacillus licheniformis*. Int J Pure Appl Sci Technol 10(2):12–19

Samuel J, Paul ML, Pulimi M, Nirmala MJ, Chandrasekaran N, Mukherjee A (2012) Hexavalent chromium bioremoval through adaptation and consortia development from sukinda chromite mine isolates. Ind Eng Chem Res 51:3740–3749

Sasaki Y, Minakawa T, Miyazaki A, Silver S, Kusano T (2005) Functional dissection of a mercuric ion transporter Mer C from *Acidithiobacillus ferrooxidans*. Biosci Biotechnol Biochem 69:1394–1402

Schut S, Zauner S, Hampel G, Konig H, Claus H (2011) Biosorption of copper by wine-relevant *lactobacilli*. Int J Food Microbiol 145:126–131

Shahid M, Dumat C, Khalid S, Schreck E, Xiong T, Niazi NK (2017) Foliar heavy metal uptake, toxicity and detoxification in plants: a comparison of foliar and root metal uptake. J Hazard Mater 325:36–58

Shanab S, Essa A, Shalaby E (2012) Bioremoval capacity of three heavy metals by some microcode species (Egyptian Isolates). Plant Signal Behav 7:392–399

Shi T, Ma J, Wu X, Ju T, Lin X, Zhang Y, Li X, Gong Y, Hou H, Zhao H, Wu F (2018) Inventories of heavy metal inputs and outputs to and from agricultural soils: a review. Ecotoxicol Environ Saf 164:118–124

Siddiquee S, Rovina K, Azad SA, Naher L, Suryani S, Chaikaew P (2015) Heavy metal contaminants removal from wastewater using the potential filamentous fungi biomass: a review. J Microb Biochem Technol 7:384–393

Sikander S, Khansa M, Mohammad F (2012) Uptake of toxic Cr (VI) by biomass of exopolysaccharides producing bacterial strains. Afr J Microbiol Res 6:3329–3336

Singh S, Kang SH, Mulchandani A, Chen W (2008) Bioremediation: environmental cleanup through pathway engineering. Curr Opin Biotechnol 19:437–444

Singh R, Chadetrik R, Kumar R, Bishnoi K, Bhatia D, Kumar A, Bishnoi NR, Singh N (2010) Biosorption optimization of lead(II), cadmium(II) and copper(II) using response surface methodology and applicability in isotherms and thermodynamics modeling. J Hazard Mater 174:623–634

Singh TP, Goel S, Majumder C (2018) Biosorption of heavy metals by acclimated microbial species, *Acinetobacter baumannii*. Innovare J Life Sci 6:5–9

Sinha A, Pant KK, Khare SK (2012) Studies on mercury bioremediation by alginate immobilized mercury tolerant *Bacillus cereus* cells. Int Biodeterior Biodegrad 71:1–8

Sobol Z, Schiestl RH (2012) Intracellular and extracellular factors influencing Cr(VI) and Cr(III) genotoxicity. Environ Mol Mutagen 53:94–100

Spormann AM, Widdel F (2000) Metabolism of alkylbenzenes, alkanes, and other hydrocarbons in anaerobic bacteria. Biodegradation 11:85–105

Srinath T, Verma T, Ramteke PW, Garg SK (2002) Chromium (VI) biosorption and bioaccumulation by chromate resistant bacteria. Chemosphere 48:427–435

Sriprang R, Hayashi M, Ono H, Takagi M, Hirata K, Murooka Y (2003) Enhanced accumulation of Cd2+ by a *Mesorhizobium* sp. transformed with a gene from Arabidopsis thaliana coding for phytochelatin synthase. Appl Environ Microbiol 69:1791–1796

Sudha Bai R, Abraham TE (2001) Biosorption of Cr (VI) from aqueous solution by *Rhizopus nigricans*. Bioresour Technol 79:73–81

Sulaymon AH, Mohammed AA, Al-Musawi TJ (2012) Competitive biosorption of lead, cadmium, copper, and arsenic ions using algae. Environ Sci Pollut Res Int 20:3011–3023

Taiwo AM, Gbadebo AM, Oyedepo JA, Ojekunle ZO, Alo OM, Oyeniran AA, Onalaja OJ, Ogunjimi D, Taiwo OT (2016) Bioremediation of industrially contaminated soil using compost and plant technology. J Hazard Mater 304:166–172

Tan T, Cheng P (2003) Biosorption of metal ions with *Penicillium chrysogenum*. Appl Biochem Biotechnol 104:119–128

Taniguchi J, Hemmi H, Tanahashi N, Amano N, Nakayama N, Nishino T (2000) Zinc biosorption by a zinc-resistant bacterium, *Brevibacterium* sp. strain HZM-1. Appl Microbiol Biotechnol 54:581–588

Thatoi H, Das S, Mishra J, Rath BP, Das N (2014) Bacterial chromate reductase, a potential enzyme for bioremediation of hexavalent chromium: a review. J Environ Manag 146:383–399

Tobin JM, Cooper DG, Neufield R (1984) Uptake of metal ions by *Rhizopus arrhizus* biomass. Appl Environ Microbiol 47:821–824

Townsley CC, Ross IS, Atkins AS (1986) Biorecovery of metallic residues from various industrial effluents using filamentous fungi. In: Lawrence RW, Branion RMR, Ebner HG (eds) Fundamental and applied biohydrometallurgy. Elsevier, Amsterdam, pp 279–289

Tsekova K, Todorova D, Dencheva V, Ganeva S (2010) Biosorption of copper(II) and cadmium (II) from aqueous solutions by free and immobilized biomass of *Aspergillus niger*. Bioresour Technol 101:1727–1731

Ueda M (2016) Establishment of cell surface engineering and its development. Biosci Biotechnol Biochem 80:1243–1253. https://doi.org/10.1080/09168451.2016.1153953

Ullah A, Heng S, Munis MFH, Fahad S, Yang X (2015) Phytoremediation of heavy metals assisted by plant growth promoting (PGP) bacteria: a review. Environ Exp Bot 117:28–40

Vardhan KH, Kumar PS, Panda RC (2019) A review on heavy metal pollution, toxicity and remedial measures: Current trends and future perspectives. J Mol Liq 290:111197

Vasudevan P, Padmavathy V, Dhingra SC (2002) Biosorption of monovalent and divalent ions on baker's yeast. Bioresour Technol 82:285–289

Venil CK, Mohan V, Lakshmanaperumalsamy P, Yerima MB (2011) Optimization of chromium removal by the indigenous bacterium *Bacillus* spp. REP02 Using the Response Surface Methodology. ISRN Microbiol 2011:951694

Verma S, Kuila A (2019) Bioremediation of heavy metals by microbial process. Environ Technol Innov 14:100369

Verma A, Shalu Singh A, Bishnoi NR, Gupta A (2013) Biosorption of Cu (II) using free and immobilized biomass of *Penicillium citrinum*. Ecol Eng 61:486–490

Volesky B, Holan ZR (1995) Biosorption of heavy metals review. Biotechnol Prog 11:235–250

Volesky B, May H (1995) Biosorption of heavy metals by *Saccharomyces cerevisiae*. Appl Microbiol Biotechnol 42:797–806

Weerasundara L, Amarasekara RWK, Magana-Arachchi DN, Ziyath AM, Karunaratne DGGP, Goonetilleke A, Vithanage M (2017) Microorganisms and heavy metals associated with atmospheric deposition in a congested urban environment of a developing country: Sri Lanka. Sci Total Environ 584(585):803–812

Wu CH, Wood TK, Mulchandani A, Chen W (2006) Engineering plant-microbe symbiosis for rhizoremediation of heavy metals. Appl Environ Microbiol 72:1129–1134

Xu X, Hui D, King AW, Song X, Thornton PE, Zhang L (2015) Convergence of microbial assimilations of soil carbon, nitrogen, phosphorus, and sulfur in terrestrial ecosystems. Sci Rep 5:17445

Xun E, Zhang Y, Zhao J, Guo J (2018) Heavy metals in nectar modify behaviors of pollinators and nectar robbers: consequences for plant fitness. Environ Pollut 242:1166–1175

Yalcinkaya Y, Arica MY, Soysal L, Denzili A, Genc O, Bektas S (2002) Cadmium and mercury uptake by immobilized *Pleuritus spadius*. Turk J Chem 26:441–452

Yan G, Viraraghavan T (2000) Effect of pretreatment on the bioadsorption of heavy metals on *Mucor rouxii*. Watermark 26:119–124

Yan G, Viraraghavan T (2001) Heavy metal removal in a biosorption column by immobilized *Mucor rouxii* biomass. Bioresour Technol 78:243–249

Yee N, Fein JB (2001) Cd adsorption onto bacterial surfaces, a universal adsorption edge? Geochim Cosmochim Acta 65:2037–2042

Yin K, Lv M, Wang Q, Wu Y, Liao C, Zhang W, Chen L (2016) Simultaneous bioremediation and biodetection of mercury ion through surface display of carboxylesterase E2 from *Pseudomonas aeruginosa* PA1. Water Res 103:383–390

Yin K, Wanga Q, Lva M, Chen L (2019) Microorganism remediation strategies towards heavy metals. Chem Eng J 360:1553–1563

Yu Q, Kaewsarn P, Duong LV (2000) Electron microscopy study of bioscience from marine macroalgae *Durvillaea potatorum*. Chemosphere 41:589–594

Yuan L, Zhi W, Liu Y, Karyala S, Vikesland PJ, Chen X, Zhang H (2015) Lead toxicity to the performance, viability, and community composition of activated sludge microorganisms. Environ Sci Technol 49:824–830

Zouboulis AI, Loukidou MX, Matis KA (2004) Biosorption of toxic metals from aqueous solutions by bacteria strains isolated from metal-polluted soils. Process Biochem 39:909–916

Plant–Microbe Interaction in Attenuation of Toxic Wastes in Ecosystem

13

Kingsley Erhons Enerijiofi and Beckley Ikhajiagbe

Abstract

The use of plant–microbial interactions in mitigating the effect of toxic waste in the environment has increased tremendously as a result of the high success rate. This could be attributed to various survival mechanisms of plants–microbes in contaminated environment. However, important factors such as plants ability to produce biomass, active root proliferation and/or root activities with root symbiosis establishment and others determine the efficacy of phytoremediation technology which has proved to be effective. More rapidly growing plants with high phytoextraction abilities should be identified for the remediation of pollutants from soil. Plant–microbial interactions are very crucial for the sustenance of environmental sustainability through toxic waste attenuation.

Keywords

Bioremediation · Ecosystem · Plant · Microbes · Toxic wastes

K. E. Enerijiofi (✉)
Department of Biological Sciences, Samuel Adegboyega University, Ogwa, Edo State, Nigeria

Applied Environmental Bioscience and Public Health Research Group, Department of Microbiology, University of Benin, Benin, Nigeria
e-mail: kenerijiofi@sau.edu.ng

B. Ikhajiagbe
Applied Environmental Bioscience and Public Health Research Group, Department of Microbiology, University of Benin, Benin, Nigeria

Environmental Biotechnology and Sustainability Research Group, Department of Plant Biology and Biotechnology, University of Benin, Benin, Nigeria

© The Author(s), under exclusive licence to Springer Nature Singapore Pte Ltd. 2021

V. Kumar et al. (eds.), *Rhizobiont in Bioremediation of Hazardous Waste*,
https://doi.org/10.1007/978-981-16-0602-1_13

13.1 Introduction

Higher Plants live together with other biotic and abiotic components of the environment, thereby participating in a number of relationships. This is so as they cannot live in complete isolation from each other. The biotic components are the living forms of life which include microorganisms and higher animals, while the abiotic are the non-living things made up of the physical, chemical, and cultural features (Enerijiofi 2014). However, the interactions between plants, microorganisms, and other environmental constituents are quintessential for continuous survival of plants on earth as well as balance of the environment.

13.2 Plant Interaction with Soil

The interaction between plants and soil occurs in the region known as rhizosphere. However, Hiltner (1904) was first to draw attention to the scientific domain of the word rhizosphere which involves the promotion of microbial growth round the roots of leguminous plants. There exist different meanings of rhizosphere (Marschner 1995; Uren 2001). Uren (2001) defined rhizosphere as the interface between the soil and plant root which is characterized by lots of mineral nutrients, pH, redox processes, root exudates as well as lots of microorganisms which results from increased activities of microorganisms. The rhizosphere region of plants is made up of two regions; ectorhizosphere and endorhizosphere. The ectorhizosphere is the layer of soil that immediately surrounds the roots of plants while in the endorhizosphere, microorganisms colonize the internal tissues of the root. The health of soil determines the health of plant as well as humans, due largely to the dependence on its products for survival (Enerijiofi 2014). Mycorrhizae perhaps encompass the best conspicuous and nearby forms of mutualistic plant–fungal relationships (Fester et al. 2014).

13.3 Plant Interaction with Microbes

Though plant–microbial interactions are not visible to the human eye, they interact at different facets and levels. Almost, all plant organs undergo interactions with microbes at one phase or the other in their life and it is not essentially a harmful one for the plant. Plants as well as other living and non-living components make up a great chunk of diverse environments for microorganisms. The specific environments may include noxious combinations of compounds in which there may be inadequate supply of nutrients which are important in supporting the growth of microorganisms (Fester et al. 2014). The various classes of microbes like the prokaryotes and eukaryotes undergo interactions with plants and sustain their wellbeing in a variety of ways. These include enhancement of the growth of plant and harvest, control of diseases, ability to survive and recover from hostile ecological disorders such as lack of water, etc. (Adesemoye et al. 2009; Reid and Greene 2012).

They are associated with millions of other microbes. The functions of the aforementioned plant-associated microorganisms are still under investigation, though they are known to support plants which enable them withstand the abiotic and biotic stresses, thereby aiding the host in water and assimilation of other nutrients as well as the production of plant hormones, siderophores and inhibitory allelochemicals (Weyens et al. 2009a, b; Bulgarelli et al. 2013). However, under extreme contamination conditions, plants have a resilient influence on the microbial communities of soil and they are regularly in control of the building and power-driven firmness of a given system. Though in real situations, plants in association with microorganisms always seem to be the actual actors intervening the impact of plant on the transformation of contaminants (Ingham et al. 2011).

13.4 Positive Interactions Between Plant and Microbes in Soil

Series of microbes are famous in the colonization of the rhizosphere area. Though, members of the *Streptomyces* species are distinctive in a range of ways. Their pattern of growth is filamentous, colonise soil as well as plant roots and its aerial parts, dynamically yield antibiotics and save plants from attack by disease causing bacteria species, production of unsound biological compounds that are accountable for the exceptional bouquet of new forest soils. They could also be utilized as natural control mediators in numerous agrarian practices. The actual ingenious *Streptomyces* species are made use of as biofertilizer in improving the growth of plants due to their intrinsic growth-promoting proficiencies. Their ability to form endospore gives them comparative advantage in extant severe soil situations contrary to the non-spore formers in the soil. Also, *Streptomyces* species possess innate capability to produce diverse forms of lytic enzymes which provides them the ability to break caked organic mixtures which secrete nutrients that can be used by plants (Vurukonda et al. 2018). Plant growth-promoting bacteria (PGPB) can similarly be utilized in the reduction of heavy metal polluted soils. *Helianthus tuberosus* is rich in biomass and used in the production of bio-ethanol. However, when it is exposed to a specific PGPB that is secluded from plants on heavy metal polluted soil, its ability to withstand high concentrations of heavy metals increases. The bacteria were revealed to grow endophytically in the root ensuing substantial upsurge in cadmium absorption by the plant. More so, the plant exhibited a reduction of metal-induced pressure and an enhanced growth in the presence of bacteria. Thus, these PGPB can aid in remediation and in sustainable biomass production (Montalbán et al. 2017).

Perennial ryegrass, *Lolium perenne* is an essential cool-season grass specie for fallow, silage and turf with a high yield has increased harvest and upright grass excellence as well as a compact system of root, greater tillering and fast capability to regenerate itself can easily withstand drought or to high salt concentration but PGPB are known to fully support its forbearance to dearth of water and high salinity (Su et al. 2017; He et al. 2018). Su et al. (2017) opined that valuable bacterium in soil like *Bacillus amyloliquefaciens* GB03 in a relationship with water absorbent mediator which consist in super permeable hydrogels can be used for controlling

erosion in soil thereby significantly improving the ability of perennial ryegrass to withstand drought conditions. This holds true when linked to tender single components that previously were considered to improve the ability of the plant to resist drought relative to the control. In the same distinguishing method, an innovative isolated bacterium from a C4 persistent juicy xerohalophyte tree with exceptional ability to stand long absence of water and high salt concentration was made use to meaningfully enhance development and salinity forbearance of the perennial ryegrass. In addition, is the sequencing of the bacterial genome and identification of several genes supposedly associated with promoting traits during plant growth and decreasing of abiotic stress (He et al. 2018). PGPB can support the ability to withstand drought and high salinity.

Zhang et al. (2018) studied the affirmative role of *Rhizophagus irregularis* CD1 fungus as it affect growth and proliferation of plant and the Verticillium wilt resistance of cotton. They were able to study the synergistic proficiency of 17 cotton varieties to *R. irregularis* with the most efficient being Lumian 1 which was utilized in field trial for 2 years. Nevertheless, the existence of the mycorrhizal fungus considerably amplified growth of the plant and also ability to withstand plant malady against *Verticillium dahliae* wilt. However, the negative impact on *V. dahliae* presence possibly will be as a result of mycorrhiza-induced resistance which revealed that the growth of *R. irregularis* may proportionately prevent the growth of *V. dahliae* by letting loose as yet anonymous volatiles. Consequently, microbes are utilized to absolutely alter the growth abilities of plants in order to put them at a vantage position to be able to stand against biotic and abiotic pressures like lack of water and high salinity which might probably take place far more frequently with increasingly abating change in climatic conditions.

13.5 Plant–Microbial Interaction—An Overview

Plants have just lately been known as a metaorganism with a distinct microbiome and adjacent synergistic interactions with closely related microbes (Mendes et al. 2013). They are shielded by microorganisms with some pathogens while others display a helpful effect on plant growth and development. Hitherto, a few abound merely with no clear cut function in studies of microbial ecology. The plant roots are confined by a dense cover of microorganisms in the rhizosoil. Also, plant seeds are linked with the microorganisms and are famous for having intense effect on development of plant, since they are available all through seed germination which could also have a rich outcome on the ecosystem, wellbeing, and yield of plants. The microbiome of seed consists in endophytic and exophytic (Hawkins and Crawford 2018). Microorganisms are known to be powerfully effective in motivating series of important roles in soil ecosystem (Enerijiofi 2020). Microorganisms are relevant building blocks in the recycling of major nutrients and are associated with plant roots for fruitful nutrients supply as well as reducing the effect of pathogens, thereby giving support particularly for plant and animal health and generally for life on planet earth. The exceptional act and natural ingenuity of microorganisms

particularly round the growing root of plants give credibility to the series of possible valuable microbes for the growth experienced in biotechnological field. This is relevant in improving crop yield, pathogens of plants, controlling of weeds, and more feasible methods of cleaning up polluted soils. This benign and extensive use of microorganisms has lots of prowess for making chemical methods extinct. This is found to be the relevance and its profound constituent of soils. Microorganisms are also used as soil quality indicators and in good working of the ecosystem (Enerijiofi 2020; Sherwood and Uphoff 2000).

13.6 Factors Affecting Interactions

Plant–microbial inter-relationship is implicated in the degradation of bulky quantities of contaminated waste arising from their possession of genetic metabolic machinery and their capability to withstand punitive environments. Consequently, they are a main actor in the cleanup of sites polluted with toxic wastes. Nevertheless, their potential to perform is reliant on various factors, though not limited to contaminant concentration and its chemical constituents, ability of plant–microbe interaction, and physicochemical characteristics of the location (Joutey et al. 2013). So, dynamics that affects the level of contaminants breakdown by interaction between plant and microbes is linked to plant–microbe and their nutritive supplies or related with the surrounding factors (Joutey et al. 2013).

13.6.1 Soil Factors

One of the chief ecological duties carried out by soil is filtration, others are buffering and transformation of contaminants of either organic or inorganic pollutants. This very important role guarantees worthy quality of underground water and safe production of food. When contaminants find their way to soil, they undergo series of reactions such as physicochemical, microbiological, and biochemical processes that keep, diminish, or lower their destructive capabilities. Essential characteristics of soil that affect the behaviour of pollutants encompass soil texture, quantity of soil organic matter, pH, levels of moisture, and temperature. The characteristics of soil pollutants besides are important. These include size, solubility, charge distribution, and molecular structure.

13.6.2 Plant Factors

Soils play host to series of minute forms of life. These include all classes of microorganisms viz-a-viz bacteria, fungi, nematodes, viruses, etc. The rhizosphere region, where the root of plants interacts with soil is known to contain the highest quantity of bacteria species (Ho et al. 2017). Nevertheless, the diversity of soil bacteria affects soils in any of the three means. The inter-relationship existing

between soil bacteria and soil may be helpful, detrimental, or unbiased (Weyens et al. 2009a, b). The PGPB include the free living, those with explicit harmonious inter-relationships with plants, e.g. *Cyanobacteria*. PGPB can support the growth of plant openly by empowering the capacity to have a hold on controlling the levels of plant hormone and secondarily by decreasing the resistance impact of pathogenicity and plant growth by standing in as proxies of biocontrol (Glick 2012).

13.6.3 Climate Factor

The change in global climatic condition is linked with lots of factors including increase in atmospheric temperature and high concentration of carbon (iv) oxide (Srivastava et al. 2014). The community of microbes in soil environment is known to play important function in cycling of carbon as microorganisms have enlarged potential to degrade organic matter in soil at high carbon (iv) oxide and nutrient concentration which are primarily affected by biotic and abiotic factors. There are no proof that can be traced to the influence of change in climatic condition on bioremediation except the physicochemical parameters which have influence on the metabolic process of the microbial community thereby affecting bioremediation (Sowerby et al. 2005; Castro et al. 2010; Srivastava et al. 2014). The extracellular enzymes production by microorganisms could be attributed to the microbial activities and physicochemical characteristics of the soil environment which are affected by the climatic conditions (Sowerby et al. 2005; Enerijiofi 2020). A study reported that an increase in temperature arising from change in climatic conditions positively boosts the community of microorganisms to properly utilize recalcitrant compounds in soil (Bardgett et al. 2008; Frey et al. 2013). Also, increase in the concentration of carbon (iv) oxide is directly proportionate to the bacterial richness and indirectly proportionate to the fungal richness (Frey et al. 2008; Castro et al. 2010). The reduction in fungal biomass at elevated temperature and during dry seasons is responsible for the reduction in the fungal/bacterial biomass ratio in soil (Sowerby et al. 2005). This showed reduced degree of organic matter recycling in the environment which in addition distorts the normal course of degradation by indigenous microorganisms that are skilled at cometabolic reaction in breaking down precarious compounds made possible by the availability of natural carbon. Baldrian et al. (2013) predicted that metabolic activities of microbes rise significantly if the temperature of soil increases arising from change in global climatic conditions.

13.6.4 Microbial Factors

The catabolic and anabolic abilities of microorganisms are referred to as microbial factor. The biotic factors influencing microorganism destructive activities of biological combinations have uninterrupted hindrance to enzymatic activities and multiplication routes of microbes involved in the degradation process. For example, inhibition can take place when there is struggle between microbes for limited

resources like carbon, hostile inter-relationships between microbes, or the predation of microbes by bacteriophages and protozoa (Riser-Roberts 1998). The extent of breakdown of precarious waste is mainly due to the quantity of the toxic material as well as the catalytic agent that is available for the process to take place. In furtherance of the aforementioned, the extent to which the toxic waste is degraded is mostly due to the capability of the specific enzymes implicated, affinity for the toxic waste as well as the degree of the bioavailable fractions (Enerijiofi 2020). Also, adequate quantities of oxygen and nutrients should be present in readily available form as well as in precise amounts as this support the substantial growth and multiplication of microorganisms (Riser-Roberts 1998).

13.6.5 Environmental Factors

The soil type and the concentration of organic matter play important function in the capability of the noxious waste to adsorb to the compact surface of the soil. In absorption which is a corresponding procedure, toxic waste infiltrates into the major mass of the soil medium. However, both adsorption and absorption reduce the accessibility of the toxic waste to a greater chuck of plant and microbes interactions at the rhizosphere region and the degree of element absorbed is directly condensed. In the soil matrix, the ability of passing on gases like oxygen, carbon (iv) oxide, and methane is reduced in finely coarse soils and sediments and also when soils are water logged which arises from poor porosity. They also affect plant and microbial growth which regulates the degree and kind of biodegradation that occurs. The reduction–oxidation prowess of a soil is the ability of its electron compactness of the system. Energy is gained through the breakdown of compounds in which electrons are conveyed from one oxidized compound to another during electron transport chain known as electron acceptors. A low electron mass with Eh $>$ 50 mV specifies breaking down and aerobic situations, while high electron mass (Eh $<$ 50 mV) points to reduction and anaerobic conditions. Series of other additional environmental factors that affect biodegradation rate of toxic waste are temperature, pH, and moisture. Biological enzymes that have an important function in degradation pathway need an optimum temperature for best performance, below or above the optimum temperature is a proportionate degradation metabolic rate (van der Heul 2009). According to Riser-Roberts (1998), the degree of breaking down declines approximately by 50% for each 10 °C diminution in temperature. In terms of pH, breakdown takes place in a wide range, but, a pH range of 6.5–8.5 is mostly best for biodegradation process in most terrestrial and aquatic environments. The water content performs a very important function in the metabolism of toxic waste in the ecosystem because it regulates the solubility, type, and amount of decipherable materials as well as the growth of the microorganisms that partake in the process, osmotic pressure as well as pH of both aquatic and terrestrial ecosystem (Cases and de Lorenzo 2005).

13.6.6 Biological Factors

These are only noticeable when bioremediation techniques are being implemented. However, there exist many intrinsic characteristics of microorganisms that perform roles in the degradation of substrate. Example is plasmid-encoded genes that make available the exact enzyme for the specific substrates but, naturally, it has been known that microorganisms mostly bacteria have different specificity for diverse nutrients (Mars et al. 1997). The control of chemotaxis by bacterial cells places them at a vantage position to be able to degrade obstinate biological molecules (Pandey and Jain 2002). It is worthy to note that the use of single isolate is not as active as microbial communities in accomplishing comprehensive degradation of xenobiotic compounds. The microbial communities required for bioremediation is mostly reliant on complex interactions. Maphosa et al. (2010) posited that metagenomics which encompasses genome sequencing aid in making data available regarding the species of microorganisms that contribute to substrate degradation. More so, the peak of microbial growth conditions cannot be determined (Ingham et al. 2007). Microbes are important in ensuring proficiency in the working of ecologies on earth and issues influencing growth, development, arrangement, and richness of microorganisms and microbial populations may perturb the biomes (Nweke et al. 2007). Chakraborty et al. (2012) posited that Allelopathic response of plants in the terrestrial environment on the community of microorganisms may affect the degradative abilities of soil microorganisms negatively. Aerobic degradative actions of microbes are restricted by organic carbon solubility and lack of oxygen. However, certain microorganisms can utilize supplementary sources of biological carbon, electron acceptor, and energy as cometabolic substrates in so doing degrading the recalcitrants compounds, e.g. *Mycobacterium gilvum* can breakdown pyrene in the presence of oxygen in the rhizosphere of *Phragmites australis* concurrently with the breakdown of benzo(a)pyrene (Toyama et al. 2011). Pandey and Jain (2002) opined that injurious pressure applied by toxics on microorganisms quickly modifies their enzymes which play vital function in microbial degradation of refractory compounds.

13.7 Microbial Diversity Implicated in Plant Interactions

A lot of studies have documented a number of microorganisms that are implicated in plant–microbe interactions (Montesinos et al. 2002; Garbeva et al. 2004; Vimal et al. 2017). Microbes found in soil are important in the preservation of soil role in both regular and succeeded agrarian soils arising from their involvement in significant practices like soil structure formation, decomposition of organic compounds, toxins elimination, and recycling of nutrients like carbon, etc. (van Elsas and Trevors 1997). Also, microbes perform important function in subduing soil borne diseases of plant, encouraging plant growth and fluctuations in flora.

Though microbiologists had studied the influence of different microorganisms on the firmness of environment role since the 1960s, Harrison et al. (1968) stated that

there is now intensified attention of its influence on functioning and resilience of the ecology to turbulences in soil ecosystems. Microorganisms have established quite a number of approaches to ensure successful acclimatization to the environment of the plant, together with helpful or harmful interrelationships. Valuable interrelationships are triggered by synergetic or non-synergetic bacteria and by a very specific kind of fungi, the mycorrhizae. The harmful interrelationships of microorganisms with plants comprise different microbial types with contagious diseases upsetting the kingdom Plantae. In agricultural soils, perhaps 80% of the nitrogen fixed biologically originates from an extensive variety of soil bacteria like the *Rhizobium*, *Sinorhizobium*, and *Allorhizobium* of the family Rhizobiaceae in relationship with leguminous root of plants (Vimal et al. 2017). These endophytes generally invade the root structures of leguminous plants giving rise to nodules thereby stimulating the growth of plants unswervingly or incidentally (Zimmer et al. 2016).

The genetic basis of plant–microbial interaction is sturdily clarified by the gene-for-gene elicitor-receptor model. On this premise, numerous investigations have utilized plant pathogenic bacteria of the genera *Pseudomonas* and *Xanthomonas*. A group of genes have been rapt comprising of the hypersensitivity reaction (HR) and pathogenicity (hrp) which impact the limit of bacteria to create HR in non-host plants (Montesinos et al. 2002). Majority of plants are not proficient in gathering enough biomass for obvious steps of remediation within the sight of high degree of contaminants (Harvey et al. 2009; Chakraborty et al. 2005). The cleanup route of polluted ecosystem is restricted and delayed due to inadequate nutrient level. Soil microorganisms are assumed to exercise affirmative influence on the wellbeing of plant through mutualistic associations between them. Conversely, microorganisms are subtle to contamination and reduction in their population through the types as well as biomass which regularly take place in such polluted soils (Shi et al. 2002). A stress in the biotic or abiotic conditions through a little change in the physicochemical and natural characteristics of rhizospheric soils may prompt exceptional impact on plant–microbial interaction. The utilization of Plant growth-promoting microorganisms as inocula in rhizosphere is gaining more ground as its prospects is on the increase in phytoremediation process; though, it partially subject to the capacity of the plant to withstand the toxic nature of the metal and give adequate harvest. The exudates at the plant roots are utilized by microbes in the rhizosphere region as nutrients for growth and subsequent multiplication. It is projected that the amount of the remaining photosynthetic carbon transported to plant roots varies amid 30–60% and 10–20% of root requirements originates from rhizodeposition (Marschner 1995; Salt et al. 1998). The exudates are basically made up of low as well as high molecular weight organic acids. Their total amount determined in plant roots falls within the range of 10–20 mM, by and large consisting of acetate, lactate, succinate, oxalate, fumarate, malate and aconitate while the remainder of biological solutes in roots are sugars (90 mM) and amino acids (10–20 mM) (Jones 1998).

Bioremediation is the practice of eliminating environmental pollutants utilizing living organisms which are mostly microbes. This is one of the most reliable

methods for cleanup and restoration of polluted ecosystems. The frequent use of some plants for cleanup of precarious toxins in the ecosystem in a recently developed method is known as phytoremediation. They are known as hyperaccumulators which grow optimally in heavy metals rich soil. Alkorta and Garbisu (2001) have reported phytoremediation to be real, in situ, artistically attractive, reduced effort socially acknowledged technique for the cleanup of contaminated soil. These cleanup may be through phytostabilization, rhizofiltration, phytoextraction, and phytovolatilization. It is not only cleanup of the ecosystem contaminations but plant–microbe interrelationship also adds to viable improvement of agriculture. These days, there exist a major issue in production of crops with decreased utilization of pesticides and inorganic fertilizers. So the use of PGPR to improve yield of harvests has demonstrated to be an earth benevolent technique as a substitute to such issues.

As soon as a site becomes contaminated, the masterpiece of the autochthonous microbial population in the site as well as the underground water will acclimatize to the new condition. The microbial species that are able to use the pollutants as foundation of substrates for growth will proliferate and turn out to be dominant (Liu and Suflita 1993; Gkorezis et al. 2016). The normal, non-planned process of xenobiotic breakdown by the native microbial species is known as normal diminution and it is considered the modest method of bioremediation. The Environmental Protection Agency (EPA, United States) describes innate remediation as a combination of degradation, dispersion, dilution, sorption, volatilization, chemical and biochemical balance of pollutants. Though, in earlier times, this "treatment" technique was regularly talk about as an important method, it gradually has become a vital instrument to remediate polluted sites. Natural attenuation is already a success for BTEX compounds which is associated with underground water (USEPA 2001). It has been useful mostly on locations with "low" public worth, especially when there is enough time, since cleanup could last a while when other kind of restoration technologies are not appropriate. Normal cleanup is not allowed at sites near home with great ecological worth, such as natural resorts. Time is also a restraining influence because the ability of native microorganisms to adapt could take decades, contingent on the nature of the xenobiotic that is available (Ojuederie and Babalola 2017). The by-products that arise from incomplete breakdown of other contaminants can be lethal. For example, toxic 1-napthol arises from oxygenic conversion of naphthalene, while the actual carcinogenic compound vinyl chloride comes from anaerobic conversion of tri-chloroethylene (Liu et al. 2007). Heavy metals are recalcitrant so they cannot be damaged by normal degradation; nevertheless, they are subjected to volatilization. Also, microorganisms that have appropriate catabolic genes may not be present on the site for all xenobiotic compounds, which is confirmed by the buildup of hazardous and obstinate mixtures found in the ecosystem (Vimal et al. 2017).

13.8 Plant–Microbial Interaction During Remediation

The interaction between plant and microorganisms can be accomplished through various immediate: nutrient transfer (originating from nutrient or siderophore production, air nitrogen fixation, enzymatic deterioration of organic matter in soil, or transformation of inorganic minerals to dissolvable constituents, particularly phosphorous), direct encouragement of growth through phytohormones, (for example, ethylene or indole acetic acid), antipathy towards pathogenic microorganisms, and mitigation of salt stress. The soil is exceptional in possessing a life-dependent structure and offers ecosystem services that are vital for global roles, comprising principally production, regulation of biogenic gases, earth's climate, biogeochemical and water cycling, as well as biodiversity maintenance (Magdoff and Es 2000; Welbaum et al. 2004). A substantial quantity of the land is polluted arising from different human influences and a steady upsurge of this level is anticipated in years ahead. The microorganisms inhabiting the soils form a very vital component of living things. The relationship between bacteria and plants in the different ecological niches including the rhizosphere contributes to the rise in promoting the growth by directly affecting plant anabolic and catabolic reactions in the absence of most important pathogen. These bacteria fit into different genera, including *Acetobacter, Achromobacter, Anabaena, Azotobacter, Bacillus, Hydrogenophaga, Kluyvera, Pseudomonas,* and *Rhizobium* (Bashan et al. 2008).

There are important factors that determine the efficiency of phytoremediation. These include setting up of important plants with the ability to produce biomass, vigorous root as well as root activities with the root network, aiding cleanup using plants in the rhizosphere region. Likewise, the association of different groups of microorganisms can be of advantage to the plant. In addition to the numerous positive interrelationships, there exists competition of resources between plants and microorganisms (Kaye and Hart 1997). Arising from the restrictions of scarce nutrients and its struggle, which usually take place at contaminated locations, the proliferation of microorganisms as well as biodegradability could be restricted (Joner et al. 2006; Unterbrunner et al. 2007). Though, supply of too much nutrients can be responsible for appropriate conditions for encouraging heterotrophic and pollutant bacteria that have become acclimatized, this may not essentially result in realizing improved rates of phytoremediation. This has been reported in the degradation of hydrocarbon in oil contaminated ecosystems. The degradation of the contaminant was not influenced or subdued by nutrient addition (Chaineau et al. 2005).

The microbial communities found in soil that show diverse competences of hereditary capabilities and endeavours can differ widely in soils which may also impact on the functioning capacities of soil, arising from their involvement in important metabolic reactions (Nannipieri et al. 2003). The relationship that exists between microorganisms is constrained by precise compounds and is accountable for significant natural processes, such as organic matter decomposition, and safeguarding of plant wellbeing just as soil quality (Barea et al. 2004). The development of enormous amounts of metabolically active inhabitants of useful microorganisms in soil is required for distinctive bioremediation (Metting Jr

1992). In the aforementioned microorganisms, the motivating aspects are high ability to acclimatize to different environmental conditions, fast growth rate, and biochemical resourcefulness to fully utilize different types of normal and xenobiotic chemicals for an entrenched ecosystem (Narasimhan et al. 2003).

13.9 Role of Plant Growth-Promoting Rhizobacteria

Plant growth-promoting rhizobacteria play critical function in the promotion of plant growth leading to viable agricultural development. They assist plant growth promotion by direct and indirect machineries. The direct consist in fixing of nitrogen in the atmosphere, solubilization of phosphorus, siderophore production for iron chelation, and providing siderophore–iron complex to plant resulting in the synthesis of different plant hormones. While indirect method includes control of pathogenic plant pathogens via antibiotics production, reduction of iron in the soil, and eventually encouraging the growth of plants. Plant growth-promoting Rhizobacteria are classified into two based on their association with host plant: (1) cooperative rhizobacteria, which assault and colonize the inward piece of the plant cell to endure, e.g. bacteria forming nodule, and (2) free-living rhizobacteria that exist outside the plant and are likewise popular as extracellular PGPR, e.g. *Azotobacter, Burkholderia*, and *Bacillus* (Babalola 2010; Khan 2006). Microbes like PGPR can improve the supply of supplements in the rhizosphere (Choudhary et al. 2011; Kumar et al. 2017). For instance, nitrogen, the best controlling variable related with the development of plant is not promptly open for plant use, yet *Azospirillum* existing in grain biological system can fix free nitrogen accordingly, advancing the yield of harvests (Tejera et al. 2005). Besides, phosphate is likewise provided in the accessible form by PGPR (Vacheron et al. 2013), making it to be promptly used by plants. Vejan et al. (2016) posited that Lavakush Yadav et al. (2014) completed a trial on PGPR strain like *Pseudomonas putida* and *Pseudomonas fluorescens* relating to their impact on take-up of uptake of nutrient during the growth of rice.

Certain rhizospherical strains possess the capability to give up a variety of substrates such as antimicrobials, hydrocyanic acid, indoleacetic acid (IAA), siderophores which is integral to expanding the bioavailability and admission of hefty metals by plant root, for both fundamental (e.g. Fe and Mn) and superfluous (e.g. Cd) nutrients (Barber and Lee 1974; Crowley et al. 1991; Salt et al. 1998). An examination was completed which indicated connection between metal opposition and metal activation capacities of rhizobacteria under weighty metal pressure. Phosphate solubilizers had the most extensive level of the biochemical movement of all segregates and against metal opposition; trailed by siderophore makers and in conclusion acid producers. This points to the fact that the aforementioned group of microorganisms is utilized by rhizobacteria and be responsible for metals mobilization in soil (Abou-Shanab et al. 2005). The take up and movement of non-essential elements might differ significantly and regularly influenced by different genera and form of minor elements. To the varying degree, the various metals display different

rates of mobility, and the conscription rate might remain higher for some than others for a specific metal inside a plant.

13.10 Hormones in Enhancing Growth During Remediation

Some rhizospheric microorganisms produce plant hormones which support root growth and in so doing discharge root secretions. The plant secretions incorporate carbohydrates, amino acids, lipophilic mixes, and chelating specialists secreted from the roots of plants and set forth constructive outcomes to keep up an assortment of microbial networks in the rhizosphere (Anderson et al. 1993). Plants that are low in phosphorus try to summon phosphorous components that are accessible in soil by expanding citrus extract level in root exudates (Hooda 2007). A coagulated oil alluded to as mucigel is needed for root entrance which is emitted by it cells and adds to expanding the root mass apically during growth in the soil. The microbes in soil use these mixes for development to create the plant rhizosphere (Anderson et al. 1993). The survival of plants in contaminated and nutrient limiting environments is stimulated via inter-relationships existing between microorganisms associated with plant roots and plants itself in the rhizosphere. Several metal ions have low bioavailability due to their reduced solubility in aqueous solution and resilient affinity for soil particles which render them immobile thereby hampering utilization by plants. However, microbes that colonize the roots of plant can contribute to increased metal uptake by increasing the bioavailability (Hooda 2007).

13.11 Role of Endophytes and Mycorrhiza

The degradation of contaminants has also been implicated in endophytic microorganisms as well as those involved in plant–microbial interactions. The endophytic bacteria colonize internal plant tissues without necessarily impeding plant development (Lodewyckx et al. 2002; Schulz et al. 2006). Plant–endophyte interactions are such that plants provide nutrients and shelter for the endophyte, whereas the latter provide growth enhancement conditions for the plant through the production and release of useful metabolites (Bacon and White 2000; Garbeva et al. 2001; Tan and Zou 2001). Generally, many common easily grown endophytic species are *Pseudomonaceae, Burkholderiaceae*, and *Enterobacteriaceae* (Mastretta et al. 2006). This association has also been exploited in remediation of contaminants. The photoautotrophic capacities of plants make for the possibility that associating rhizospheric microorganisms would have the capacity to biodegrade and/or utilize petroleum hydrocarbons even when they are poorly soluble in water. Haichar et al. (2008) earlier reported that the soils with enhanced plant cover usually had more diverse microorganisms and as such are most likely to be easily remediated. Plants release exudates, mucilages, lysates, vitamins, organic acids, ligands, enzymes, or otherwise rhizodeposits (Olson et al. 2003). These are carbon sources that enhance

soil microbial proliferation and eventual biodegradative capacities (Chaudhry et al. 2005).

13.12 Mechanism of Rhizoremediation

The ability of plants to cleanup contaminants from either terrestrial or aquatic environments relies basically on its rooting capacities. The root is the major organ for nutrient absorption, adsorption, and accumulation. Plant capacities to associate with soil microorganisms that are critical for plant development also rest, to a very large extent, on the roots. Therefore, bioremediation of contaminants is better appreciated at rhizospheric levels. There are a number of mechanisms of contaminant remediation in the roots—this however depends first on the types of contaminants. Whereas inorganic contaminants are basically absorbed or adsorbed either by direct flow or upon enhancement by ligand and chelators, organic contaminants are degraded or sequestered around the rhizosphere or rhizoplane. The role of microorganisms in achieving these capacities is imperative. The process of bioremediation can be carried out either using oxygen or not, according to the requirement of the organism involved. This means bioremediation can be of two form, aerobic or anaerobic (Malik and Ahmed 2012). It is however common to ascribe the mechanism of remediation to aerobic route due to the overly abundance of aerobic organisms involved in bioremediation. Below are the equations for bioremediation.

Aerobic biodegradation:

$$\begin{aligned}&\text{Biota} + \text{Hydrocarbon compound} + \text{Oxygen } (O_2) \pm \text{Enzyme(s)}\\ &\quad = \text{Biota} + \text{Water} + \text{Residue(s)}\end{aligned}$$

Anaerobic biodegradation:

$$\begin{aligned}&\text{Biota} + \text{Hydrocarbon compound} + \text{Carbon (iv) oxide} \pm \text{Enzyme(s)}\\ &\quad = \text{Biota} + \text{methane } (CH_4) + \text{Water} + \text{Residue(s)}\end{aligned}$$

Many genera of bacteria have been reported to be useful in bioremediation. Among the aerobic bacteria involved are *Bacillus, Micrococcus, Sphingobium, Rhodococcus*, those of the anaerobic are *Pelatomaculum, Desulphovibrio, Desulfotomaculum, Aromatoleum aromaticum, Dechloromonas aromatica*, *Desulfitobacterium hafniense* (Cao et al. 2009), and *Syntrophus* (Shimao 2001; Jayasekara et al. 2005).

The process by which the microorganism carry out remediation can be ascribed to mineralization, a process whereby the pollutant is converted into intermediate substance, usually according to the pathway the organism uses in remediation. The whole process involves absorbing the pollutant into the cell, followed by the release of enzymes and organic acids such as citric acid, and malic acid, etc., which acts on them thereby converting them into intermediate product. However, before

absorption the pollutants are converted into less toxic compound by complete oxidation using an electron acceptor, oxygen in the case of aerobic respiration.

13.13 Enzymes and Genetic Implications of Hydrocarbon Biodegradation

In most cases of hydrocarbon pollution, the process of remediation is usually preceded by the release of extracellular enzymes such as oxygenase. This is usually observed in fungi which are known to degrade their substrate extracellularly before taking it in using enzymes such as lignin peroxidases (LiP), laccases, etc. (Asemoloye et al. 2017). These enzymes are typically involved in the breakdown of substrate by cleaving to the bond and metabolizing hydrocarbon contaminant into phenols or trans dihydrodiols (Bogan and Lamar 1995). The functionality of these enzymes has been reported to be affected by the length and complexity of the hydrocarbon chain of the pollutant. However, some microbes have cytochrome P450 enzymes which are capable of converting long chain hydrocarbon into isoforms. Such enzymes have been isolated from *Candida* species which were able to utilize long chain aliphatic hydrocarbon. A typical example is the alkaneoxygenase which is able to oxidize alkane and some other methane monooxygenases which contain copper (Scheller et al. 1998; Van Beilen and Funhoff 2005).

13.14 Synergistic Rhizosphere Mechanisms for the Removal of Hydrocarbons in Polluted Soils

Biodegradation requires reduced energy and it involves the use of life organisms in the cleaning up of contaminated soils (Segura and Ramos 2013). It is a generally accepted technology because of its cost effectiveness and more ecofriendly when compared to other conventional remediation methods. Using this method, one major challenge is the ability to establish the plant in the remediation process, due to the toxic property of the pollutant. The roots of plants are important in the remediation of both land and soil but with increase in the rooting ability of the plant in the land or water to be remediated there is increase the rate of remediation by way of reducing the amount of contaminant left in the field (Gunawardana et al. 2011). Some level of pollution will however inhibit the rate of rooting in plants, this has been the major problem in rhizoremediation (Abhilash et al. 2012; Li et al. 2013; Ukaegbu-Obi and Mbakwem-Aniebo 2014). Ways have been looked into, to be able to increase root proliferation in this type of situation, such as trying different form of techniques. Treatment of root of plants in hydrocarbon polluted soils with organic fertilizers and selected microbes is known to improve plants abilities to remediate polluted soils. The microbes which can be native or introduced have been said to symbiotically promote root system of the plant (Escalante-Espinosa et al. 2005; Huang et al. 2004;

Johnson et al. 2005; Joner et al. 2006; Leigh et al. 2006; Gerhardt et al. 2009; Weyens et al. 2009a, b; Glick 2010; Guo et al. 2014).

13.14.1 Biosurfactants

Most microbes, including bacteria, yeast, and the filamentous fungi have been reported to synthesize several biomolecules. Many of these biomolecules produced by these organisms have shown surface activity, because they comprise both hydrophilic and lipophilic properties. These compounds are made up of a water loving acids, peptide positive and negative charged ions, and a hydrophobic moiety of unsaturated or saturated hydrocarbon chains or lipids (Banat et al. 2010). They can be of two type, the first being the low mass compounds called biosurfactants, known for reducing surface and interfacial tensions, and they include lipopeptides, glycolipids, and proteins (Nguyen and Sabatini 2011; Banat et al. 2014; Dobler et al. 2016; Santos et al. 2016). The high mass are the bioemulsifiers such as the lipopolysaccharides, polysaccharides. Bioemulsifiers balance out oil-in-water emulsions and possess reduced ability to bring down surface pressure than biosurfactants (Neu 1996; Smyth et al. 2010a, b; Uzoigwe et al. 2015). The aforementioned properties have been attributed to enhance microbial growth by expanding the surface territory among oil and water through emulsification, as well as through expansion of the pseudosolubility by apportioning into micelles (Volkering et al. 1997). The whole procedure will enhance the bioavailability of the contaminant to degradation by microorganisms (Mulligan 2009; Pacwa-Plociniczak et al. 2011; Lawniczak et al. 2013).

Typical examples have been reported, like the case of *Bacillus circulans* which produces lipopeptide and *Pseudomonas aeruginosa* which produces both lipopeptides and protein-starch-lipids have increased biodegradation (Bordoloi and Konwar 2009; Das et al. 2008). Another is the comparative study between Triton X-100 and the commercial rhamnolipid JBR-515 (Jeneil Biosurfactant Company, USA) using *Burkholderia multivorans* (NG1) shows that Triton X-100 increased bioavailability by emulsification and sustained interfacial take-up, while the rhamnolipid mixture JBR-515 considerably did not emulsify hydrocarbons, improving bioavailability in its place by solubilization of the micelle (Mohanty and Mukherji 2013). Colores et al. (2000) have however posited that the presence of surfactants of biological origin and that of non-biological origin may be inhibitory to the process of biodegradation. This is because the Micelle cores formation which will trap the organic contaminants can create a hydrophilic barrier between the organic contaminant and the hydrophobic microorganisms making it less available for degradation (Colores et al. 2000).

Another case observed in *Pseudomonas aeruginosa* is the use of a mechanism not so different to pinocytosis for the uptake of rhamnolipid-coated hexadecane droplets which can be referred to as the internalization of biosurfactant layered hydrocarbon droplet. Some microbes have been reported to even emulsify hydrocarbons without absorbing the hydrocarbon. This have prompted the attention to the surface property

of the cell to be associated with emulsification, due to the connection of the oil–water interface by broad hydrophobic communications as opposed to explicit acknowledgment of the substrate. It is said that the microorganisms cells may serve as fine strong units at interface, meaning that stationary-phase or hydrophobic microorganisms can settle oil–water emulsions by clinging to the oil–water interface because of the cell surface hydrophobicity in a population of different microbes, the production of biosurfactants by the microbes or the plants or the one introduced into the medium may be suitable substrate for species that naturally degrade hydrocarbon, thus reducing the remediation yield. Biosurfactant of external and internal origin is however poisonous to certain microorganisms by impairing permeability of the membrane, hence meddling with chemotaxis driven motility, and upsetting the formation of biofilm.

Biofilms, bacterial networks encompassed by self-produced polymeric matrices reversibly committed to a passive surface are a survival strategy against harsh physicochemical environments, to aid exchange of cations, gene transfer, and regulation of redox ability of their ecosystem (Costerton et al. 1995; Gorbushina and Broughton 2009; Shemesh et al. 2010). Biofilm milieus are made up of extracellular polysaccharides (EPSs), deoxyribonucleic acids, and proteins (Sutherland 2001; Branda et al. 2005; Rinaudi and Gonzalez 2009), with EPS influencing the water holding capacity, thickness, moisture content, and mechanical firmness of biofilms (Flemming and Wingender 2010).

Biofilms, however, have the property of enhancing PHC bioremediation courses by aggregating the accessibility of the contaminant (Wick et al. 2002; Johnsen and Karlson 2004). The production of high molecular weight compounds is usually proportional to the formation of production of biofilm; therefore, in the event that release of polymers by microbes is trailed by production of biofilms on the superficials of inexplicable hydrocarbons. This put those microbes particularly well prepared for the management of unruly combinations due to their great microorganism biomass inside biofilm. However, biofilm formation enhances remediation process by preserving best situations of pH, limited concentrations of solute as well as redox ability in the presence of the cells.

13.15 Environmental Factors Affecting Bioremediation of Contaminants by Plant–Microbe Interactions

Competition for resource and interference by chemicals lead to harmful associations among plants. Also, exudates from plants root are a possible factor that can affect the three instruments of intervention. For some species of plant, the exudates from root perform vital function as phytotoxins (i.e. allelopathy). Also, these exudates are crucial for improvement of interrelationships among some plants parasite and their hosts. Lastly, release from the roots also performs crucial secondary roles in the struggle for resources, this is done by interfering with soil chemistry, various soil processes, and the population of microorganisms. Root exudates sometimes control positive interactions between plants. In some situations, root exudates induce plant

defence that helps decrease vulnerability to infections from pathogen, but in opposite conditions, these immunities result in the manufacture and discharge of green volatiles which attracts killers of plant adversaries. Also, the different influences of releases from the root positively impact on the soil processes, and population of microorganisms as well as the surrounding plants.

Allelopathy or chemical enhanced plant interference is one method used by plants to have a lead on their rivals. Plants do this by producing and releasing potent phytotoxins to inhibit or diminish the instituting, growth, or existence of vulnerable plant neighbours, this will help reduce or eliminate competition and then increase the availability of resources. Some of the phytotoxins released could be located in rotten foliage and root matter that might have been discarded by the plant. These phytotoxins show differences in their chemical structures, mechanisms of activity and influence on plant growth and metabolism. The various phytotoxins present in root exudates affect various processes like the production of metabolites, photosynthesis, root growth, etc.

Root exudates are critical factors required for establishing important relationships between microorganisms and plant roots or even between other biota and plant roots. Plant capacity for survival also rests on this. Plant association with other biota may not necessarily be always beneficial. Whereas some associations are synergistic, others could be parasitic, neutral, or commensalistic. Root exudates can influence better association.

13.16 Conclusion

This paper reviewed toxic waste, plant–microbial interactions, survival mechanisms of plants–microbes and their interactions in contaminated environment. It also took a cursory view on the genetic implications of plant–microbes interactions involved in the conversion of toxic waste in the ecosystem. Environmental factors affect enzyme responses during ecosystem cleanup. These can be as little as can induce free radical activity that would change the course of enzyme activity that would ultimately influence remediation capacities and performance. It re-echoes the overwhelming importance of synergistic relationship between plants and their counterpart rhizospheric microbes during the conversion of toxic waste making it a better and sustainable alternative for the elimination of poisonous wastes (organic and inorganic) within the surrounding. Microbes and plants have innate natural machineries that support their survival under environmental conditions and eliminate the toxics from the ecosystem. Additional fast developing plants with great phytoextraction potentials need to be identified for the cleanup of contaminants in soil.

13.17 Future Perspectives

There are new ways of studying plant–microbial interactions. These are chromatography, sequencing, microscopy, mass spectrometry, phospholipid fatty acid (PLFA), real-time PCR (RT-PCR), etc. Additional development in this genomic age will open up avenues for improved knowledge of the inter-relationships of endophytes, plant–pathogen and plant protection. There is need for improved remediation techniques to meet the challenge of pollution. In plants, together with their microbiomes, lies huge unexploited potential for purifying both environmental pollution particularly soil.

References

Abhilash PC, Powell JR, Singh HB, Singh BK (2012) Plant–microbe interactions: novel applications for exploitation in multipurpose remediation technologies. Trends Biotechnol 30:416–420. https://doi.org/10.1016/j.tibtech.2012.04.004

Abou-Shanab RA, Ghozlan H, Ghanem K, Moawad H (2005) Behaviour of bacterial populations isolated from rhizosphere of *Diplachne fusca* dominant in industrial sites. World J Microbiol Biotechnol 21:1095–1101

Adesemoye AO, Torbert HA, Kloepper JW (2009) Plant growth-promoting rhizobacteria allow reduced application rates of chemical fertilizers. Microb Ecol 58:921–929

Alkorta I, Garbisu C (2001) Phytoremediation of organic contaminants. Bioresour Technol 79 (3):273–276. https://doi.org/10.1016/S0960-8524(01)00016-5

Anderson TA, Guthrie EA, Walton BT (1993) Bioremediation in the rhizosphere: plant roots and associated microbes clean contaminated soil. Environ Sci Technol 27(13):2630–2636. https://doi.org/10.1021/es00049a001

Asemoloye MD, Ahmad R, Jonathan SG (2017) Synergistic action of rhizospheric fungi with megathyrsus maximus root speeds up hydrocarbon degradation kinetics in oil polluted soil. Chemosphere 187:1–12

Babalola OO (2010) Beneficial bacteria of agricultural importance. Biotechnol Lett 32:1559–1570

Bacon C, White J (2000) Microbial endophytes. Marcel Dekker, New York

Baldrian PS, Najdr J, Merhautova V, Dobiasova P, Cajthaml T, Valaskova V (2013) Responses of the extracellular enzyme activities in hardwood forest to soil temperature and seasonality and the potential effects of climate change. Soil Biol Biochem 56:60–68

Banat IM, Franzetti A, Gandolfi I, Bestetti G, Martinotti MG, Fracchia L et al (2010) Microbial biosurfactants production, applications and future potential. Appl Microbiol Biotechnol 87:427–444. https://doi.org/10.1007/s00253-010-2589-0

Banat IM, Satpute SK, Cameotra SS, Patil R, Nyayanit NV (2014) Cost effective technologies and renewable substrates for biosurfactants' production. Front Microbiol 5:697. https://doi.org/10.3389/fmicb.2014.00697

Barber SA, Lee RB (1974) The effect of microorganisms on the absorption of manganese by plants. New Phytol 73:97–106

Bardgett RD, Freeman C, Ostle NJ (2008) Microbial contributions to climate change through carbon cycle feed backs. ISME J 2:805–814

Barea JM, Azcón R, Azcón-Aguilar C (2004) Mycorrhizal fungi and plant growth promoting rhizobacteria. In: Varma A, Abbott L, Werner D, Hampp R (eds) Plant surface microbiology. Springer, Heidelberg, pp 351–371

Bashan Y, Puente ME, De-Bashan LE, Hernandez JP (2008) Environmental uses of plant growth-promoting bacteria. In: Barka EA, Clément C (eds) Plant microbe interactions. Research Signpost, Kerala, pp 69–93

Bogan BW, Lamar RT (1995) One-electron oxidation in the degradation of creosote polycyclic aromatic hydrocarbons by Phanerochaete chrysosporium. Appl Environ Microbiol 61 (7):2631–2635

Bordoloi NK, Konwar BK (2009) Bacterial biosurfactant in enhancing solubility and metabolism of petroleum hydrocarbons. J Hazard Mater 170:495–505. https://doi.org/10.1016/j.jhazmat.2009.04.136

Branda SS, Vik A, Friedman L, Kolter R (2005) Biofilms: the matrix revisited. Trends Microbiol 13:20–26. https://doi.org/10.1016/j.tim.2004.11.006

Bulgarelli D, Schlaeppi K, Spaepen S, Ver Loren van Themaat E, Schulze-Lefert P (2013) Structure and functions of the bacterial microbiota of plants. Annu Rev Plant Biol 64:807–838

Cao YR, Chen SY, Zhang JS (2009) Ethylene signaling regulates salt stress response: an overview. Plant Signal Behav 3(761–763):52

Cases I, de Lorenzo V (2005) Genetically modified organisms for the environment: stories of success and failure and what we have learned from them. Int Microbiol 8:213–222

Castro HF, Classen AT, Austin EE, Norby RJ, Schadt CW (2010) Soil microbial community responses to multiple experimental climate change drivers. Appl Environ Microbiol 76 (4):999–1007

Chaineau CH, Rougeux G, Yepremian C, Oudot J (2005) Effects of nutrient concentration on the biodegradation of crude oil and associated microbial populations in the soil. Soil Biol Biochem 37:1490–1497

Chakraborty R, O'Connor SM, Chan E, Coates JD (2005) Anaerobic degradation of benzene, toluene, ethylbenzene, and xylene compounds by Dechloromonas strain RCB. Appl Environ Microbiol 71:8649–8655

Chakraborty S, Pangga IB, Roper AM (2012) Climate change and multitrophic interactions in soil: the primacy of plants and functional domains. Glob Chang Biol 18:2111–2125

Chaudhry Q, Blom-Zandstra M, Gupta SK, Joner E (2005) Utilising the synergy between plants and rhizosphere microorganisms to enhance breakdown of organic pollutants in the environment. Environ Sci Pollut Res 12:34–48

Choudhary DK, Sharma KP, Gaur RK (2011) Biotechnological perspectives of microbes in agro-ecosystems. Biotechnol Lett 33:1905–1910

Colores GM, Macur RE, Ward DM, Inskeep WP (2000) Molecular analysis of surfactant-driven microbial population shifts in hydrocarbon-contaminated soil. Appl Environ Microbiol 66:2959–2964. https://doi.org/10.1128/AEM.66.7.2959-2964.2000

Costerton JW, Lewandowski Z, Caldwell DE, Korber DR, Lappinscott HM (1995) Microbial biofilms. Annu Rev Microbiol 49:711–745. https://doi.org/10.1146/annurev.mi.49.100195.003431

Crowley DE, Wang YC, Reid CPP, Szaniszlo PJ (1991) Mechanisms of iron acquisition from siderophores by microorganisms and plants. Plant Soil 130:179–198

Das P, Mukherjee S, Sen R (2008) Improved bioavailability and biodegradation of a model polyaromatic hydrocarbon by a biosurfactant producing bacterium of marine origin. Chemosphere 72:1229–1234. https://doi.org/10.1016/j.Chemosphere.2008.05.015

Dobler L, Vilela LF, Almeida RV, Neves BC (2016) Rhamnolipids in perspective: gene regulatory pathways, metabolic engineering, production and technological forecasting. New Biotechnol 33:123–135. https://doi.org/10.1016/j.nbt.2015.09.005

Enerijiofi KE (2014) Elements of environmental studies. In: Ogbe FM, Inegbeboh BO, Ngamen Kouassi C, Esezobor EA (eds) General studies compendium, vol 2. Samuel Adegboyega University, Ogwa, pp 177–188

Enerijiofi KE (2020) Bioremediation of environmental contaminants: a sustainable alternative to environmental management. In: Saxena G, Kumar V, Shah MP (eds) Bioremediation for environmental sustainability: toxicity, mechanisms of contaminants degradation, detoxification and challenges, vol 2. Elsevier, New York, pp 461–480

Escalante-Espinosa E, Gallegos-Martinez ME, Favela-Torres E, Gutierrez Rojas M (2005) Improvement of the hydrocarbon phytoremediation rate by Cyperus laxus lam. Inoculated

with a microbial consortium in a model system. Chemosphere 59:405–413. https://doi.org/10.1016/j.chemosphere.2004.10.034
Fester T, Giebler J, Wick LY, Schlosser D, Kastner M (2014) Plant–microbe interactions as drivers of ecosystem functions relevant for the biodegradation of organic contaminants. Curr Opin Biotechnol 27:168–175
Flemming HC, Wingender J (2010) The biofilm matrix. Nat Rev Microbiol 8:623–633. https://doi.org/10.1038/nrmicro2415
Frey SD, Drijber R, Smith H, Melillo J (2008) Microbial biomass functional capacity and community structure after 12 years of soil warming. Soil Biol Biochem 40:2904–2907
Frey SD, Lee J, Melillo JM, Six J (2013) The temperature response of soil microbial efficiency and its feedback to climate. Nat Clim Chang 3:395–398
Garbeva P, Overbeek LS, Vuurde JW et al (2001) Analysis of endophytic bacterial communities of potato by plating and denaturing gradient gel electrophoresis (dgge) of 16s rdna based pcr fragments. Microb Ecol 41:369–383
Garbeva P, van Veen JA, Elsas JD (2004) Microbial diversity in soil: selection of microbial populations by plant and soil type and implications for disease Suppressiveness. Annu Rev Phytopathol 42:243–270
Gerhardt KE, Huang XD, Glick BR, Greenberg BM (2009) Phytoremediation and rhizoremediation of organic soil contaminants: potential and challenges. Plant Sci 176(1):20–30. https://doi.org/10.1016/j.plantsci.2008.09.014
Gkorezis P, Daghio M, Franzetti A, Va Hamme JD, Silen W, Vangronsveld J (2016) The interactions between plants and bacteria in the remediation of petroleum hydrocarbons: an environmental perspective. Front Microbiol 7:1–28
Glick BR (2010) Using soil bacteria to facilitate phytoremediation. Biotechnol Adv 28(3):367–374. https://doi.org/10.1016/j.biotechadv.2010.02.001
Glick BR (2012) Plant growth-promoting bacteria: mechanisms and applications. Forensic Sci 12:1–15
Gorbushina AA, Broughton WJ (2009) Microbiology of the atmosphererock interface: how biological interactions and physical stresses modulate a sophisticated microbial ecosystem. Annu Rev Microbiol 63:431–450. https://doi.org/10.1146/annurev.micro.091208.073349
Gunawardana B, Singhal N, Johnson A (2011) Effects of amendments on copper, cadmium, and lead phytoextraction by Lolium perenne from multiple-metal contaminated solution. Int J Phytoremed 13(3):215–232. https://doi.org/10.1080/15226510903567448
Guo S, Fan R, Li T, Hartog N, Li F, Yang X (2014) Synergistic effects of bioremediation and electrokinetics in the remediation of petroleum-contaminated soil. Chemosphere 109:226–233. https://doi.org/10.1016/j.chemosphere.02.007
Haichar FZ, Marol C, Berge O, Rangel-Castro JI, Prosser JI et al (2008) Plant host habitat and root exudates shape soil bacterial community structure. ISME J 2:1221–1230. https://doi.org/10.1038/ismej.2008.80
Harrison NG, Allan JD, Colwell RK, Futuyma DJ, Howell J et al (1968) The relationship between species diversity and stability: an experimental approach with protozoa and bacteria. Ecology 49:1091–1101
Harvey PR, Warren RA, Wakelin S (2009) Potential to improve root access to phosphorus: the role of non-symbiotic microbial inoculants in the rhizosphere. Crop Pasture Sci 60:144–151
Hawkins AP, Crawford KM (2018) Interactions between plants and soil microbes may alter the relative importance of intraspecific and interspecific plant competition in a changing climate. AoB 10:1–11
He AL, Niu SQ, Zhao Q, Li YS, Gou JY, Gao HJ, Suo SZ, Zhang JL (2018) Induced salt tolerance of perennial ryegrass by a novel bacterium strain from the rhizosphere of a desert shrub Haloxylon ammodendron. Int J Mol Sci 19:469
Hiltner L (1904) Über neuere Erfahrungen und Probleme auf dem Gebiete der Bodenbakteriologie unter besonderer Berücksichtigung der Gründungung und Brache. Arb Dtsch Landwirtsch Ges 98:59–78

Ho YN, Mathew DC, Huang CC (2017) Plant-microbe ecology: interactions of plants and symbiotic microbial communities, vol 6. Intech Open, London, pp 93–119

Hooda V (2007) Phytoremediation of toxic metals from soil and wastewater. J Environ Biol 28:367–376

Huang XD, El-Alawi Y, Penrose DM, Glick BR, Greenberg BM (2004) A multi-process phytoremediation system for removal of polycyclic aromatic hydrocarbons from contaminated soils. Environ Pollut 130(3):465–476. https://doi.org/10.1016/j.envpol.2003.09.031

Ingham CJ, Sprenkels A, Bomer J, Molenaar D, Van Den Berg A, van Hylckama Vlieg JE, de Vos WM (2007) The micro petri dish, a million-well growth chip for the culture and high-throughput screening of microorganisms. Proc Natl Acad Sci USA 104:18217–18222

Ingham CJ, Kalisman O, Finkelshtein A, Ben-Jacob E (2011) Mutually facilitated dispersal between the nonmotile fungus *Aspergillus fumigatus* and the swarming bacterium *Paenibacillus vortex*. Proc Natl Acad Sci USA 108:19731–19736

Jayasekara R, Harding I, Bowater I, Lonergan G (2005) Biodegradability of selected range of polymers and polymer blends and standard methods for assessment of biodegradation. J Polym Environ 13(3):231–250. https://doi.org/10.1007/s10924-005-4758-2

Johnsen AR, Karlson U (2004) Evaluation of bacterial strategies to promote the bioavailability of polycyclic aromatic hydrocarbons. Appl Microbiol Biotechnol 63:452–459. https://doi.org/10.1007/s00253-003-1265

Johnson DL, Maguire KL, Anderson DR, McGrath SP (2005) Enhanced dissipation of chrysene in planted soil: the impact of a rhizobial inoculum. Soil Biol Biochem 36:33–38. https://doi.org/10.1016/j.soilbio.2003.07.004

Joner EJ, Hirmann D, Szolar OH, Todorovic D, Leyval C, Loibner AP (2006) Priming effects on PAH degradation and ecotoxicity during a phytoremediation experiment. Environ Pollut 128:429–435. https://doi.org/10.1016/j.envpol.2003.09.005

Jones D (1998) Organic acids in the rhizosphere - a critical review. Plant Soil 205:24–44

Joutey NT, Bahafid W, Sayel H, El Ghachtouli N (2013) Biodegradation: involved microorganisms and genetically engineered microorganisms. In: Biodegradation—life science. IntechOpen, London, pp 289–320

Kaye JP, Hart SC (1997) Competition for nitrogen between plants and soil microorganisms. Trends Ecol Evol 12:139–143

Khan AG (2006) Mycorrhizoremediation—an enhanced form of phytoremediation. J Zhejiang Univ Sci 7:503–514

Kumar V, Kumar M, Sharma S, Prasad R (2017) Probiotics and plant health. Springer, Singapore

Lavakush Yadav J, Verma JP, Jaiswal DK, Kumar A (2014) Evaluation of PGPR and different concentration of phosphorus level on plant growth, yield and nutrient content of rice (*Oryzasativa*). Ecol Eng 62:123–128. https://doi.org/10.1016/j.ecoleng.2013.10.013

Lawniczak L, Marecik R, Chrzanowski L (2013) Contributions of biosurfactants to natural or induced bioremediation. Appl Microbiol Biotechnol 97:2327–2339. https://doi.org/10.1007/s00253-013-4740-1

Leigh MB, Prouzova P, Mackova M, Macek T, Nagle DP, Fletcher JS (2006) Polychlorinated biphenyl (PCB)-degrading bacteria associated with trees in a PCB-contaminated site. Appl Environ Microbiol 72(4):2331–2342. https://doi.org/10.1128/AEM.72.4.2331-2342.2006

Li HY, Chen J, Jiang L (2013) Elevated critical micelle concentration in soil water system and its implication on PAH removal and surfactant selecting. Environ Earth Sci 71(9):3991–3998. https://doi.org/10.1007/s12665-013-2783-3

Liu S, Suflita JM (1993) Ecology and evolution of microbial populations for bioremediation. Tibtech 11:344–352

Liu L, Jiang CY, Liu XY, Wu JF, Han JG, Liu SJ (2007) Plant–microbe association for rhizoremediation of chloronitroaromatic pollutants with *Comamonas* sp. strain CNB-1. Environ Microbiol 9(2):465–473. https://doi.org/10.1111/j.1462-2920.2006.01163.x

Lodewyckx C, Mergeay M, Vangronsveld J, Clijsters H, Van Der Lelie D (2002) Isolation, characterization, and identification of bacteria. Front Microbiol 7:14

Magdoff F, van Es H (2000) Building soils for better crops. In: Sustainable agriculture network handbook series, 2nd edn. University of Vermont, Burlington

Malik ZA, Ahmed S (2012) Degradation of petroleum hydrocarbons by oil field isolated bacterial consortium. Afr J Biotechnol 11:650–658. https://doi.org/10.5897/AJB11.036.

Maphosa F, Smidt H, De Vos WM, Roling WFM (2010) Microbial community and metabolite dynamics of an anoxic dechlorinating bioreactor. Environ Sci Technol 44:4884–4890

Mars AE, Kasberg T, Kaschabek SR, van-Agteren MH, Janssen DB, Reineke W (1997) Microbial degradation of chloroaromatics: use of the meta-cleavage pathway for mineralization of chlorobenzene. J Bacteriol 179:4530–4537

Marschner H (1995) Mineral nutrition of higher plants. Academic Press, London, p 889

Mastretta C, Barac T, Vangronsveld J, Newman L, Taghavi S, van der Lelie D (2006) Endophytic bacteria and their potential application to improve the phytoremediation of contaminated environments. Biotechnol Genet Eng Rev 23:175–207

Mendes R, Garbeva P, Raaijmakers JM (2013) The rhizosphere microbiome: significance of plant beneficial, plant pathogenic, and human pathogenic microorganisms. FEMS Microbiol Rev 37 (5):634–663

Metting FB Jr (1992) Structure and physiological ecology of soil microbial communities. In: Metting FB Jr (ed) Soil microbial ecology. Marcel Dekker, New York, pp 3–25

Mohanty S, Mukherji S (2013) Surfactant aided biodegradation of NAPLs by *Burkholderia multivorans*: comparison between triton X-100 and rhamnolipid JBR-515. Colloids Sur B-Biointer 102:644–652. https://doi.org/10.1016/j.colsurfb.2012.08.064

Montalbán B, Thijs S, Lobo MC, Weyens N, Ameloot M, Vangronsveld J, Pérez-Sanz A (2017) Cultivar and metal-specific effects of endophytic bacteria in Helianthus tuberosus exposed to Cd and Zn. Int J Mol Sci 18:2026

Montesinos E, Bonaterra A, Badosa E, Frances J, Alemany J, Llorente I, Moragrega C (2002) Plant-microbe interactions and the new biotechnological methods of plant disease control. Int Microbiol 5:169–175

Mulligan CN (2009) Recent advances in the environmental applications of biosurfactants. Curr Opin Colloid Interface Sci 14:372–378. https://doi.org/10.1016/j.cocis.2009.06.005

Nannipieri P, Ascher J, Ceccherini MT et al (2003) Microbial diversity and soil functions. Eur J Soil Sci 54:655–670

Narasimhan K, Basheer C, Bajic VB, Swarup S (2003) Enhancement of plant–microbe interactions using a rhizosphere metabolomics driven approach and its application in the removal of polychlorinated biphenyls. Plant Physiol 132:146–153

Neu TR (1996) Significance of bacterial surface-active compounds in interaction of bacteria with interfaces. Microbiol Rev 60:151–166

Nguyen TT, Sabatini DA (2011) Characterization and emulsification properties of rhamnolipid and sophorolipid biosurfactants and their applications. Int J Mol Sci 12:1232–1244. https://doi.org/10.3390/ijms12021232

Nweke CO, Alisi CS, Okolo JC, Nwanyanwu CE (2007) Toxicity of zinc heterotrophic bacteria from a tropical river sediment. Appl Ecol Environ Res 5(1):123–132

Ojuederie OB, Babalola OO (2017) Microbial and plant-assisted bioremediation of heavy metal polluted environments: a review. Int J Environ Res Public Health 14(1):26. https://doi.org/10.3390/ijerph14121504

Olson PE, Reardon KF, Pilon-Smits EAH (2003) Ecology of rhizosphere bioremediation. In: McCutcheon SC, Schnoor JL (eds) Phytoremediation: transformation and control of contaminants. Wiley, Hoboken, pp 317–353

Pacwa-Plociniczak M, Plaza GA, Piotrowska-Seget Z, Cameotra SS (2011) Environmental applications of biosurfactants: recent advances. Int J Mol Sci 12:633–654. https://doi.org/10.3390/ijms12010633

Pandey G, Jain RK (2002) Bacterial chemotaxis towards environmental pollutants: role in bioremediation. Appl Environ Microbiol 68(12):5789–5795

Reid A, Greene SE (2012) How microbes can help feed the world. Report of an American Academy of Microbiology Colloquium, p 3

Rinaudi LV, Gonzalez JE (2009) The low-molecular-weight fraction of exopolysaccharide II from Sinorhizobium meliloti is a crucial determinant of biofilm formation. J Bacteriol 191:7216–7224. https://doi.org/10.1128/JB.01063-09

Riser-Roberts E (1998) Remediation of petroleum contaminated soils. In: Biological, physical, and chemical process. CRC Press, New York, pp 1–542

Salt DE, Smith RD, Raskin I (1998) Phytoremediation. Annu Rev Plant Physiol 49:643–668

Santos DKF, Rufino RD, Luna JM, Santos VA, Sarubbo LA (2016) Biosurfactants: multifunctional biomolecules of the 21st century. Int J Mol Sci 17:401. https://doi.org/10.3390/ijms17030401

Scheller U, Zimmer T, Becher D, Schauer F, Schunck WH (1998) Oxygenation cascade in conversion of n-alkanes to alpha, omegadioic acids catalyzed by cytochrome P450 52A3. J Biol Chem 273(49):32528–32534

Schulz BJE, Boyle CJC, Sieber TN (eds) (2006) Microbial root endophytes. Springer, Berlin. https://doi.org/10.1007/3-540-33526-9

Segura A, Ramos JL (2013) Plant–bacteria interactions in the removal of pollutants. Curr Opin Biotechnol 24(3):467–473. https://doi.org/10.1016/j.copbio.2012.09.011

Shemesh M, Kolter R, Losick R (2010) The biocide chlorine dioxide stimulates biofilm formation in *Bacillus subtilis* by activation of the histidine kinase Kin C. J Bacteriol 192:6352–6356. https://doi.org/10.1128/JB.01025-10

Sherwood S, Uphoff N (2000) Soil health: Research, practice and policy for a more regenerative agriculture. Appl Soil Ecol 15:85–97

Shi W, Becker J, Bischoff M et al (2002) Association of microbial community composition and activity with lead, chromium, and hydrocarbon contamination. Appl Environ Microbiol 68:3859–3866

Shimao M (2001) Biodegradation of plastics. Curr Opin Biotechnol 12(3):242–247. https://doi.org/10.1016/S0958-1669(00)00206-8

Smyth TJP, Perfumo A, Marchant R, Banat IM (2010a) Isolation and analysis of low molecular weight microbial glycolipids. In: Timmis KN (ed) Handbook of hydrocarbon and lipid microbiology. Springer, Berlin, pp 3705–3723

Smyth TJP, Perfumo A, McClean S, Marchant R, Banat IM (2010b) Isolation and analysis of lipopeptides and high molecular weight biosurfactants. In: Timmis KN (ed) Handbook of hydrocarbon and lipid microbiology. Springer, Berlin, pp 3689–3704

Sowerby A, Emmett B, Beier C, Tietema A, Periuelas J, Estiarte M, van Meeteren MJM, Hughes S, Freeman C (2005) Microbial community changes in heath land soil communities along a geographical gradient: interaction with climate change manipulations. Soil Biol Biochem 37 (10):1805–1813

Srivastava J, Naraian R, Kalra SJS, Chandra H (2014) Advances in microbial bioremediation and the factors influencing the process. Int J Environ Sci Technol 11:1787–1800

Su AY, Niu SQ, Liu YZ, He AL, Zhao Q, Paré P, Li MF, Han QQ, Ali Khan S, Zhang JL (2017) Synergistic effects of *Bacillus amyloliquefaciens* (GB03) and water retaining agent on drought tolerance of perennial ryegrass. Int J Mol Sci 18:2651

Sutherland IW (2001) Exopolysaccharides in biofilms, flocs and related structures. Water Sci Technol 43:77–86

Tan R, Zou W (2001) Endophytes: a rich source of functional metabolites. Nat Prod Rep 18:448–459

Tejera N, Lluch C, Martínez-Toledo MV (2005) Isolation and characterization of *Azotobacter* and *Azospirillum* strains from the sugarcane rhizosphere. Plant and Soil 270:223–232

Toyama T, Furukawa T, Maeda N, Inoue D, Sei K, Mori K, Kikuchi S, Ike M (2011) Accelerated biodegradation of pyrene and benzo(a)pyrene in the Phragmites australis rhizosphere by bacteria-root exudates interactions. Water Res 45(4):1629–1638

Ukaegbu-Obi KM, Mbakwem-Aniebo CC (2014) Bioremediation potentials of bacteria isolated from rhizosphere of some plants of oil contaminated soil of Niger Delta. J Appl Enviorn Microbiol 2(4):194–197. https://doi.org/10.12691/jaem-2-4-13

Unterbrunner R, Wieshammer G, Hollender U et al (2007) Plant and fertiliser effects on rhizodegradation of crude oil in two soils with different nutrient status. Plant Soil 300:117–126

Uren NC (2001) Types, amounts, and possible functions of compounds released into the rhizosphere by soil-grown plants. In: Pinton R, Varanini Z, Nannipieri P (eds) The rhizosphere: biochemistry and organic substances at the soil-plant interface. Marcel Dekker, New York, pp 19–40

USEPA (Environmental Protection Agency) (2001) A citizen's guide to monitored natural attenuation. EPA 542-F-01-004, U.S. Environmental Protection Agency, Washington, DC

Uzoigwe C, Burgess JG, Ennis CJ, Rahman PKSM (2015) Bioemulsifiers are not biosurfactants and require different screening approaches. Front Microbiol 6:245. https://doi.org/10.3389/fmicb.2015.00245

Vacheron J, Desbrosses G, Bouffaud M-L, Touraine B, Moenne Loceoz Y, Muller D, Legendre L, Wisniewski Dye F, Prigent Combaret P (2013) Plant growth promoting Rhizobacteria and root system functioning. Front Plant Sci 4:1–19. https://doi.org/10.3389/fpls.2013.00356

Van Beilen JB, Funhoff EG (2005) Expanding the alkane oxygenase toolbox: new enzymes and applications. Curr Opin Biotechnol 16(3):308–314. https://doi.org/10.1016/j.copbio.2005.04.005

van der Heul RM (2009) Environmental Degradation of petroleum hydrocarbons

van Elsas JD, Trevors JT (1997) Modern soil microbiology. Marcel Dekker, New York

Vejan P, Abdullah R, Khadiran T, Ismail S, Nasrulhaq BA (2016) Role of plant growth promoting rhizobacteria in agricultural sustainability—a review. Molecules 21:573

Vimal SR, Singh JS, Arora NK, Singh S (2017) Soil-plant-microbe interactions in stressed agriculture management: a review. Pedosphere 27(2):177–192

Volkering F, Breure AM, Rulkens WH (1997) Microbiological aspects of surfactant use for biological soil remediation. Biodegradation 8:401–417. https://doi.org/10.1023/A:1008291130109

Vurukonda SSKP, Giovanardi D, Stefani E (2018) Plant growth promoting and biocontrol activity of *Streptomyces* spp. as endophytes. Int J Mol Sci 19:952

Welbaum G, Sturz AV, Dong Z, Nowak J (2004) Fertilising soil microorganisms to improve productivity of agroecosystems. Crit Rev Plant Sci 23:175–193

Weyens N, Taghavi S, Barac T, van der Lelie D, Boulet J, Artois T et al (2009a) Bacteria associated with oak and ash on a TCE-contaminated site: characterization of isolates with potential to avoid evapotranspiration of TCE. Environ Sci Pollut Res 16:830–843

Weyens N, van der Lelie D, Taghavi S, Newman L, Vangronsveld J (2009b) Exploiting plant–microbe partnerships for improving biomass production and remediation. Trends Biotechnol 27:591–598

Wick LY, de Munain AR, Springael D, Harms H (2002) Responses of *Mycobacterium* sp. LB501T to the low bioavailability of solid anthracene. Appl Microbiol Biotechnol 58:378–385. https://doi.org/10.1007/s00253-001-0898-z

Zhang Q, Gao X, Ren Y, Ding X, Qiu J, Li N, Zen F, Chu Z (2018) Improvement of *Verticillium* wilt resistance by applying arbuscular mycorrhizal fungi to a cotton variety with high symbiotic efficiency under field conditions. Int J Mol Sci 19:241

Zimmer S, Messmer M, Haase T, Piepho PH, Mindermann A, Schulz H, Habekuß A, Ordon F, Wilbois KP, Heß J (2016) Effects of soybean variety and *Bradyrhizobium* strains on yield, protein content and biological nitrogen fixation under cool growing conditions in Germany. Eur J Agron 72:38–46

PGPR in Management of Soil Toxicity

14

Jupinder Kaur

Abstract

Intensive agricultural practices, development of industries and several other human activities are adding significant amount of pollutants in soil. When these pollutants are present in soil beyond their normal concentration then they act as danger to soil health, human health and environment. Such pollutants which can result in soil toxicity include heavy metals, non-metals (like ammonia) and various other organic compounds (chlorinated as well as non-chlorinated compounds). To overcome the problem of soil toxicity, low cost, efficient and nature friendly remediation techniques are needed. Most of the remediation techniques face limitations due to the toxic nature of pollutants. The battle of soil toxicity can be conquered by using the plant growth promoting rhizobacteria (PGPR). PGPR possess many functional activities, some of which can be used as a tool for remediation of soil toxicity. So, these rhizobacteria not only play role in plant growth promotion and biological control of diseases but they may also help in reducing the toxicity of various pollutants in soil. The use of PGPR for curing soil toxicity is gaining much interest as it offers environment friendly, economical and natural aesthetic benefits.

Keywords

Heavy metals · PGPR · Rhizobacteria · Soil contamination · Soil toxicity

J. Kaur (✉)
Department of Microbiology, Punjab Agricultural University, Ludhiana, Punjab, India
e-mail: jupinderkaur@pau.edu

© The Author(s), under exclusive licence to Springer Nature Singapore Pte Ltd. 2021

V. Kumar et al. (eds.), *Rhizobiont in Bioremediation of Hazardous Waste*,
https://doi.org/10.1007/978-981-16-0602-1_14

14.1 Introduction

Soil is a dynamic and biologically active medium in which soil constituents, soil organisms and plants interact with each other. It acts as a major sink for pollutants released by various natural and human activities (Adriano 2001). The worldwide intensive agricultural practices, industrialization and various other anthropogenic activities like mining release toxic substances such as heavy metals, various non-metals, organic pollutants, etc. which lead to contamination of soil. Toxicity of soil negatively impacts the soil structure and growth of plants resulting in stress and consequently leading to agricultural losses (economic). These problems of soil toxicity can be managed by used of microbes as the various transformations occurring in the soil are associated with the biological activities (microbes) of soil–plant systems (Adriano et al. 2004). Microorganisms perform a wide variety of functions in plant soil ecosystems. A wide range of transformation reactions are carried out by bacteria that cannot be carried out easily by any other species (Rovira et al. 1983). The ability of microbes to adapt and live in various habitats and their vital role in various biogeochemical cycles and other transformations made microbes a suitable candidate for the elimination of various toxic pollutants. Free living rhizobacteria that trigger plant growth and exert other beneficial effects are known as Plant Growth Promoting Rhizobacteria (Kloepper et al. 1989). These soil beneficial bacteria facilitate the growth of plant directly as well as indirectly (Glick 1995). Fixation of atmospheric nitrogen, solubilization of insoluble phosphorous, production of phytohormones, sequestration of iron by siderophore production, etc. are some of the direct mechanisms used by plant growth promoting rhizobacteria for stimulation of plant growth, whereas the protection of plant from diseases by acting as biocontrol agent is the indirect mechanism of PGPR to boost plant productivity (Glick and Bashan 1997). Microorganisms are responsible for the transformation of at least one third elements of the periodic table. The activities of these microbes are affected by environmental factors also (Kaur and Gosal 2015; Kaur and Gosal 2017). The inoculation of PGPRs with diverse functional activities also help the plant to withstand various stresses like salt stress, osmotic stress, heavy metals stress, etc. These transformation reactions help the microbes to metabolize the soil pollutants also. The processes of microbes like assimilation or incorporation into cell biomass, dissimilation to obtain energy or detoxification, etc. act as remediation processes for various soil pollutants (Stolz and Oremland 1999; Upadhyay et al. 2017). This means PGPRs adapt even in the conditions of soil toxicity. So, the activities of microorganisms present in soil are not a prerequisite only for healthy and fertile soil but these microbes are indispensable for degradation of various substances also (Alexander 1999). So, in this chapter we will discuss about sources of soil toxicity, their classification and management of soil toxicity using rhizobacteria.

14.2 Soil Toxicity and Soil Health

Soil is thin layer of loose soil particles covering the rocky surface of Earth. Dirt, mud and ground are the other names of it. Soil is composed of inorganic (fragment of rocks) and organic materials (derived from decaying remains of plants and animals) apart from air, water and various organisms residing in it. Due to its heterogeneity, it is considered as one of the complex system. Soils are formed over many years by the decomposition of parent bed rock and organic matter. It is the basis of agricultural productivity. The productivity of crops for feeding of human and animals are dependent on soil (Belluck et al. 2003). Composition of parent bed rock, climatic conditions and influence of various other factors affect the soil properties like the ability to retain water, cycling of nutrients, micro- and macro-biota it can inhabit, etc. Soil contains various chemical elements as part of the soil minerals. All the soil nutrients and various reactions occurring in soil contribute towards soil health. 'Soil health' term is often used interchangeably with 'soil quality' by the farmers. Soil is considered as healthy if it has good structure, proper amount of organic matter and diverse range of organisms (Brevik et al. 2013). To get maximum productivity of any agricultural crop, soil must be healthy and fertile. As soil is a universal sink, thus it bears the burden of pollution. To maintain soil health, fertility and productivity of agricultural ecosystem, soil pollution needs to be controlled. Moreover, the health of the soil also determines the fate of soil contaminants.

Any soil element or any other chemical which is present at higher concentration than its normal concentration is considered as pollutant. Pollutants adversely affect the non-targeted organisms and can result in toxicity of soil. Presence of pollutants in soil is the worst example of contamination as it causes irreversible damage due to build-up of toxicity. Soil toxicity may be referred to as the higher quantity of any chemical beyond its threshold limit that lead to undesirable physio-chemical and biological changes in properties of soil which disturb various biotic and abiotic components of ecosystem. There are number of ways in which soil can be polluted. The chemical or substances which are responsible for soil toxicity can be natural as well as anthropogenic. The natural sources of waste such as dead plants, remains of animals, rotten fruits and vegetables, only add to the soil fertility. But, the waste produced from anthropogenic sources is full of chemicals and cause soil pollution. Human activities have intentionally added many harmful contaminants in the soil. Heavy metals and pesticides are the most important contaminants encountered in soil. Presence of these toxic substances in soil can adversely affect the soil health and fertility (Upadhyay et al. 2017). Soil toxicity can be considered as hidden danger as it is difficult to perceive it visually and cannot be directly assessed.

14.3 How Toxic Compounds Reach Soil

Presence of toxic compound in soil interferes with the various transformation reactions occurring in soil and can adversely affect the soil properties. Most of the toxic substances enter into the soil environment by accidental discharge of sewage,

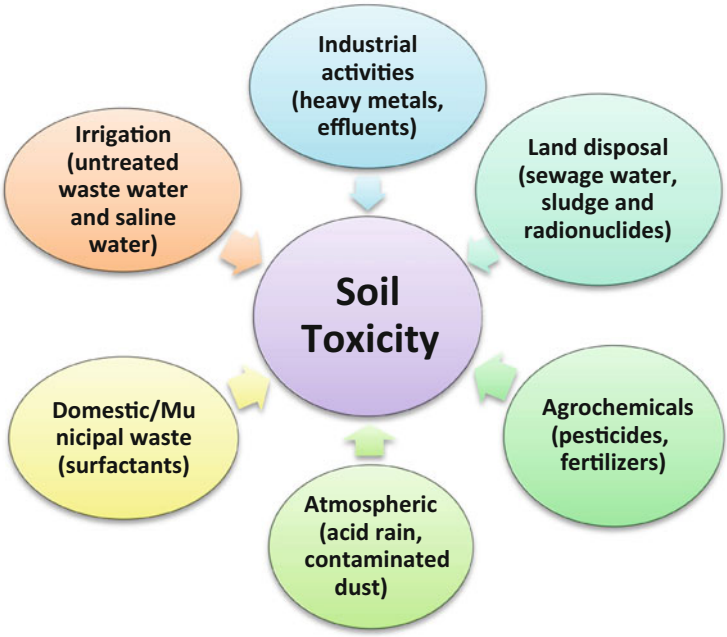


Fig. 14.1 The various causes of soil pollution resulting in soil toxicity

industrial or domestic effluents and sometimes they are part of some beneficial products. There are many ways in which soil become polluted leading to its toxic nature (Fig. 14.1). The release of these pollutant chemicals into the soil is either accidentally (leaching from landfills) or intentionally (fertilizers, pesticides, sewage sludge application, irrigation with untreated waste water). Pollution from anthropogenic sources may work in conjunction with pollution from natural sources resulting in increasing the levels of toxicity in soil. The various routes for entry of toxic compounds into soil are described below.

14.3.1 Industrial

Chemicals are integral part of industries. Industrial activities have been the biggest contributors towards the pollution problems. Industrial activities release various substances or chemicals which pollute soil, air and water. The agricultural waste containing inorganic residues poses serious threats to ecosystem. These inorganic residues contain heavy metals which have high potential for causing soil toxicity. The effluents released from industries also emit a large quantity of sulphur dioxide and arsenic dioxide (Richardson et al. 2006). Soil can become very acidic due to the sulphur dioxide released by industrial effluents. In the atmosphere of phosphoric acid, superphosphate, steel, aluminium and ceramic industries, fluorides are found.

The presence of these metals in the atmospheric waste can destroy vegetation and lead to leaf injury also.

The other metals like cadmium, nickel, arsenic, lead, copper mercury reach the soil through industrial effluents and mine washings. These metals accumulate in soil and cause soil toxicity. Soil particles adsorb the smoke released from automobiles, which is toxic to growth of plants (Van 1996). Radionuclides and gaseous pollutants released from industries reach soil via atmosphere (acid rain/atmospheric deposition). Improper storage of chemicals and direct discharge of industrial waste into soil also lead to soil toxicity. Soil salinity is also a problem in areas near to industries involved in soap and detergent production, ceramic manufacturing, production of textile, glass and rubber, metal processing, animal hide processing and leather tanning, etc. (Saha et al. 2017). The expansion of lead based industries also contributes towards soil toxicity (Zahran et al. 2013). The fertilizer manufacturing industries are among the leading users of heavy metals (mercury, cadmium, arsenic, lead, copper and nickel) and natural radionuclides (^{238}U, ^{232}Th and ^{210}Po). The by-products of industries dealing with mineral extraction are mostly contaminated. These by-products if not disposed properly, will linger on soil surface and this, contribute towards its toxicity.

14.3.2 Land Disposal

The incrementation of human population at an alarming rate consequently results in increased waste production. This is becoming a dangerous situation due to the lack of municipal services dealing with waste management. So, the way of our waste disposal is a main concern in soil toxicity problem. Usually this waste is managed either by disposal in landfills or by incineration. But in both cases, pollutants (heavy metals, pharmaceutical compounds, polyaromatic hydrocarbons, etc.) and their derivatives accumulate in soil (Swati et al. 2014) in the form of landfill leachate or ash fallout from incineration plants which lead to soil pollution and thus, contribute towards its toxicity (Mirsal 2008). By urine or faeces, human also produce certain amount of waste. Part of this waste is directly dumped to landfills and part of it moves to sewage, which ultimately ends at the landfill. The toxins or chemicals present in waste seeps into the land and result in soil toxicity. Sewage sludge is also the chief source of soil pollution. It is the source of various heavy metals like zinc, copper, nickel, lead and chromium toxicity in soil (Wang et al. 2016). If sewage sludge is repeatedly applied to soil in large quantities, then heavy metal accumulation occur in soil and consequently soil can even become unable to support plant growth.

Radionuclides existing in the environment have both natural as well as anthropogenic origin (Mehra et al. 2010). After any radioactive incident, radionuclides become the part of land disposals. Radionuclides have long half-lives.^{40}K,^{238}U, ^{232}Th, ^{90}Sr and ^{137}Cs are among the frequently occurring radionuclides in soil with natural and anthropogenic basis (Wallova et al. 2012).

Nuclear accidents, fallouts during the nuclear weapon testing, mining of radioactive ores, nuclear waste handling and mineral fertilizers, etc. (Ulrich et al. 2014) are main anthropogenic sources of radionuclides. After reaching in soil, these radionuclides are taken up by plants and thus reach various trophic levels through food chain (Zhu and Shaw 2000). These radionuclides remain bioavailable in soils for long time (Falciglia et al. 2014). It is not possible to remove the top layer after any radioactive accident (as it will generate large amount of radioactive waste) so, agricultural countermeasures (like abandoning the soil for years) should be followed to restrict the entry of radionuclides into various level of our food chain (Vandenhove and Turcanu 2011).

14.3.3 Agrochemicals

To get higher productivity of agricultural crops, vast range of chemicals are used. Agrochemicals such as fertilizers, manures and pesticides are source of soil pollution and contribute towards its toxicity. Metals such as arsenic, copper, lead, cadmium and mercury released from these agrochemicals result in soil toxicity. This soil toxicity due to these metals decreases the productivity of crops by impairment with the metabolism of plants. Fungicides used in agricultural production also contain copper and mercury, thus contribute towards soil toxicity. Spillage of agrochemicals during their transport and storage or spillage of hydrocarbons in agricultural soils used as fuel for machine are also among the point sources of pollution contributing towards soil toxicity (Prakash et al. 2014).

More than recommended dose of application of fertilizers or manures or injudicious use of macronutrients like nitrogen, phosphorous can result in mineral toxicity in soil (Kanter 2018). Excessive application of fertilizers pollutes the soil and has negative impact on soil microflora. This can also result in soil salinity, accumulation of nitrate, eutrophication of water bodies which negatively impacts environment as well as act as big threat to human health. Adequate management and handling of fertilizers is the utmost need to prevent the soil from mineral toxicity (Stewart et al. 2005). Instead of inorganic fertilizers, biofertilizers, compost and animal residues can be used as these are good source of nutrients. These provide nutrients and increase organic matter content thus, decrease the dependence on agrochemicals and save the environment and soil from negative impacts (Shiralipour et al. 1992).

Pesticides also contribute towards soil toxicity. Pesticides are the chemical formulations or their combinations used to restrict, eliminate, or lessen the damage caused by any pest. Use of pesticides helps in good security as their application protects the crop from any damage caused by any pest. But, the application of pesticides has negative impacts on soil, environment as well as on human health (FAO and ITPS 2017). Some pesticides are highly persistent, so residues of such pesticides remain in soil for long time thus interfering with the soil properties. Improper storage of pesticide stocks result in its leakage to surroundings thus, polluting the soil, water and environment.

14.3.4 Atmospheric (Acid Rain, Contaminated Dust Such as Sulphur Dust)

Atmosphere also contributes towards the soil toxicity. The gaseous pollutants released from the industries mix up in the air. This air when come in contact with the rain water it reaches soil and cause soil pollution. Acid rain is the most common example. Acid rain occurs when pollutants (like H_2S gas) present in air mix up with the rain (leading to formation of sulphuric acid) and falls back on earth. This polluted rain water on reaching the soil will change the soil properties and contributes towards its toxicity. The chemicals that can travel more easily through air as fine particulate matter are highly risky. The toxic and foul gases emitted from the landfills also pollute the air leading to dust contamination. Contaminated dust also causes serious problems. It also produces the unpleasant smell creating inconvenience. Such chemicals which adhere to dust or move as fine particulate matter are very resistant to degradation and can bio accumulate in living organisms. Construction dust easily spread through air. Due to its lower particle size, it is highly dangerous (as it cause respiratory illness and even cancer). Demolition of older buildings release asbestos, a toxic chemical that poisons the soil.

14.3.5 Domestic/Municipal

Increase in population also lead to generation of more waste. Organic waste of various types causes soil toxicity. When municipal sewage and domestic garbage is inadequately disposed, it affects soil, plant, animals and human health. This waste contains large quantities of detergents, borates and phosphates. If this waste is disposed without any treatment, it can cause soil toxicity.

14.3.6 Irrigation (Untreated Waste Water and Saline Water)

If the untreated waste water, sewage water or saline water is used for irrigation, then it can also cause soil pollution. The presence of toxic substances such as heavy metals, excess of inorganic elements like nitrogen, phosphorous not only causes soil toxicity, but also disturbs, water quality and human health and food security once they enter the food chain (FAO and ITPS 2015).

14.4 Classification of Soil Toxic Compounds

The pollutants present in soil responsible for its toxicity usually originates from anthropogenic processes. Although some substances are present naturally in soil yet human interventions are main contributors towards soil toxicity. The most common toxic substances generally encountered in soil can be classified on the basis of their persistence as well as their chemical nature (Fig. 14.2). Apart from these two main

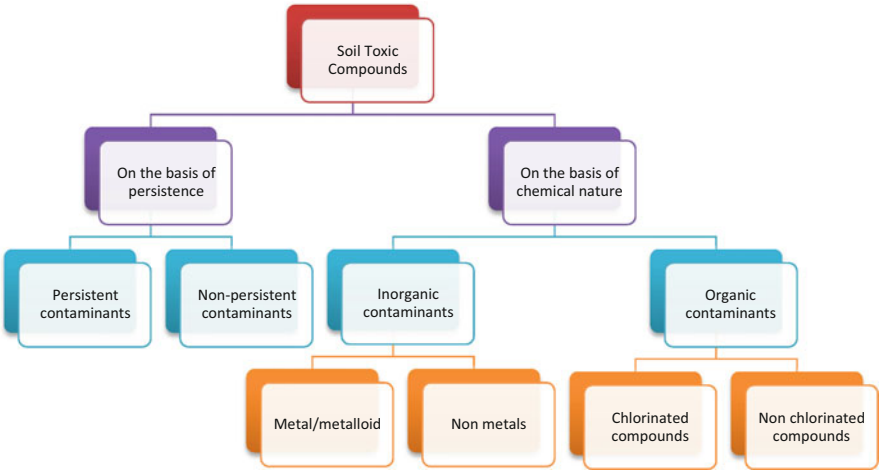


Fig. 14.2 Classification of contaminants responsible for soil toxicity

categorizations, pollutants can be classified on some other basis also but that can result in the overlapping among various classification groups.

14.4.1 On the Basis of Persistence

On the basis of persistence, soil toxic compounds can be persistent or non-persistent. The term persistent or non-persistent refers to how long a pollutant stays in soil.

14.4.1.1 Persistent Pollutants

Persistent pollutants are those which are resistant to degradation. These pollutants accumulate in the food chain and impose negative impact on soil, water quality and human health (UNEP 2018). A number of factors may be responsible for persistence nature of pollutants such as structure that is resistant to microbial degradation, strong sorption or hydrophobicity. Persistent organic pollutants are very common as they are used in agricultural as well as in many industries. Persistent organic pollutants include chlorinated as well as brominated aromatics, polychlorinated biphenyls, organochlorine pesticides such as DDT, etc. Other toxic chemicals like dioxins (polychlorinated dibenzo-p-dioxins and –furans), which are produced from industrial activities and during the ignition of waste, also exist in this category for their long-term persistence. These organic pollutants are hydrophobic in nature which increases their affinity for the lipid membranes of cells and thus allows them to persist in the fatty tissues of living organisms (Jones and de Voogt 1999). They keep on accumulating in the food chain as they move from one organism to the next (Biomagnification). The Stockholm Convention has registered around 20 POPs so far (Stockholm Convention 2018) (Vasseur and Cossu-Leguille 2006). Persistent pollutants persist in soil and contribute towards its toxicity.

14.4.1.2 Non-persistent Pollutants

Non-persistent pollutants are those pollutants which stay in soil for a brief period after their release. These pollutants are biodegradable in nature. Although, the damage caused by non-persistent pollutant is reversible but these pollutants have more immediate toxic action than persistent pollutants. Once the non-persistent pollutants undergo degradation, they no longer cause toxicity in soil and are not a threat for soil, environment and human health. The half-life of these pollutants is also very short (hours to weeks at most). Domestic sewage, fertilizers, chlorinated hydrocarbons such as endosulfan and organophosphates such as malathion are among the examples of non-persistent pollutants.

14.4.2 On the Basis of Chemical Nature

Categorization of chemicals on the basis of their chemical nature was proposed by Swartjes (Swartjes 2011). This is the most systematic way of categorization of pollutants and is very useful in understanding them.

14.4.2.1 Inorganic

The inorganic pollutants include metals, metalloids and non-metals which are described in detail as under:

Metal

Heavy metals are defined as group of metals or metalloids possessing high density (usually greater than 4.5 g cm^{-3}). The metals such as lead, zinc, cadmium, copper, mercury and tin; along with some non-metals such as arsenic, selenium and antimony are also included in this group due to their density and toxic nature (Kemp 1998). Most heavy metals appear in uncontaminated soils during the weathering of parent bed rock. The concentration of heavy metals remains very low in soil under natural conditions. Plants and animals require these elements in trace amounts.

Heavy metals cause phytotoxicity, when present in high concentration. In soil, these metals get strongly adsorbed on organic or inorganic colloidal particles. Being persistent in nature, the remediation of heavy metals is difficult. Due to non-biodegradable in nature, these accumulate in the tissues of living organisms thus; they are threat to soil quality, crop productivity and human health. Among the various metals responsible for soil toxicity, zinc, nickel, cobalt and copper are more toxic to plants whereas cadmium, mercury, lead, arsenic and chromium are more toxic to animals (McBride 1994). Arsenic, lead, cadmium, mercury and selenium are main contaminates of food chain.

The main sources of heavy metals toxicity in soil are anthropogenic such as urban and industrial aerosols, atmospheric deposition, fuel combustion, heavy metal waste disposal, spillage from petrochemicals, animals and human derived solid or liquid material, mining effluent and agrochemicals, etc. (Alloway 2013). Arsenic is introduced in soil with the application of agrochemicals; livestock based manures and mining activities. Weathering of parent bed rock can also result in high arsenic

concentration in soil. Metals such as copper reach the soil due to pesticides (Komarek et al. 2010).

Nonmetal (Cyanide, Ammonia, Sulphur)
Apart from metals, some nutrients or compounds like cyanide, ammonia and sulphur, etc. also affect the soil ecosystem. These nutrients or compounds are added into soil through natural as well as anthropogenic methods. The decrease as well increase in concentration of these nutrients above a certain limit can result in toxic nature of soil. Ammonia fertilizers are added to agricultural soil for the provision of nitrogen to the growing crop. But these fertilizers are often added to soils in high dosage in order to get higher productivity. High amount of mineral nitrogen in soil is not appropriate for good soil health. Excess of ammonia in soil also enhances the process of nitrification which is the process of soluble nitrates formation from the elemental atmospheric nitrogen or ammonia and this process contributes towards soil toxicity as high level of nitrate in soil is toxic to plants as well as organisms. These nitrates also contribute towards water pollution as the nitrates leach out from soil and contaminate groundwater. So, inorganic nitrates and phosphates are responsible for soil contamination as well as result in eutrophication. The decomposition or organic material in soil can release sulphur compounds.

14.5 Organic Compounds

Apart from inorganic compounds, the organic compounds such as chlorinated as well as non-chlorinated compounds are also main contributors towards soil toxicity.

14.5.1 Chlorinated

The chlorinated compounds which contribute towards soil toxicity include alkenes, dioxins, polychlorinated biphenyls, chlorinated pesticides, etc. Dioxin is chemically 2,3,7,8-tetrachlorodibenzoparadioxin (TCDD). Generally, the group of chemicals structurally and functionally related to polychlorinated dibenzo-para-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) the named as ‘dioxins’.

Sometimes, compounds with the same toxicity like polychlorinated biphenyls (PCBs) are also categorized as ‘dioxins’. So far 419 chemical compositions have been grouped under dioxin-related compounds, but only 30 among these are found toxic, with TCDD being the most toxic. These are persistent organic pollutants that are highly toxic in nature. Dioxins undergo biomagnification and keep on accumulating in food chain. Highest level of dioxins is found in animals, which are at the top of food chain. Dioxins can cause developmental and reproductive problems, can cause cancer, interfere with hormones and can also decrease the immunity (WHO 2013).

Other carbon based organic pollutants include persistent organic pollutants (POP’s) which are not easily degradable in the environment. POP’s include

Table 14.1 General description and environmental behaviour of some organic pollutants

POPs	Half–lives	Environmental behaviour in soil
Aldrin	10,000–30,000	Persistent
Chlordane	10,000–30,000	Persistent
DDT	10,000–30,000	Persistent
Hexachlorobenzene	>30,000	Persistent
Mirex	>30,000	Persistent
PCBs	>10,000	Persistent
Polychlorinated dioxins	3000–10,000	Persistent
Polychlorinated furans	10,000–30,000	Persistent
Phenanthrene	2.5–4400	Mineralization
Flouranthrene	2.5–4400	Persistent
Benzopyrene	1368–13,000	Persistent

polycyclic aromatic hydrocarbons (PAH), polychlorinated dibenzofurans (PCDFs), polychlorinated biphenyls (PCBs), polybrominated biphenyls and pesticides such as organophosphorous and carbamates (ex DDT), etc. There are only few studies which deal with the toxicity of these organic pollutants in soil (Burgess 2013). Polycyclic aromatic hydrocarbons (PAHs) pollutants in soil are of major concern due to their recalcitrant and carcinogenic properties (Wilson and Jones 1993). Incomplete combustion of organic material in volcanic activities, burning of fossil fuels, forest fires and hydrothermal wells are important natural sources of PAHs.

Polychlorinated biphenyls are wide spread in all environments due to their use as additives in plastics, electrical insulators, in pesticides, etc. PCBs are introduced into soil through various routes such as application of pesticides or deposition of air particles, etc. Pesticides such as DDT (Dichlorodiphenyltrichloroethane) are also hazardous to soil health due to their persistent nature and their ability to undergo bioaccumulation via process called biomagnification. The general description, half-lives and environmental behaviour of some organic pollutants is given in Table 14.1.

These organic pollutants have structural composition with atoms (such as bromine, sulphur or and chlorine) placed at some unusual positions not commonly found in nature. Due to their persistent nature, these synthetic organic chemicals do not break down easily and consequently prove toxic to living creatures. Hence, these pollutants build up over time in body tissues, or become magnified along food chains. The industries create these compounds in very large quantities; many POPs are actually by-products of these processes.

14.5.2 Non-chlorinated

Apart from, chlorinated compounds, non-chlorinated chemicals also contribute towards soil toxicity. These compounds include volatile organic compounds mainly. Non-chlorinated compounds are diverse and ubiquitous. The main non-chlorinated

compounds which play role in soil toxicity are alkenes such as ethane; aliphatic such benzene, ethyl benzene, xylene or toluene.

14.6 Solution to Soil Toxicity

Soil is the most valuable resource of the nature. As soil is a source of human food also so, healthy and productive soil is essential for the survival of mankind. But, modern agricultural practices, rapid industrialization and many other anthropogenic activities contribute a significant amount of pollutants to soil resulting in soil toxicity. Soil toxicity has many negative effects as it affects soil biological activities as well as soil physico-chemical properties. It is threat to soil fertility and crop productivity as it changes the original nature of soil. With the widespread awareness regarding adverse impacts of soil toxicity, there has been increasing interest in techniques that carry out remediation of soil toxicity. There are many strategies used as a solution to soil toxicity. The strategies in which total concentration of pollutant must be lowered are termed as 'Clean up technologies'. While the strategies that do not aim to lower the pollutant concentration but aims to measure the exposure to pollutant along with taking into consideration the health and environmental risks are called 'Containment technologies'. All these strategies can broadly be categorized into four classes (Fig. 14.3). These classes are described below:

14.7 Thermal Methods

Thermal methods (Fig. 14.4) hold a significant position in remediation of soil pollution as they meet the clean-up standards. Thermal methods remediate the soil pollution site very efficiently and quickly. There are many thermal operations which are used for remediation of toxic soil. These methods are described under:

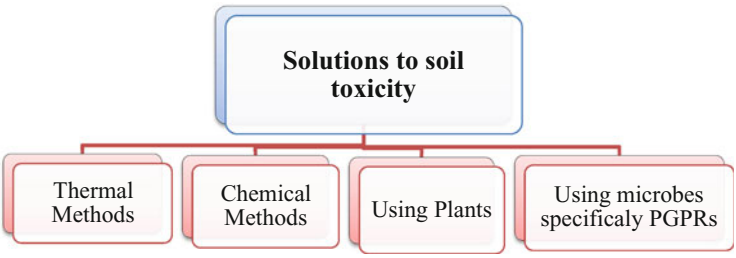


Fig. 14.3 The various solutions for the management of soil toxicity

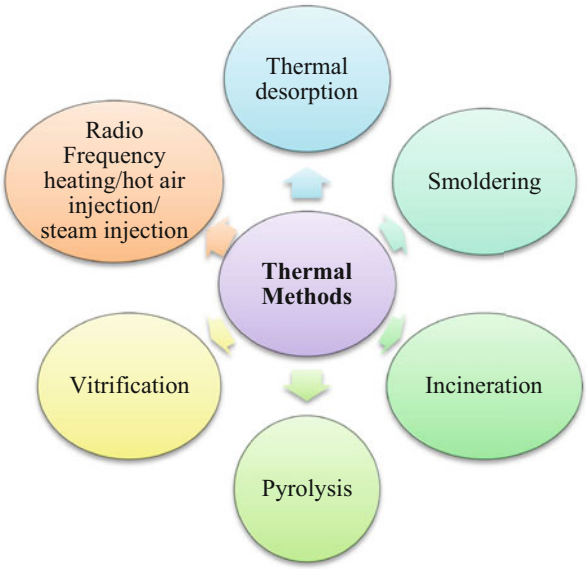


Fig. 14.4 Thermal methods for the management of soil toxicity

14.7.1 Thermal Desorption (TD)

This method involves heating of toxic soil so that the toxic pollutants present in soil either volatilize or get desorbed. The pollutants after volatilization or desorption are removed by vacuum or gas stream. Then these are destroyed by carbon adsorption or incineration (Roberts 1998). There are two variations of TD; one is LTTD and other is HTTD.

- *LTTD*: It refers to low temperature thermal desorption. In this temperature are 100–300 °C.
- *HTTD*: It refers to high-temperature thermal desorption. In this temperature varies from 300 to 550 °C.

Thermal desorption can be carried out ex situ as well as in situ. In ex situ thermal desorption, contaminated soil is excavated and then subjected to thermal desorption units such as rotary drums or thermal screws for heating. Desorbed pollutants are incinerated or disposed using activated charcoal after they are swept away from heating unit. In situ TD involves, use of vacuum wells or dual heaters to desorb and remove soil toxic pollutants using vapour extraction. Gases evolving during the process can be collected for reuse or disposed. Both the methods are highly effective and remove contaminants quickly and efficiently. The cost for TD depends on the contaminated soil. This technique is highly useful for removal of volatile or semi-volatile toxic pollutants.

14.7.2 Smoldering

Smoldering is the exothermic flameless combustion process. Heat, water and carbon dioxide are the final end products after the combustion process. The average temperature in smoldering process ranges from 600 to 1100 °C (Hasan et al. 2015). This process is widely used for oil contaminated sites. During the early phase, combustion is initiated by providing air injection and heating. After ignition, heating can be stopped but air injection will continue as long as the remediation process is not completed. Conduction and convection heat up the soil. This lead to desorption of contaminants as the temperature rises. Pyrolysis can also occur. Therefore, smoldering is a process of exploiting a self-sustained flaming wave to destroy soil pollutants. Off gases are collected for disposal or reuse. Smoldering is useful in treating soils that are hampered with heavy hydrocarbons. Studies have claimed successful removal of significant levels of hydrocarbons through smoldering.

14.7.3 Incineration

Incineration refers to the complete removal of contaminants from polluted soil through combustion at very high temperature. This technology has been found suitable to remove toxic hydrocarbon, municipal and many other hazardous wastes. Depending upon the site of action, it can be on-land or onsite incineration with no excavation of contaminated soil. However, this method of on-land or open burning is problematic, unpredictable and expensive. Therefore, more reliable is the ex situ incineration technology that involves the excavation of contaminated soils followed by combustion in controlled incineration units (Fingas 2010).

Incineration demands the maintenance of high temperature for a continuous period which makes it an expensive technology. Despite, it is a widely used remediation technology owing to its efficiency and effect on a broad range of target contaminants. It can also destroy nearly flammable pollutants.

14.7.4 Pyrolysis

Pyrolysis is defined as the heating of impacted soils in anoxic atmospheres, typically to 400–1200 °C for a variety of hazardous waste. When applied to soils, pyrolysis can function in two different ways. If soil temperature is increased gradually, the pollutants with low molecular weight will first undergo thermal desorption when heated to their boiling temperature. Later, at temperature >250–300 °C, the high energy chemical bonds of the contaminant destroy and it may generate reactive radicals. These bonds and the order in which they are cleaved usually involve C-heteroatom (i.e., C–S) bonds, followed by C–H and then C–C bonds. The reactive radicals may continue their self-destruction reactions (beta-scission) or may initiate a

chain of aromatic condensation reactions that results information of a carbonaceous material (char) with very low H/C ratio (Shearer 1991).

Pyrolysis can remove the soil contaminants at low temperature. It saves energy and sequesters carbon in the form of char.

14.7.5 Vitrification

In vitrification, contaminants are heated to very high temperatures (1600–2000 °C), melted and fused with soil to form a glass-like solid. Radioactive wastes are mostly treated by using this method. It works on the principle that contaminant solid in its molten state develops properties similar to an obsidian and with strength ten times greater than concrete (Shearer 1991). Further, rapid cooling of these molten contaminants prevents crystallization and it develops into stable glass from the non-volatile materials. Soils rich in a variety of organic contaminants such as petroleum or those receiving hazardous inorganic wastes such as heavy metals are best cured by vitrification.

14.7.6 Radio Frequency Heating/Hot Air Injection/Steam Injection

Heating the contaminant by high frequency radio waves (RFH, i.e., microwave heating) can serve as one of the remediation techniques that enhance the efficiency of other processes such as air sparging, bioremediation and enhanced vapour recovery. RFH removes low molecular weight hydrocarbons by causing their volatilization and desorption, improves bioavailability, decreases viscosity and speeds degradation by microbes (Price et al. 1999).

Hot air injection is a soil vapour extraction remediation which functions by increasing mobility and extraction efficiency of the contaminant. More often, steam is used as an additional component with hot air for more efficient transmission of desorbed organics into the vacuum well. The heating capacity of steam is higher than hot air, therefore provides more efficient means for heating soils; when easily accessible (Roberts 1998).

Despite such advantages, thermal methods have disadvantages also. In thermal operations, heating the toxic soil is quite labour intensive and it is very costly also. High temperature used during thermochemical operations can destroy soil organic matter, soil minerals and even soil microbial biota. So although, thermochemical methods efficiently remove the contaminants from soil, yet they are not so much desirable due to their negative impact on soil and plant growth.

14.8 Chemical Methods

Technicians are putting continuous efforts in developing strategies that are environment friendly, simple and economical to maintain and restore quality of soil. A number of chemical based technologies are prevalent to treat polluted soils. These include the small scale remediation approaches with simpler technology; as well as those occurring at a large scale that often encounter more difficulties due to complexity, high costs and several side effects. Chemical treatments (Fig. 14.5) commonly used for the remediation of polluted soil are discussed below:

14.8.1 Encapsulation

In this chemical treatment method, contaminated soils are isolated through low permeability walls or caps to prevent the infiltration of precipitation. The commonly used polymers as barrier for encapsulation are polyethylene, EIA (ethylene interpolymer alloy) and PVC (Poly vinyl chloride). The method of encapsulation for the treatment of toxic soil is economical and simple method. This method has some disadvantages like there is no complete destruction of the contaminant, i.e. it remains at the site of remediation, also the efficiency of this method is limited by time. A number of other factors like properties of the contaminated site and depth of contaminant also influence this remediation process (Mulligan et al. 2001).

14.8.2 Chemical Oxidation

This method relies on a redox reaction involving the formation of stable organometallic complexes through the percolation of organic and inorganic reagents by reduction of metals to their lowest valence state. The most effective oxidizing agents for both inorganic and organic contaminants are chlorine dioxide, hydrogen peroxide and potassium permanganate. Although chemical oxidation is low-cost method

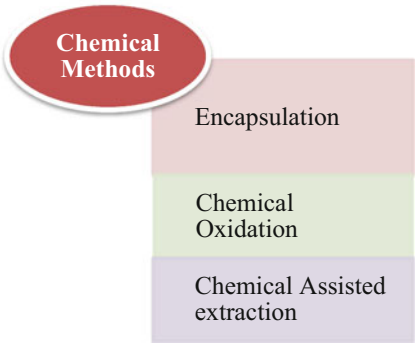


Fig. 14.5 Chemical Methods for the management of soil toxicity

yet it is rather expensive in the case of high-contaminant concentrations (FRTR 2002).

14.8.3 Chemical Assisted Extraction

This method involves the action of chemicals like EDTA (ethylene diaminetetraacetic acid) for abstraction of metals during vigorous mixing. These function as metal chelators that cause the removal of metals from the contaminated soil via extraction. This method is cost effective and even efficient for high dose of metals; but it has been found that the chelator itself may persist long in soil and have harmful effects on plants and other soil biota (Tandy et al. 2004).

14.9 Use of Plants in Toxicity Removal

Traditionally used thermal or chemical soil remediation methods are costly and often result in several harmful side effects. Application of biological methods as a solution to soil toxicity problems is the most desirable and cost effective approach as it has many benefits over thermochemical methods. Green technologies involving phytoremediation have gained popularity due to its environment friendly nature. This technique utilizes green plants for the remediation of pollutants from the environment (Bisht et al. 2014a). It is quite popular and acceptable among the society due to its environment sustainability and aesthetic appeal. Phytoremediation is an autotrophic system, simple to handle with very less requirement of nutrients. There are many plants which are capable of accumulating much diverse range of toxic pollutants into their vegetative or reproductive parts. There are many features which are desirable in plant for its use in phytoremediation. These desirable features are listed below:

- Plant should be fast growing.
- It should have high biomass production.
- It should be native species with extensive root system.
- It should be highly tolerant and capable of accumulating various toxic pollutants.

Phytoremediation of heavy metal polluted soils can be achieved via different mechanisms which include phytoextraction, phytostabilization and phytovolatilization. The first step in phytoremediation is the extraction of soil pollutant from the soil solution (Bisht et al. 2014b). This is followed by the mobilization of pollutant towards surface of roots. The toxic pollutants then bind to root cells and are uptake by roots after recognition and then these pollutants are transported to aerial parts of plants. Transporter proteins along with vascular system are involved in this transportation process.

Being a cost effective, environmental friendly approach, this technique is quite successful when the toxicity levels are low. But, when there is high amount of toxic

Table 14.2 Variations of phytoremediation technique

Phytoextraction	• It is the most common form of phytoremediation • It includes pollutant accumulation; especially heavy metals, in the roots and shoots of phytoremediating plants (can cause problem in food chain). These plants are later harvested and incinerated • Plants used for phytoextractions should have high growth rate, high biomass, extensive root system, and ability to tolerate high amounts of heavy metals
Phytostabilization	• It involves immobilization of metals by plants, resulting in reduced metal bioavailability via leaching and erosion • It is often practiced when phytoextraction is not desirable or even possible • Phytostabilization is the result of metalvalence reduction, precipitation, sorption, or complexation • The plants used for phytostabilization should necessarily have (1) ability to tolerate variable soil conditions, (2) dense root system, (3) rapid growth to provide adequate ground coverage, (4) ease of establishment and maintenance underfield conditions, (5) longevity and (6) ability to self-propagate
Phytovolatilization	• Phytovolatilization is when the plants are allowed to take up pollutants from the soil and then these pollutants undergo transformation into volatile compounds which are transpired into the atmosphere through aerial parts of the plant
Phytodegradation	• It involves the role of plant associated microbes that degrade metal rich organic contaminants
Rhizofiltration	• Plant roots serve as filters to absorb metals from waste in soil

pollutants, the growth of plants retards with less biomass yield. There are many variations in phytoremediation which are described in Table 14.2.

14.10 Use of Microbes Specifically PGPR's in Toxicity Reduction

The limitation of phytoremediation technique, in high toxicity level necessitates the need of other biological sources. The disadvantage of phytoremediation can be overcome using rhizobacteria for the remediation of soil toxicity. PGPR represent a wide array of soil bacteria which, when allowed to grown in association with plant roots, causes the stimulation of the host growth (Vessey 2003). PGPR can impose a positive effect on plant growth by two mechanisms: direct and indirect. During direct growth promotion, these bacteria synthesize various phytohormones, reduces the root membrane potential for better nutrient absorption, synthesize enzymes like ACC deaminase that influence plant hormone production, fixes atmospheric N, produce organic acids to solubilize of inorganic phosphate, mineralize organic phosphorus compounds, mobilize phosphorous to the plants. Indirect promotion of plant growth by PGPR involve activities that induce plant stress response through hormonal signaling or those reducing the deleterious effect of pathogenic microorganisms like synthesis of antibiotics or siderophores.

Apart from the plant growth promoting mechanisms, PGPR strains reduce the toxicity of by converting the pollutants into less toxic form, helping in disease management, modulating bioavailability and help in mitigation of soil toxicity. Several PGPR (*Pseudomonas putida, Bacillus subtilis* and *Enterobacter cloacae*) have been effectively used for the remediation of heavy metals. Some bacteria also enhance the efficiency of phytoremediation by promoting plant growth, alleviating pollutant phytotoxicity, altering bioavailability of pollutants in soil and increasing translocation within the plant.

Use of PGPR in the remediation of soil pollutants is emerging as one of the most effective ways as microbes possess the ability to use these compounds as carbon and nitrogen source.

14.11 Mechanism of PGPR Action

Bacteria remediate organic contaminants through unique degradation pathways of their metabolism (Boopathy 2000). However, bacterial bioremediation may limit in terms of rate and efficiency when the polluted in soil is specifically recalcitrant hydrocarbons (Grishchenkov et al. 2000). PGPR along with the assistance of plants helps in remediation of various toxic pollutants. For example: the plant rhizosphere is rich in root exudates which serve as substrate for microbial growth and metabolism; as well as it maintains soil pH to favour microbial activities (Kumar et al. 2017) The various mechanisms used by PGPR (Fig. 14.6) for the management of soil toxicity are described below:

14.11.1 Acting as a Metal Chelator

In natural environments, the pollutants which are soluble in soil solution like metals are readily absorbed by plant. Whereas, those pollutants present in insoluble

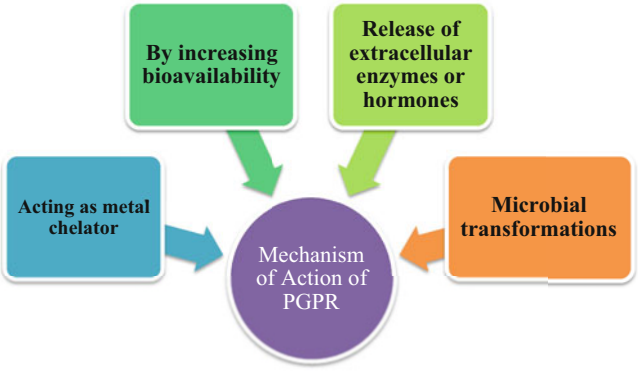


Fig. 14.6 Various mechanisms of PGPR action

precipitate form are unavailable for plant uptake. These recalcitrant pollutants are made available to plants by the application of chelators that causes precipitation and sorption by forming metal chelate complexes. This improves the availability of these pollutants in soil solution (Marques et al. 2009). Addition of chelates has been found an effective approach for improved transport of metal pollutants through the precipitate dissolution and desorption (Norvell 1984). PGPR also release chelating agents to increase the biological availability of pollutants. Examples of chelates include EDDHA (ethylenediamine-di-o-hydroxyphenylacetic acid), EDTA (ethylenediaminetetraacetic acid), EDDS (SS-ethylenediaminedisuccinic acid), HEDTA (N-hydroxyethylenediaminetriacetic acid) and DTPA (diethylenetriaminepentaacetic acid).

PGPR are known to produce organic acids like malic and citric acid; which have an effective chelating ability and therefore; can improve phytoextraction of pollutants from soils. The main disadvantage of using chelates for pollutant bio-availability is the risk of their leaching and the groundwater contamination (Lombi et al. 2001).Synthetic chelates are also available but these may have toxic effect on plants and disturb soil microbial dynamics if used in concentration too high (Chen et al. 2004).

14.11.2 Increases Bioavailability

Bioavailability refers to the amount of element which is available for organism to uptake or adsorption across cellular membrane. In soil toxicity context, it refers to the availability of contaminants. Toxic pollutants can only be taken up if they are in available form (dissolved in water). But, the contaminants are not always present in available or dissolved form. Organic contaminants may become sorbed or sequestered in organic matter. Heavy metals get precipitated into the solid phase. Volatile compounds can be lost as aerosols to the atmosphere. So, in all these forms pollutants are not available for uptake by microbes or plants. So, these toxic contaminants must be dissolved in soil solution to become biologically available. PGPR increase the bioavailability of various pollutants for their degradation.

14.11.3 Release of Extracellular Enzymes/Hormones

Many enzymes are produced by microbes (Kaur et al. 2020). These enzymes also act as indicator of soil health (Kaur et al. 2014). Enzymatic breakdown mediated degradation of pollutants is one of the most important mechanisms used by PGPR. Many hydrolytic enzymes are released by PGPR. These enzymes serve as an essential factor in biocontrol and nutrient recycling. Microbial hydrolytic enzymes can easily hydrolyse the various toxic pollutants. Pollutant rich in cellulose can serve as substrate for microbial cellulose enzyme while keratin for keratinase and chitin for chitinase. Kraft pulp degradation is observed in the presence of both xylanase and β-xylosidase, and sewage sludge is acted upon by protease and phosphatase.

Similarly, synthetic insoluble pollutants like nylon can undergo hydrolysis by enzymes like Mn-dependent peroxidase (MnP), polyacrylate by cellobiose dehydrogenase, polyurethane by esterase, poly-l-lactic acid by depolymerase and alkaline protease (Gramms et al. 1999).

Mostly the bacteria which are used as PGPRs can also produce these enzymes. Understanding the role of PGPRs with activities like ACC deaminase; in mitigating plant stress conditions is currently the focus of researchers. Pollutants having inorganic nitrogen and phosphorous, are utilized by PGPR having nitrogenase and phytase enzyme, respectively. Dehalogenase enzyme hydrolyses chlorine and fluorine from halogenated aliphatic and aromatic hydrocarbons. Laccase, peroxidases and dioxygenase help in the degradation of various organic pollutants. Nitrilase enzyme remove cyanide group from nitriles whereas the nitroreductase enzyme removes nitro group from various nitro compounds (Pieper et al. 2004).

14.11.4 Through Microbial Transformation

Many substances used by microbes are structurally similar to pollutants (Singer 2006). This structural similarity (analogy) favours the accidental uptake of pollutants by microbes called microbial co-metabolism. The oxidative breakdown of a non-growth substrate in the presence of another other growth substrate is termed as co-metabolism. It is observed as a major pathway behind the microbial transformation of pollutants or other complex substrates in environment. Biotransformation refers to the structural modification in chemical compounds (pollutants) that may lead to the formation of new molecules with less toxicity. This mechanism has been developed by microbes to acclimatize to environmental changes and it is functional in a wide range of biotechnological processes. Examples of major microbial transformation are as under:

1. Steroids and sterols.
2. Non steroid compounds.
3. Antibiotics.
4. Pesticides.
5. Other pollutants.

14.12 Role of PGPR in Managing Soil Toxicity

PGPRs are an intact part of bioremediation clean up strategies which aim to reduce the whole proportion of toxic pollutant in soil through various degradative activities of microbes. These microbial groups participating in soil toxicity reduction are also categorized as degraders. These degraders use the pollutants as a source of nutrients and energy. Enrichment of polluted site with specific strains of degrader microbes to boost the remediation process is also practiced as technique named bioaugmentation. A number of remediation trials using non-indigenous strains of degrader PGPRs

have been reported by researchers at site with varying degrees of pollution. However, so far; no strong evidence has been documented indicating significant remediation by non-native microorganisms for tested situations.

The benefit of using PGPR in soil toxicity remediation is that they can are very cost effective. However, microbial bioremediation is more time consuming than other thermochemical or phytoremediation treatments. This is because microbial activities are more sensitive to even minute changes in the degrading environment, nature and dose of the pollutant. Although, not all soil pollutants are amenable to be managed by PGPR yet, but successful results has been observed for soils polluted with petroleum hydrocarbons, wood preservatives, pesticides, solvents and other organic or inorganic chemicals.

14.12.1 Use of Inorganic Compounds

The genus *Bacillus;* specifically *B. subtilis,* has been found with ability to reduce nonmetallic compounds. Garbisu et al. (1995) recorded reduction of toxic selenite to a less toxic product by application of *B. subtilis*. More interestingly, chelating effect of *B. thuringiensis* and *B. cereus* has also been reported for the increased bioavailability of Cd and Zn in soil polluted with waste from metal industry(Mohideena et al. 2010). The chelators facilitating extraction were the siderophores produced (Fe complexing molecules) by these bacteria in soil. It was emphasized that presence of heavy metals must have induced the production and release of siderophore by bacteria which consequently improved metal bioavailability (Lelie et al. 1999). Another bacteria with sulphate reducing ability (*Desulfovibrio desulfuricans*) can also remediate polluted soils; indirectly by bioprecipitation. It reduces the sulphate sulphur to hydrogen sulphate which further reacts with heavy metals such as Cd and Zn to form of metal sulphides.

14.12.2 Use of Organic Compounds

Plant Growth Promoting Rhizobacteria plays a key role in the degradation or removal of contaminants and provides an environmental friendly zone for the plant to thrive (Schwab and Banks 1994). Rhizobacteria are extensively used for remediating soils with organic pollutants. However, results are found more efficient with the synergistic action of plants and microorganisms. The combined approach offers greater efficiency because plant roots can penetrate through the varied substrates and layers of soil and expose the entrapped pollutant to microbes that might have previously been inaccessible (Parrish et al. 2005). In addition, the plant roots can provide natural niche to the degrader microbes; which in turn can stimulate plant based phytoremediation in conditions of stress (Huang et al. 2004a). These benefits from mutual action may have limited the overall efficiency of remediation process probably by effect on the transport of waste from roots to shoots, which is necessary because organic pollutants inhibit photosynthesis (Huang et al. 2004b).

Organic pollutants are generally categorized as recalcitrant xenobiotic pollutants mostly present in high residual concentrations in soils. These generate a significant environmental concern due to their hazardous nature, ability to exist as mutagen or carcinogen (Baek et al. 1991).Phytoremediation of organic pollutants have been attempted several times (Shann and Boyle 1994). However, the presence and survival of beneficial PGPR in organic pollutant rich environment is rarely observed. The success of microbial based bioremediation in such conditions entirely relies on the rhizosphere competence of microbes (Weller and Thomashow 1994). It reflects by the ability of the selected microbes to establish in the plant rhizosphere, sustain insufficient numbers, compete for exudate nutrients, survive the changing environment and keep colonizing the developing root system efficiently (Lugtenberg and Kamilova 2009).

It has been observed in a study that varying doses of TPH undergo successful reduction with the help of two PGPRs strains *Enterobacter cloacae* UW4 and *E. cloacae* CAL2. It was the enzyme aminocyclopropane-1-carboxylate (ACC) deaminase released by PGPR that played the key role in degradation process by reducing the ethylene levels of total petroleum hydrocarbons (TPHs) and making it degradable. Similarly, polycyclic aromatic hydrocarbons (PAHs) have been remediated by enzymes: dioxygenases (e.g., 1,2-dihydroxynaphthalene dioxygenase), dehydrogenases (e.g., 1,2-dihydroxy-l,2-dihydronaphthalenedehydrogenase) and aldolases (e.g., cis-2-hydroxybenzalpyruvate aldolase) released by *Pseudomonas paucimobilis*Q1. One of the most prevalent organic pollutants is polychlorinated biphenyls (PCBs); successfully remediated with enzyme biphenyl dioxygenases of microbial origin. Recombinant *Pseudomonas fluorescens* has been found effective in remediating trichloroethylene (TCE) by producing toluene o-monooxygenase. Microbial enzymes like lignin peroxidase (LiP) and Mn-dependent peroxidase (MnP) are able to degrade biopolymers such as kraft and lignin or trinitrotoluene (TNT).

14.13 Future Advancement

Once it is confirmed that soil is toxic and need for its remediation is recognized, then the next step is the selection of best technology for the soil remediation. The best available technology is dependent on many factors like the origin of the contaminant, nature and degree of toxicity, the conditions of soil containing pollutant (pH, moisture, temperature, organic matter, nutrients, microflora), the time available for remediation, the social acceptance and process economics. These different criteria vary widely among all the technologies. But the major need is the development of low-cost, low-input technologies that can tackle remediation of polluted soils.

Owing to ever-rising community concern for the harm posed by soil pollution, the development of more efficient, multi-action strategies in future is quite expected for human welfare. But at present, with emphasis on being cost effective, sustainable and environmental friendly technologies, PGPR are considered as the best method for the management of soil toxicity. Rapid advancements occurring in molecular

biology will offer a better understanding of the microbial mechanisms involved in remediation of soil toxicity. This knowledge is of fundamental importance in order to optimize these processes.

14.14 Conclusion

Toxicity of soil is an important problem affecting soil properties, agriculture productivity and even human health. Remediation of soil toxicity with sustainable methods is gaining interest of researchers. Among all the approaches used for remediation of soil toxicity, biological systems using PGPR are getting popularity as they are eco-friendly and cost effective. But, a key element in use of PGPR in remediation methods is the understanding of the microbe–plant interaction. Despite many progress made in the soil toxicity remediation, the research is still at its infancy. Molecular engineering of degrader microbes and/or plants is an aspect still unexplored. It would provide opportunities to enhance efficiency or manipulate microbial metabolism for remediation of various soil pollutants. As a result, some PGPRs even have potential to increase plant tolerance to degraded soil and other extreme conditions.

References

Adriano DC (2001) Trace elements in terrestrial environments: biogeochemistry, bioavailability and risks of metals, 2nd edn. Springer, New York

Adriano DC, Wenzel WW, Vangronsveld J, Bolan NS (2004) Role of assisted natural remediation in environmental cleanup. Geoderma 122:121–142

Alexander M (1999) Biodegradation and bioremediation, 2nd edn. Academic Press, San Diego, p 453

Alloway BJ (2013) Heavy metals in soils: trace metals and metalloids in soils and their bioavailability. In: Environmental pollution, 3rd edn. Springer, Dordrecht

Baek SO, Field RA, Goldstone ME, Kirk PW, Lester JN, Perry R (1991) A review of atmospheric polycyclic aromatic-hydrocarbons—sources, fate and behavior. Water Air Soil Pollut 60:279–300

Belluck DA, Benjamin SL, Baveye P, Sampson J, Johnson B (2003) Widespread arsenic contamination of soils in residential areas and public spaces: an emerging regulatory or medical crisis? Int J Toxicol 22:109–128

Bisht S, Pandey P, Kaur G, Aggarwal H, Sood A, Sharma S, Kumar V, Bisht NS (2014a) Utilization of endophytic strain *Bacillus* sp. SBER3 for biodegradation of polyaromatic hydrocarbons (PAH) in soil model system. European J. soil. Biol 60:67–76

Bisht S, Kumar V, Kumar M, Sharma S (2014b) Inoculant technology in *Populusdeltoides*rhizosphere for effective bioremediation of Polyaromatic hydrocarbons (PAHs) in contaminated soil, Northern India. Emirates J Food Agric 26(9):458–470. https://doi.org/10.9755/ejfa.v26i9.18436

Boopathy R (2000) Factors limiting bioremediation technologies. Bioresour Technol 74(1):63–67

Brevik EC, Burgess LC (2013) Soils and human health. CRC Press, Boca Raton

Burgess LC (2013) Organic pollutants in soil. In: Brevik EC, Burgess LC (eds) Soils and human health. CRC Press, Boca Raton, pp 83–102

Chen Y, Li X, Shen Z (2004) Leaching and uptake of heavy metals by ten different species of plants during an EDTA assisted phytoextraction process. Chemosphere 57(3):187–196
Falciglia PP, Cannata S, Romano S, Vagliasindi FG (2014) Stabilisation/solidification of radionuclide polluted soils—part I: assessment of setting time, mechanical resistance, g-radiation shielding and leachate g-radiation. J Geochem Explor 142:104–111
FAO and ITPS (2015) Status of the world's soil resources (SWSR)—main report. Food and Agriculture Organization of the United Nations and Intergovernmental Technical Panel on Soils, Rome. Available at http://www.fao.org/3/a-i5199e.pdf
FAO and ITPS (2017) Global assessment of the impact of plant protection products on soil functions and soil ecosystems. Food and Agriculture Organization of the United Nations, Rome. Available at http://www.fao.org/3/I8168EN/i8168en.pdf
Fingas M (2010) An overview of in-situ burning. In: Fingas M (ed) Oil spill science and technology. Gulf Professional Publishing, Burlington, pp 737–903
FRTR (Federal Remediation Technology Roundtable) (2002) Remediation technologies screening matrix and reference guide. Version 4.0. http://www.frtr.gov/matrix2
Garbisu C, Gonzalez S, Yang WH (1995) Physiological mechanisms regulating the conversion of selenite to elemental selenium by *Bacillus subtilis*. Bio Factors 5:29–37
Glick BR (1995) The enhancement of plant growth by free-living bacteria. Can J Microbiol 41:109–117
Glick BR, Bashan Y (1997) Genetic manipulation of plant growth-promoting bacteria to enhance biocontrol of fungal phytopathogens. Biotechnol Adv 15:353–378
Gramms G, Voigt KD, Kirsche B (1999) Oxidoreductase enzymes liberated by plant roots and their effects on soil humic material. Chemosphere 38:1481–1494
Grishchenkov VG, Townsend RT, McDonald TJ, Autenrieth RL, Bonner JS, Boronin AM (2000) Degradation of petroleum hydrocarbons by facultative anaerobic bacteria under aerobic and anaerobic conditions. Process Biochem 35(9):889–896
Hasan T, Gerhard JI, Hadden R, Rein G (2015) Self-sustaining smouldering combustion of coal tar for the remediation of contaminated sand: two-dimensional experiments and computational simulations. Fuel 150:288–297
Huang XD, El-Alawi Y, Penrose DM, Glick BR, Greenberg BM (2004a) Responses of three grass species to creosote duringphytoremediation. Environ Pollut 130:453–463
Huang XD, El-Alawi Y, Penrose DM, Glick BR, Greenberg BM (2004b) A multi-process phytoremediation system for removal of polycyclic aromatic hydrocarbons from contaminated soils. Environ Pollut 130:465–476
Jones KC, de Voogt P (1999) Persistent organic pollutants (POPs): state of them science. Environ Pollut 100(1–3):209–221
Kanter DR (2018) Nitrogen pollution: a key building block for addressing climate change. Clim Change 147(1–2):11–21. https://doi.org/10.1007/s10584-017-2126-6
Kaur J, Gosal SK (2015) Influence of weather parameters on activities of bacterial population associated with rhizospheric soil of rice crop. Eco Env Cons 21(3):1255–1262
Kaur J, Gosal SK (2017) Influence of environmental factors on activities of bacterial population associated with rhizospheric soil of wheat crop. Eco Env Cons 21(3):1255–1262
Kaur J, Gosal SK, Kaur P (2014) Effects of climate change on plant associated microbial communities and enzyme activities. Afr J Microbiol Res 8(33):3087–3093
Kaur J, Gosal SK, Khurana S (2020) Soil enzymes: an agricultural perspective. In: New perspectives in agricultural sciences. Lambert Academic Publishing, Latvia, pp 59–82
Kemp DD (1998) The environment dictionary. Routledge, London; New York
Kloepper JW, Lifshitz R, Zablotowicz RM (1989) Free-living bacterial inocula for enhancing crop productivity. Trends Biotechnol 7:39–43
Komárek M, Cadková E, Chrastný V, Bordas F, Bollinger JC (2010) Contamination of vineyard soils with fungicides: a review of environmental and toxicological aspects. Environ Int 36 (1):138–151. https://doi.org/10.1016/j.envint.2009.10.005

Kumar V, Kumar M, Sharma S, Prasad R (2017) Probiotics in agroecosystem. Springer, Singapore. https://doi.org/10.1007/978-981-10-4059-7

Lelie DV, Corbisier P, Diels L (1999) The role of bacteria in the phytoremediation of heavy metals. In: Terry N, Banuelos E (eds) Phytoremediation of contaminated soil and water. Lewis, Boca Raton, pp 265–281

Lombi E, Zhao FJ, Dunham SJ, McGrath SP (2001) Phytoremediation of heavy metal-contaminated soils: natural hyperaccumulation versus chemically enhanced phytoextraction. J Environ Qual 30(6):1919–1926

Lugtenberg B, Kamilova F (2009) Plant-growth-promoting rhizobacteria. Annu Rev Microbiol 63:541–556

Marques APGC, Rangel AOSS, Castro PML (2009) Remediation of heavy metal contaminated soils: Phytoremediation as a potentially promising clean-up technology. Crit Rev Environ Sci Technol 39(8):622–654

McBride MB (1994) Environmental chemistry of soils. Oxford University Press, New York

Mehra R, Kumar S, Sonkawade R, Singh NP, Badhan K (2010) Analysis of terrestrial naturally occurring radionuclides in soil samples from some areas of Sirsa district of Haryana, India using gamma ray spectrometry. Environ Earth Sci 59(5):1159–1164. https://doi.org/10.1007/s12665-009-0108-3

Mirsal I (2008) Soil pollution: origin, monitoring & remediation. Springer, Berlin, pp 310–321

Mohideena RAH, Thirumalai AV, Narayananb KR, Zahir HMI (2010) Bioremediation of heavy metal contaminated soil by the exigo bacterium and accumulation of Cd, Ni, Zn and Cu from soil environment. Int J Biol Technol 1(2):94–101

Mulligan CN, Yong RN, Gibbs BF (2001) Remediation technologies for metal-contaminated soils and groundwater: an evaluation. Eng Geol 60:193–207

Norvell WA (1984) Comparison of chelating agents as extractants for metals in diverse soil materials. Soil Sci Soc America J 48(6):1285–1292

Parrish ZD, Banks MK, Schwab AP (2005) Assessment of contaminant lability during phytoremediation of polycyclic aromatic hydrocarbon impacted soil. Environ Pollut 137:187–197

Pieper DH, Martins VPS, Golyshin PN (2004) Genomic and mechanistic insights into the biodegradation of organic pollutants. Curr Opin Biotechnol 15:215–224

Prakash A, Bisht S, Singh J, Teotia P, Kela R, Kumar V (2014) Biodegradation potential of petroleum hydrocarbons (PHCs) by bacteria and mixed bacterial consortium isolated from contaminated sites. Turkish J Eng Env Sci 38(1):31–40

Price SL, Kasevich RS, Johnson MA, Wiberg D, Marley MC (1999) Radio frequency heating for soil remediation. J Air Waste Manage Assoc 49(2):136–145

Richardson GM, Bright DA, Dodd M (2006) Do current standards of practice in Canada measure what is relevant to human exposure at contaminated sites? II: oral bioaccessibility of contaminants in soil. Hum Ecol Risk Assess 12:606–618

Roberts RE (1998) Remediation of petroleum contaminated soils: biological, physical, and chemical processes. CRC Press, Boca Raton

Rovira AD, Bowden GD, Foster RC (1983) The significance of rhizospheremicroflora and mycorrhizas in plant nutrition. In: Lauechli A, Bieleski B (eds) Inorganic plant nutrition. Springer, Berlin, pp 61–93

Saha JK, Selladurai R, Coumar MV, Dotaniya ML, Kundu S, Patra AK (2017) Soil pollution—an emerging threat to agriculture. In: Environmental chemistry for a sustainable world. Springer, Singapore

Schwab AP, Banks MK (1994) Biologically mediated dissipation of polyaromatic hydrocarbons in the root-zone. In: Anderson TA, Coats JR (eds) Bioremediation through rhizosphere technology. American Chemical Society, Washington, DC, pp 132–141

Shann JR, Boyle JJ (1994) Influence of plant species on in situ rhizosphere degradation. In: Anderson TA, Coats JR (eds) Bioremediation through rhizosphere technology. American Chemical Society, Washington, DC, pp 70–81

Shearer TL (1991) A comparison of in situ vitrification and rotary kiln incineration for soils treatment. J Air Waste Manage Assoc 41(9):1259–1264
Shiralipour A, McConnel B, Smith WH (1992) Uses and benefits of MSW compost: a review and an assessment. Biomass Bioenergy 3(3–4):267–279. https://doi.org/10.1016/0961-9534(92)90031-K
Singer AC (2006) The chemical ecology of pollutant biodegradation: bioremediation and phytoremediation from mechanistic and ecological perspectives. In: Phytoremediation rhizoremediation. Springer, Berlin, pp 125–137
Stewart WM, Dibb DW, Johnston AE, Smyth TJ (2005) The contribution of commercial fertilizer nutrients to food production. Agron J 97(1):1–11. https://doi.org/10.2134/agronj2005.0001
Stockholm Convention (2018) All POPs listed in the Stockholm Convention. http://chm.pops.int/TheConvention/ThePOPs /ListingofPOPs/tabid/2509/Default.aspx
Stolz JF, Oremland RS (1999) Bacterial respiration of arsenic and selenium. FEMS Microbiol Rev 23:615–627
Swartjes FA (2011) Dealing with contaminated sites. Springer Netherlands, Dordrecht
Swati GP, Das MT, Thakur IS (2014) In vitro toxicity evaluation of organic extract of landfill soil and its detoxification by indigenous pyrene-degrading *Bacillus* sp. ISTPY1. Int Biodeter Biodegr 90:145–151. https://doi.org/10.1016/j.ibiod.2014.03.001
Tandy S, Bossart K, Mueller R, Ritschel J, Hauser L, Schulin R (2004) Extraction of heavy metals from soils using biodegradable chelating agents. Environ Sci Technol 38(3):937–944
Ulrich AE, Schnug E, Prasser HM, Frossard E (2014) Uranium endowments in phosphate rock. Sci Total Environ 478:226–234. https://doi.org/10.1016/j.scitotenv.2014.01.069
UNEP (2018) World commits to pollution-free planet at environment summit. In: UN Environment. http://www.unenvironment.org/newsandstories/press-release/world-commits-pollution-free-planet-environmentsummit
Upadhyay N, Vishwakarma K, Singh J, Mishra M, Kumar V, Rani R, Mishra RK, Chauhan DK, Tripathi DK, Sharma S (2017) Tolerance and reduction of chromium (VI) by *Bacillus* sp. MNU16 isolated from contaminated coal mining soil. Front Plant Sci 8:778–791. https://doi.org/10.3389/fpls.2017.00778
Van JA (1996) Exposure to mixtures of chemical substances: is there a need for regulations? Food Chem Toxicol 34:1033–1036
Vandenhove H, Turcanu C (2011) Agricultural land management options following large-scale environmental contamination. Integr Environ Assess Manag 7(3):385–387. https://doi.org/10.1002/ieam.234
Vasseur P, Cossu-Leguille C (2006) Linking molecular interactions to consequent effects of persistent organic pollutants (POPs) upon populations. Chemosphere 62(7):1033–1042. https://doi.org/10.1016/j.chemosphere.2005.05.043
Vessey JK (2003) Plant growth promoting rhizobacteria as biofertilizers. Plant and Soil 255 (2):571–586
Wallova G, Kandler N, Wallner G (2012) Monitoring of radionuclides in soil and bone samples from Austria. J Environ Radioact 107:44–50. https://doi.org/10.1016/j.jenvrad.2011.12.007
Wang F, Wang Z, Kou C, Ma Z, Zhao D (2016) Responses of wheat yield, macro- and micro-nutrients, and heavy metals in soil and wheat following the application of manure compost on the North China plain. PLoS One 11(1):e0146453. https://doi.org/10.1371/journal.pone.0146453
Weller DM, Thomashow LS (1994) Current challenges in introducing beneficial microorganisms into the rhizosphere. In: O'Gara F, Dowling DN, Boesten B (eds) Molecular ecology of rhizospheremicroorganisms. VCH, Weinheim, pp 1–18
WHO (2013) Ten chemicals of major health concern. www.who.int/ipcs/assessment/public_health/chemicals_phc/en/index.html
Wilson SC, Jones KC (1993) Environ Pollut 88:229–249

Zahran S, Laidlaw MAS, McElmurry SP, Filippelli GM, Taylor M (2013) Linking source and effect: resuspended soil lead, air lead, and children's blood lead levels in Detroit, Michigan. Environ Sci Technol 47(6):2839–2845. https://doi.org/10.1021/es303854c

Zhu YG, Shaw G (2000) Soil contamination with radionuclides and potential remediation. Chemosphere 41(1–2):121–128

Earthworms, Plants, and GMO's Towards Natural Bioremediation

15

Rajalakshmi Sridharan and Veena Gayathri Krishnaswamy

Abstract

The development of urbanization and increase in population has lead to the production of synthetic compounds. These compounds are toxic if not treated properly. The process of treatment of these pollutants are widely studied and explored using various methods such as physical, chemical, and biological methods. The biological method of treatment was reported to be effective in treatment of pollutants by degrading into less toxic compounds. There are also some limits in this biological process as not all the biological living systems are used for the treatment of toxic compounds. The use of microorganisms has thrown light on the remediation and degradation of pollutants. But, the range of usage of the living systems is broadened even by using plants, invertebrates, and other classes of living forms. This might be a wider area for choosing the better method in biological treatment process. Each method has it pros and cons, instead turning it into an advantage for the sustainable environment requires the input of some biotechnological knowledge by developing a new strain or modifying the native strains for enhanced results. Hence, this chapter focuses on the upcoming and hardly explored methods of bioremediation involving earthworms (vermiremediation), plants (phytoremediation), and remediation using genetically modified organisms.

Keywords

Bioremediation · Earthworms · GMO's · Plants

R. Sridharan · V. G. Krishnaswamy (✉)
Department of Biotechnology, Stella Maris College, Chennai, Tamilnadu, India
e-mail: veenagayathri@stellamariscollege.edu.in

© The Author(s), under exclusive licence to Springer Nature Singapore Pte Ltd. 2021

V. Kumar et al. (eds.), *Rhizobiont in Bioremediation of Hazardous Waste*,
https://doi.org/10.1007/978-981-16-0602-1_15

Table 15.1 Classification of earthworm (Goody 2018)

Phylum	*Annelida*
Class	*Clitellata*
Subclass	*Oligochaeta*
Order	*Haplotaxida or Lumbriculida*
Family	*Acanthodrilidae* *Ailoscolidae* *Alluroididae* *Almidae* *Criodrilidae* *Eudrilidae* *Exxidae* *Glossoscolecidae* *Hormogastridae* *Lumbricidae* *Lutodrilidae* *Megascolecidae* *Microchaetidae* *Ocnerodrilidae* *Octochaetidae* *Parganophilidae*

15.1 Introduction

Earthworms are Oligochaetes which are commonly referred to as soil engineer. Earthworms are involved in soil turning, mixing of soil zones, breaking down inorganic matters and they are collectively called pedogenesis (Carpenter et al. 2008; Coleman and Wall 2015). The classification of earthworms is given in Table 15.1.

15.2 Habitat

Earthworms are found widely in the aired and moisturized soil where the temperature is favorable. The earthworms are found abundance in temperate, tropical, and grassland regions (Curry et al. 1995). The habitats of earthworms are specified by the niche in which they live. The niche differs from family to family, species to species. The location of a niche by earthworm species indicates its physical characteristics. The niche of the earthworm can be identified by their color, size, and active movements (https://www.sciencelearn.org.nz/resources/7-niches-within-earthworms-habitat).

15.3 Classification of Earthworms Based on Niche

The earthworms, based on the niche in which they survive are classified into Epigeic (surface soil dwellers), Endogeic (topsoil dwellers), and Acenic (deep burrowing dwellers). The Fig. 15.1 shows the niches of earthworms and Table 15.2 explains the

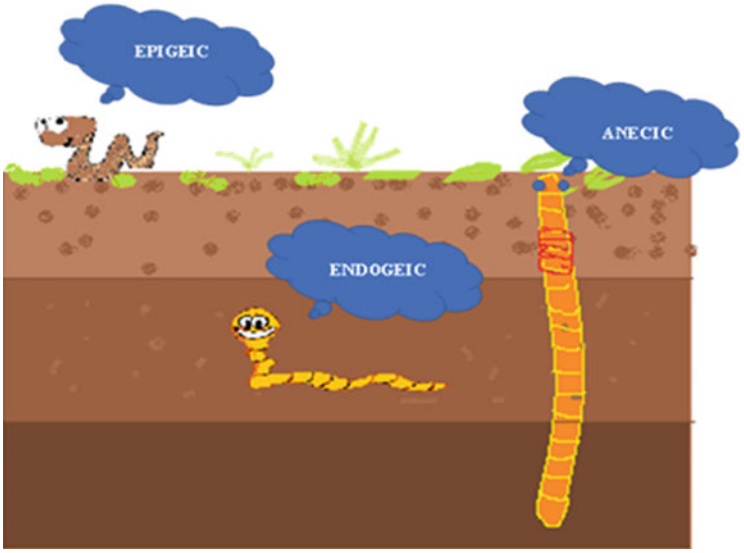


Fig. 15.1 The niches of earthworms (https://www.sciencelearn.org.nz/resources/7-niches-within-earthworms-habitat)

Table 15.2 Characteristics of earthworms based on niche (https://www.sciencelearn.org.nz/resources/7-niches-within-earthworms-habitat)

Niches	Size	Pigmentation	Movements	Channel	Soil depth
Epigeic	1–18 cm long	Dark	Quick	Not permanent	A top surface of the soil
Endogeic	2.5–30 cm long	Sparingly pigmented	Quick	Shallow semi-permanent burrows	Top 20 cm depth
Acenic	3 cm to 4 m long	Less pigmentation (mostly pale)	Sluggish	Extensive permanent burrows	3 m below the soil surface

characteristics of earthworms in each niche (https://www.sciencelearn.org.nz/resources/7-niches-within-earthworms-habitat).

15.4 Earthworms—Biomonitors of Soil Pollution

Earthworms are used as biomonitors as they accumulate the pollutants and break them with the help of microbiota and enzymes present in it or produced by it. The plants, snails, honey bees are also used as biomonitors but these organisms are not widely available and not easily cultivable (Harnly et al. 1997; Hirano et al. 2011). This explains the need for alternative biomonitors and earthworms fit the best. The earthworms are exclusively studied for its gut microbiota. Bioremediation by the microbiota and by the earthworm itself provides a new perspective. The toxicity and

concentration of the pollutants have a direct effect on earthworm population. Thus, the processes of studying the toxicity of the pollutants are called as Ecotoxicology. *Eisenia fetida* are widely used as biomonitor for testing the toxicity as it is sensitive to pollutants (Brulle et al. 2006).

15.5 Earthworm—Home for Microbiota

The microorganisms in soil are enriched by the presence of earthworms. The earthworms have diverse gut microbiome as they feed on the various inorganic matters in the soil. Soil microorganisms ingested by the earthworm constitute a part of the diet. The elimination of irrelevant microbes and assimilation of nutrients by the symbiotic microorganisms present in the gut aides in enhancing the soil fertility (Edwards and Bohlen 1996). The mucus present in the earthworm gut provides an ideal environment for the growth of microorganisms (Barois et al. 1986). Hence, the digestive system of the earthworm is considered as "mutualistic digestive system" (Barois et al. 1986; Lavelle et al. 1995).

These microorganisms develop resistance against pollutants in the soil which in turn makes the earthworm resistance to the polluted environment and aids in the survival. Thus, earthworms and its microbiome have its importance not only in composting and maintaining soil fertility but also in degrading the pollutants either by the microorganisms in the gut of earthworm or in the niche in which they survive.

The microorganisms in the earthworm gut were observed to act as plant growth-promoting factors, nitrogen fixers, and phosphate solubilizers (Loreno-Osti et al. 2004; Romero and Martínez 2001). These microbes are known to exhibit mutualism (Brown et al. 2000; Barois and Lavelle 1986). The studies showed that there was an increase in the δ-*proteobacteria* and the *Cytophaga flavobacterium* post digestion and decrease in the α-, β-, and γ- proteobacteria (Horn et al. 2003). The genus *Acidovorax*, *Streptomyces*, and *Mycobacterium* were found in the earthworm gut (Thakuria et al. 2010). The number of actinomycete and bacterial isolates was found to be higher in number in the gut than in the soil. *Allolobophora caliginosa* contained more yeast, fungi, and bacteria in its gut. The number of microorganisms varies according to the feed of earthworm (Parle 1963). It was studied that the pH of the gut content is neutral as it contains 40% to 70% of the water in it. The pH of the midgut is slightly acidic compared to the anterior and posterior gut parts (Lee 1985). The carbon and nitrogen ratio in the gut of earthworm was observed to be seven which are due to high total carbon, organic carbon, and nitrogen in the gut (Horn et al. 2003).

15.6 Evolution and Resistivity for Survival in Pollution

The concept of earthworm resistivity rose during the years 1953 and 1979, the period where the Hudson River was contaminated by approximately 53 tons of cadmium and nickel hydride. The concentration of cadmium was more than 10,000 ppm in the

river beds and the sediments. This, in turn, has to affect the survival of the earthworm population in the river sediments. Instead, the earthworm species *Limnodrilus hoffmeisteri* survived in the highly cadmium contaminated environment. Thus, it proved that the prolonged exposure of cadmium developed resistance in earthworms and this led to the survival of the earthworms. To study the concept of development of resistivity, researchers studied that the presence of the protein metallothionein (metal-binding protein) was the reason for the resistivity of cadmium/metal resistance in earthworm population. The major reason behind the resistivity was observed to be the gene that already existed in the earthworms and it was activated when the earthworms are exposed to cadmium. This reported that there is no role of evolution in the development of resistance in earthworms (Levinton et al. 2003; Blackman 2003). The heavy metals in the soil were reported to reduce the fertility, cocoon production, growth and cause earthworm mortality (Spurgeon et al. 1994; Siekierska and Urbanska-Jasik 2002; Nahmani et al. 2007; Usmani and Kumar 2015).

An outbreak in Italy by Seveso chemical plant explosion in the year 1976, in which the land was contaminated by chemical named TCDD (2, 3, 7, 8-tetrachlorodibenzo-p-dioxin). The earthworms survived by bio-accumulating the dioxin in their tissues up to 14.5-fold of its concentration (Satchell 2012). It is also reported that the earthworm can convert the fly-ash produced by coal plants into vermicompost. The heavy metals such as Cd, Cu, Ni, Pb, Zn are toxic to the earthworm species (Spurgeon and Hopkin 1995). The uptake and excretion of heavy metals by earthworms occurs either by biotransformation or biodegradation. The metals that enter the gut by ingestion get metabolized, immobilized, and excreted as non-toxic casts into the environment. The bioaccumulation of Pb occurs in the muscles, nerve chord, cerebral ganglion, seminal vesicles, and other parts which pass to the cocoon. This availability of Pb in the cocoons affects embryo development (Gupta et al. 2005). The earthworm's survival hacks are based on the process of bioaccumulation and biotransformation of heavy metals or other organic pollutants. The toxic heavy metals and pollutants get accumulated in the tissues and this cleanup process aids in the revival of the contaminated soil (Elliot 1997; Usmani and Kumar 2015). This made earthworm a potential bioindicator which helps to determine the concentration of the pollutant in the soil by assessing the quantity of pollutant accumulated in the soil (Butt 1999).

The earthworms are quoted as soil engineers as they contribute to soil structuring. This explains the importance of earthworms in agriculture as it plays a key role in the biogeochemical cycle. The application of pesticides/insecticides in the soil to prevent the loss of crops by pest invasion was developed. Thus, there is a need to test the toxicity of the pesticide on the living organisms. The toxicity of the pesticide or any other pollutant determination is achieved by performing Acute and Reproductive toxicity analysis. This includes monitoring the physical activities, growth, reproduction (cocoon formation and production), maturation, and mortality. The production of cocoons was reported to be inhibited by pesticides such as parathion, endosulfan, and fenamiphos (Yasmin and D'Souza 2010).

15.7 Vermiremediation

Vermiremediation is a process of remediation of contaminated soil using earthworms. This occurs either by absorption or bioaccumulation. The earthworm uptake the pollutants, break down to produce the non-toxic compound in the form of the cast which acts as a nutritional source to enhance fertility. The process of vermiremediation is an unexplored or flourishing technique. Vermiremediation of Poly Aromatic Hydrocarbons (PAH) (Zeb et al. 2020) and heavy metals are being widely studied. Earthworm species such as *Lumbricus rubellus*, *Eisenia fetida*, *Perionyx excavatus* are exclusively studied in the remediation of pollutants (Bhat et al. 2018).

15.8 Phytoremediation

The process of remediation which involves plants for removal of pollutants in soil or water is called the Phytoremediation. In this process, plants act as a trap or filter for removing or stabilizing or degrading the pollutants. The plants are grown in contaminated sites where the plants immobilize or degrade the inorganic pollutants. After a significant decrease in the concentration of the pollutant in the soil or water or after the plants meets its threshold, the plants are harvested and disposed of. The synergistic relationship exists between the plants, soil, and microorganisms. Plants act as a host system for aerobic and anaerobic microorganisms by providing a wide range of colonizable space. Phytoremediation has been used for the removal of pesticides, metals, PAH, solvents, explosives, and leachates (Ahalya and Ramachandra 2006). Table 15.3 explains the types of phytoremediation.

15.9 Merits and Demerits of Phytoremediation

The process includes minimum cost requirement compared to process like solidification, excavation, and leaching (Stehouwer 2014). The phytomining process includes the recovery of accumulated contaminants in the plants as it was

Table 15.3 Types of phytoremediation (http://www.cpeo.org/techtree/ttdescript/phytrem.html)

Rhizosphere biodegradation	Biodegradation by microorganisms in the root of the plants
Phyto-stabilization	Plants immobilize the compounds rather than degrading it
Phyto-accumulation/ phyto-extraction	Accumulation of pollutants in shoots and leaves of the plant
Rhizo-filtration	Ex-situ groundwater treatment by roots
Phyto-volatilization	The uptaken contaminants evaporate through the stomata in the leaves
Phyto-degradation	The contaminants are degraded with the plant tissues
Hydraulic control	The indirect remediation of contaminants by controlling the groundwater movement by the roots of trees

transformed into less toxic than the parent compound. This process is carried in many companies where the extracted contaminants were turned into a finished product. This is an eco-friendly approach which has minimal or no invasion of other species. It also structures the soil and enhances microbial growth (https://sites.google.com/site/thephytersphytoremediation/advantages-and-drawbacks). Planting trees in the contaminated sites makes the site pleasant and appealing (Sasi 2011).

The phytoremediation process also has its demerits. The major demerit that is considered is the duration of remediation. The phytoremediation is the slowest process of remediation of pollutants. This is because remediation is a dependent factor. The growth rate of the plants or trees, the ability of the plant to concentrate or accumulate or degrade the pollutant is considered as an important factor. The process may take even decades to reduce the concentration of the contaminants to half of its initial concentration (Mcgarth and Zhao 2003). The plants are known starters of the food chain. If they are applied in the remediation of pollutants, it should be monitored regularly or it might harm the living organisms at the high tropic level. There are also chances of biomagnification of the pollutants at high tropic level in the food pyramid. This can be avoided by regular monitoring and avoiding or reducing the usage of edible plants (https://sites.google.com/site/thephytersphytoremediation/advantages-and-drawbacks).

Figure 15.2 shows the process of bioaccumulation. The process of bioaccumulation, in turn, leads to the process called biomagnification. This involves the transfer of pollutants from one tropic level to another as shown in Fig. 15.3.

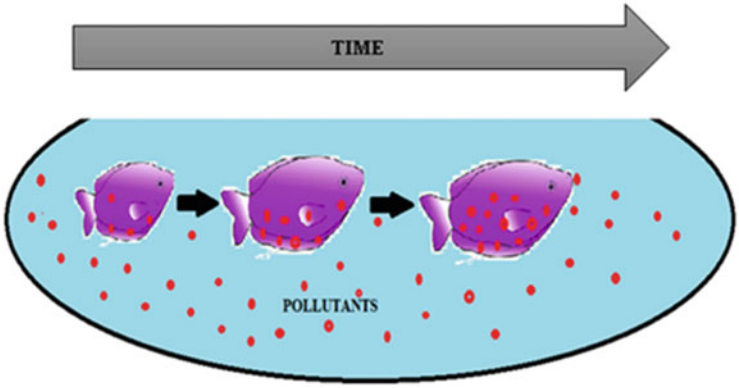


Fig. 15.2 Bioaccumulation of contaminants

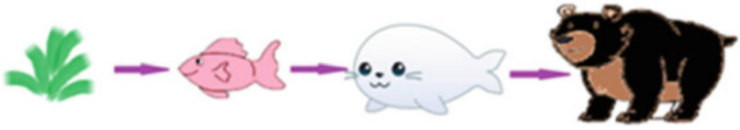


Fig. 15.3 Biomagnification of contaminants

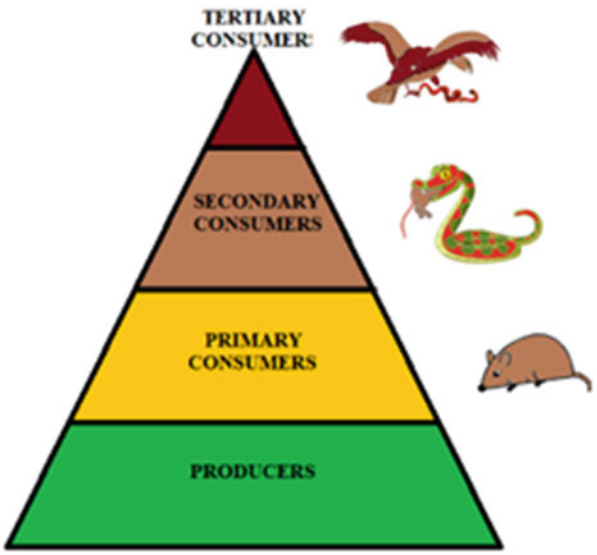


Fig. 15.4 Biomagnification in terrestrial habitats

Persistent Organic Pollutants (POPs) are the major cause of bioaccumulation and biomagnification. The POPs such as DDT, PCBs are not degraded, hence bioaccumulated. In the case of marine pollutants, the biomagnification has its base in phytoplankton. The phytoplankton accumulates the pollutants which passes to the zooplanktons and leads to the accumulation of the pollutants in higher tropic level. Figure 15.4 shows the biomagnification of pollutants in terrestrial environment. Microorganism (GEM), the factors such as target pollutant, the goal of the bioremediation process, the organism of interest and the molecular technique to be performed are to be planned and monitored. The selection of the molecular target depends on the target pollutant as shown in Fig. 15.5. The terrestrial plants that are commonly used in phytoremediation are *Brassica juncea* L (Indian mustard), *Salix* species (White willow), *Populus deltoides* (Poplor tree), *Sorghastrum nutans* (Indian Grass), and *Helianthus annus* (SunFlower) (Fig. 15.6) (Jai 2015). The plants such as alfalfa, corn, dates, and palm are also well-known plants for phytoremediation.

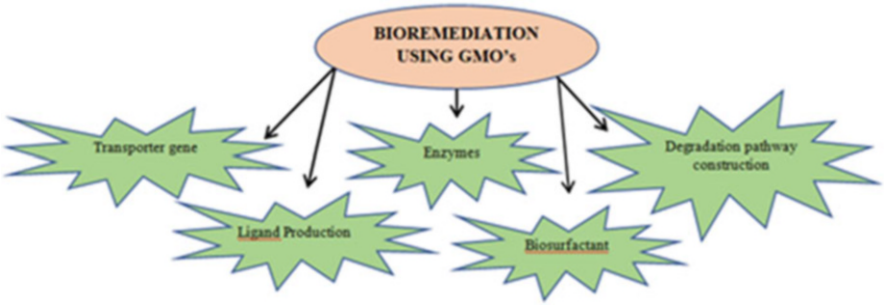


Fig. 15.5 Molecular targets for bioremediation using GEM



Fig. 15.6 *Helianthus annuus* (Sunflower) cultivated as oilseed crop and phytoremediation (https://land8.com/5-best-plants-for-phytoremediation/)

15.10 Biomagnification—A Major Disadvantage

The process of phytoremediation has a great impact on the organisms in higher trophic level. This is caused by the bioaccumulation of pollutants in plants. For this to occur, the pollutants must be lipid-soluble, biologically active, and have long half-life period (Carter 2018). These toxins enter the food web by increasing the concentration of the pollutants in an individual organism (https://cimioutdoored.org/bioaccumulation/). Figure 15.7 shows the process of bioaccumulation. The process of bioaccumulation, in turn, leads to the process called Biomagnification.

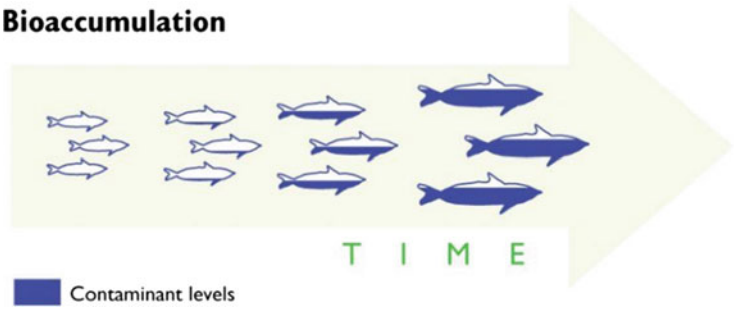


Fig. 15.7 Bioaccumulation of contaminants with increase in time (https://cimioutdoored.org/bioaccumulation/)

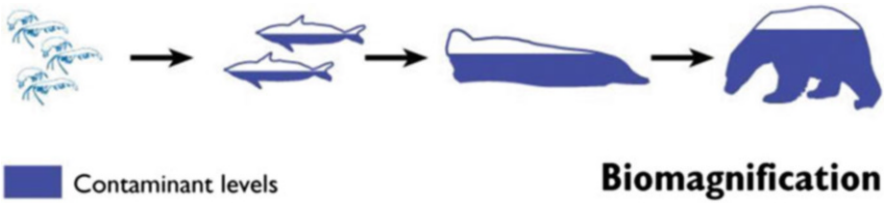


Fig. 15.8 Biomagnification of contaminants in animals (https://cimioutdoored.org/bioaccumulation/)

This involves the transfer of pollutants from one tropic level to another as shown in Fig. 15.8. Persistent Organic Pollutants or POPs are the major cause of bioaccumulation and biomagnification. The POPs such as DDT, PCBs are not degraded, hence bioaccumulated. In the case of marine pollutants, the biomagnification has its base in phytoplankton. The phytoplankton accumulates the pollutants which passes to the zooplanktons and leads to the accumulation of the pollutants in higher tropic level. Figure 15.9a and b shows the biomagnification of pollutants in aquatic and terrestrial environment.

15.11 Biomarkers in Plants

The accumulation of pollutants (mainly heavy metals) by the plants leads to the generation of reactive oxygen species (ROS). The ROS produced has an adverse effect on the plants causing cleavage of proteins, degradation of enzymes, uncoiling and breakage of DNA strands. To counteract the effects of ROS, plants possess defense mechanisms which are enzymatic and non-enzymatic. The plants synthesize enzymes such as catalase, superoxide dismutase, guaiacol peroxidase. Plants also produce compounds such as glutathione, ascorbate, proline, flavonoids, and tannins as the non-enzymatic process of defense (Emamverdian et al. 2015; Rastgoo et al. 2011). The availability of the pollutants in the plants is determined and analyzed using the biochemical markers in the plants. It helps us to compare the concentration of the pollutant in the environment and the plant cells.

There is a unique pathway for each chemical compound and is aided by the use of the specific biochemical markers. The flurocitrate is a specific biochemical marker for the fluoride incorporation in plants. This is aided by the synthesis of fluoroacetyl-CoA which converts the fluorides to flurocitrate via TCA cycle. The continuous monitoring of the plants is essential for the quantification of fluorides in plants (Meyer et al. 1992). Another specific biochemical marker in the plants is seleno proteins, proteins that are produced when plants are exposed to selenium. The plants uptake Se as they are homologous to sulfate in the soil. The plants that are sensitive to Se incorporate Se in the proteins which are not metabolized as Se–Se interaction is weak and this cause the deregulation in the metabolism of Se (Burnell 1981). In the case of Se resistant plants, seleno peptides or on-protein amino acids are produced

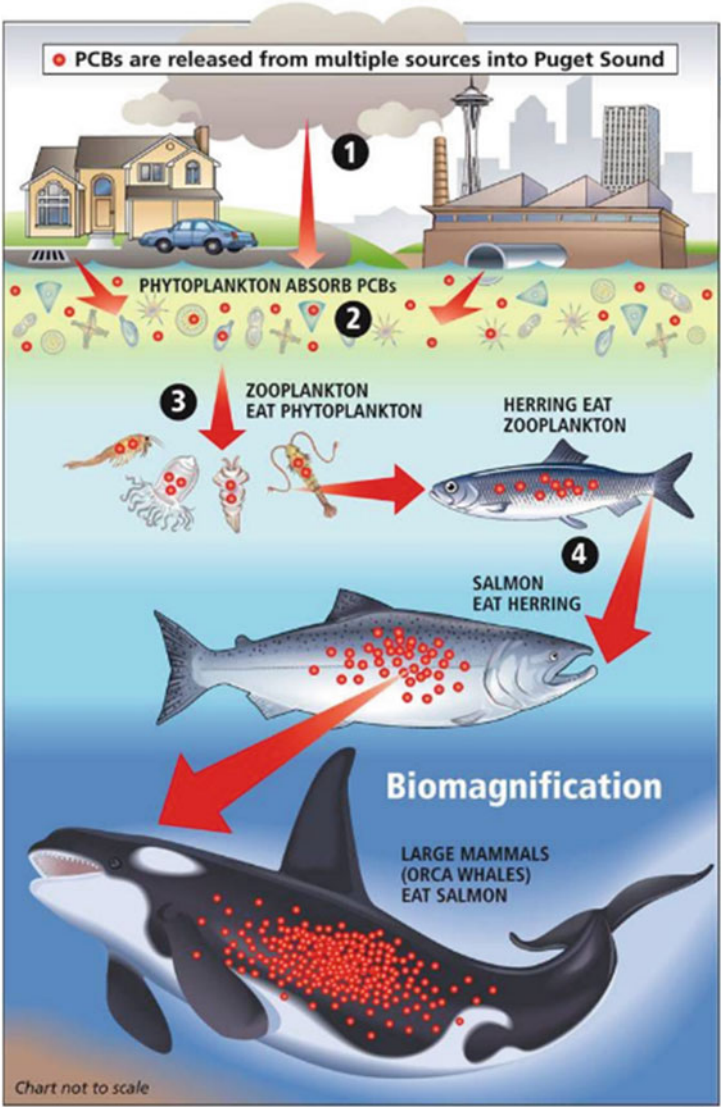


Fig. 15.9 (**a**) Biomagnification of pollutants in aquatic habitat (https://cimioutdoored.org/bioaccumulation/). (**b**) Biomagnification of pollutants in terrestrial habitats (https://cimioutdoored.org/bioaccumulation/)

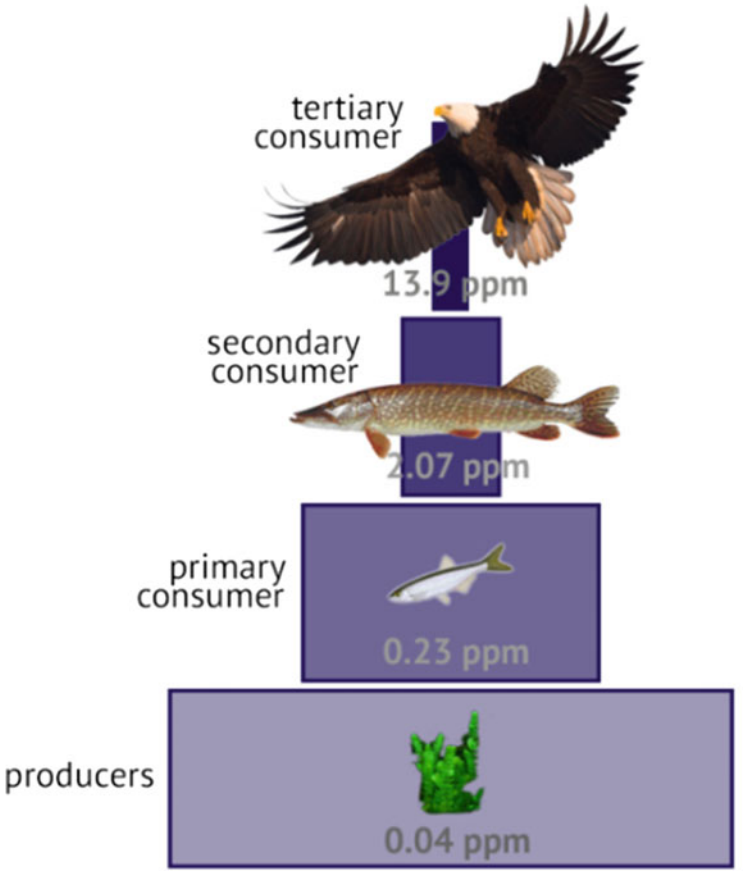


Fig. 15.9 (continued)

(Peterson and Butler 1967). Higher plants on exposure to free metal ions, produces phytochelatins (PCs) (with structure containing(gamma-Glu-Cys)nGly) in the cytoplasm of the plant cell for sulfur metabolism (Grill et al. 1985).

The effect of pollutants or the deficiency caused by the pollutants to the plants can be observed visually and hence the symptoms are the visual biomarkers. The physiological biomarkers are the change in the structure of the chloroplast, production of chlorophyll, color of the leaves, deficiency of minerals, and accumulation of heavy metals and necrosis of the plant (Ernst 1974). Jaskulak et al. (2018) studied the expression of the rbcL gene in *S. alba, R. pseudoacacia* and *I. luteus.* It inhibited growth of plants grown in the soil contaminated with heavy metals. This also showed a decrease in the Guaiacol peroxidase enzyme activity in the absence of the vermicompost. The chlorophyll content was also found to be reduced in the presence of Cd, Pb, and Zn but in contrast increase in the total phenolic compounds was observed in the plants grown in the contaminated soil than in the plants grown in

the soil containing organic manure. The rbcL gene expression was enhanced in plants grown in organic manure than in contaminated soil.

15.12 GMOs in Bioremediation

There are microorganisms available in the environment that have developed resistance to survive in the contaminated environment by utilizing the contaminants as a sole carbon source. The remediation of pollutants by the naturally occurring microbes might be a little slower and also the microbes get to be accumulated in the environment. The complex structure of pollutants is quite difficult to cleave and degrade by the microorganisms. The development of the catabolic character by the microorganisms and the existing pathways are not efficient for complete degradation or removal of the complex contaminants (Chen et al. 1999). Thus, the removal of the pollutants is enhanced by introducing exogenous microbes into the contaminated site to increase the indigenous microorganisms. This process is named as bioaugmentation. This occurs by introducing the microbes possessing catabolic genes that are responsible for the degradative ability of the microorganism or microbes are genetically modified to degrade the pollutants (Genetically Modified Microorganisms GMOs). The GMOs are produced by the transfer of the target gene between the different groups of microorganisms. By doing so, the adaptation of specific catabolic pathway for a specific contaminant could be achieved. The carbon flux is redirected and this prevents the toxic intermediate compound formation. This also modifies the affinity and specificity of the enzyme, stable catabolic activity, and increased availability of pollutants for the remediation. The first release of the GMOs commenced in the year 1996 in the US Environmental Protection Agency (EPA). The GMOs in the environment are controlled by which the bacteria are killed by the controlled suicidal process (Garbisu and Alkorta 1999). The efficient genetically modified microbes are synthesized by incorporating various promoters and regulators. The stability of the mRNA was enhanced by ligating the cassettes of DNA at 5′ of the target gene. This forms the hairpin loop in mRNA by increasing the free energy for the formation of mRNA. This increases the stability of the mRNA. The cloning vectors used for modifying the microorganisms should contain broad host range. The vectors, namely RK2, TFK, and pPP8 are widely used. The vectors with a narrow host range are pDK1, pFME4, pKME5, pNK33, and pPS10 (Singh et al. 2018).

The pollutants present in the environment are mostly aromatic. The efficiency of the degradation or removal of these aromatic compounds is aided by combining the pathway of degradation of bacteria by conjugation in a single recombinant host to degrade a wide range of aromatic compounds (Reineke 1998). The *ohh* operon from *P. aeruginosa* and *fcb* operon from *Arthrobacter globiformis* were transferred into the bacterium *Comamonas testosteroni* strain VP44 for mineralization and degradation of monochlorobiphenyls by Hrywna et al. (1999). The toluene monooxygenase gene present in the *Burkholderia cepacia* was expressed in *Pseudomonas fluorescens*. This recombinant bacterium was coated in the wheat seeds, which

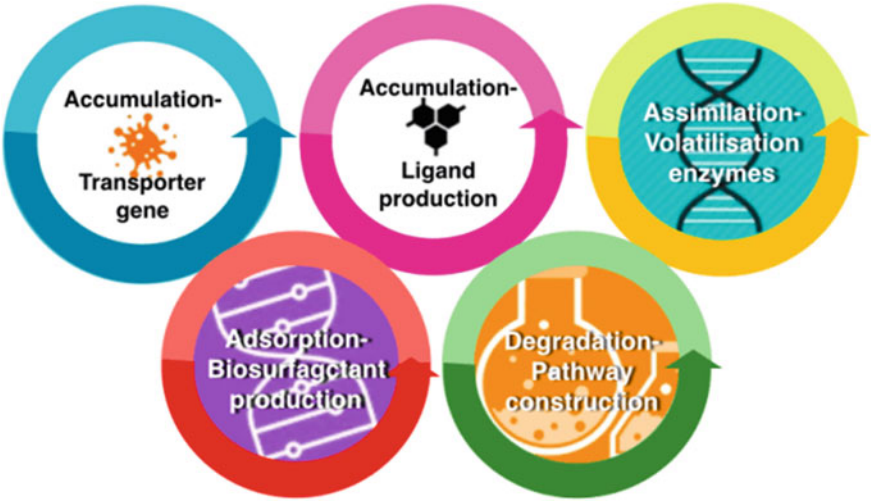


Fig. 15.10 Molecular targets for bioremediation using GEM

showed that the rhizosphere grown was more efficient in the degradation of trichloroethylene (TCE) within 4 days (Yee et al. 1998). Even though the microorganisms were able to degrade the complex pollutants, the microorganisms are sensitive to the radiations of the radioactive compounds. The bacterium *Deinococcus radiodurans* (Lange et al. 1998) and *Deinococcus geothermalis* (Brim et al. 2000) are radiation-resistant bacterium used as a host for genetic engineering.

The efficiency of the genetic engineering to enhance the bioremediation process is done either by the transformation of the new gene into the host organism or enhancing the expression of the genes existing in the microbe. To produce an efficient Genetically Engineered Microorganism (GEM), the factors such as target pollutant, the goal of the bioremediation process, the organism of interest, and the molecular technique to be performed are to be planned and monitored. The selection of the molecular target depends on the target pollutant as shown in Fig. 15.10 (Kapagunta 2017). To improve the bioremediation efficiency, the specificity of the enzymes to the pollutants should be broadened; development of effective bioprocess technology and monitoring the progression of the remediation should be performed (Joutey et al. 2013).

The phytoremediation of pollutants using genetically modified plants is performed to increase the absorption, transportation, and metabolism of pollutants. This process includes the transfer of a catabolic gene from microorganism into the plant genome (Jafari et al. 2013). Hassani et al. (2015) studied the phyto-extraction process of heavy metals by genetically engineering the *metallothionein* (*MT*) gene clones. Verbruggen et al. (2009) reported the transfer of MT-2 gene in tobacco for enhancing the Cd tolerance in plants. The genetic modification in plants modifies the metabolism, phenotypic and genotypic characters of the plants (Davison 2005). Tissue culture technique is used for the selection of genes and plants. The plants,

namely *Populus angustifolia, Nicotiana tabacum*, or *Silene cucubalis* are genetically engineered for the overexpression of glutamylcysteine synthetase (Fulekar et al. 2009). The rate limiting factor of glutathione and phytochelatin is investigated using genetically engineered *Brassica juncea* (Ow 1996). The genes such as *AtNramps*, *AtPcrs, CAD1* from the plant *Arabidopsis thaliana* was isolated and incorporated into the plants for enhancing the heavy metal removal (Thomine et al. 2000; Song et al. 2004; Ha et al. 1999). The hyperaccumulation of pollutants in the plants follows a new metabolic pathway by the transfer of *MerA* and *MerB* genes to make plants Hg tolerant (Bizily et al. 2000).

15.13 GMOs—Scope in Bioremediation

The bioremediation of pollutants using native microorganisms, containing fauna or plants that symbiotically assist the survival of microorganisms in their rhizosphere has its advantages of an eco-friendly approach. Though the presence of the native organism aids in the bioremediation of a wide range of pollutants, these organisms do not have a specific degradative pathway for the various pollutants. The process of degradation is slower and the accumulation by the native microbes is difficult to monitor. The bioaugmentation of the pollutants can be performed using the wild microbes, but this might not be an effective alternative for a speed up eco-friendly process. Thus, genetically engineering the microbes and plants to remediate a wide range of pollutant using specific degradative pathway for a specific pollutant deciphers the pathway of degradation. This adds an advantage of cloning a specific microorganism with a genes coding for the catabolism of various pollutants irrespective of the environmental condition and the concentration of the pollutants. The GMOs produced should be monitored before releasing it to the environment. The transfer of genes from the GMOs to the native microbes can be monitored using the markers and this helps to track the spreading of the GMOs in the environment. This chapter helps to understand various aspects of degradation of pollutants using biological means which can be enhanced by the application of biotechnological approaches for the betterment of the environment towards a sustainable future.

15.14 Conclusion

The synthetic chemicals are a part of our life but the way of making it less toxic lies in the treatment process. Choosing an eco-friendly, cost effective, and efficient method is the only solution. This lead to the biological treatment processes which can be applied in multiple ways. The process utilizes all the available biological system to the fullest to remediate the pollutants. Exploring the unexplored process such as vermiremediation helps to get a better perspective. The application of GMOs requires consistent monitoring while the phytoremediation requires longer duration. The choice of biological method is based on the requirement and nature of the

pollutants. Hence, this chapter provides an alternative biological treatment apart from the microbial and enzymatic process.

References

Ahalya N, Ramachandra TV (2006) Phytoremediation: processes and mechanisms. J Ecobiol 18 (1):33–38

Barois I, Lavelle P (1986) Changes in respiration rate and some physicochemical properties of a tropical soil during transit through *Pontoscolex corethrurus* (Glossoscolecidae Oligochaeta). Soil Biol Biochem 18(5):539–541

Bhat SA, Singh J, Vig AP (2018) Earthworms as organic waste managers and biofertilizer producers. Waste Biomass Valori 9(7):1073–1086

Bizily SP, Rugh CL, Meagher RB (2000) Phytodetoxification of hazardous organo-mercurials by genetically engineered plants. Nat Biotechnol 18(2):213–217

Blackman S (2003) The worm that turned (twice). *The Scientist-Daily News*

Brim H, McFarlan SC, Fredrickson JK, Minton KW, Zhai M, Wackett LP, Daly MJ (2000) Engineering *Deinococcus radiodurans* for metal remediation in radioactive mixed waste environments. Nat Biotechnol 18(1):85–90

Brown GG, Barois I, Lavelle P (2000) Regulation of soil organic matter dynamics and microbial activityin the drilosphere and the role of interactions with other edaphic functional domains. Eur J Soil Biol 36(3–4):177–198

Brulle F, Mitta G, Cocquerelle C, Vieau D, Lemière S, Leprêtre A, Vandenbulcke F (2006) Cloning and real-time PCR testing of 14 potential biomarkers in Eisenia Fetida following cadmium exposure. Environ Sci 40(8):2844–2850

Burnell JN (1981) Selenium metabolism in Neptunia amplexicaulis. Plant Physiol 67(2):316–324

Butt KR (1999) Inoculation of earthworms into reclaimed soils: the UK experience. Land Degrad Dev 10(6):565–575

Carpenter D, Hodson ME, Eggleton P, Kirk C (2008) The role of earthworm communities in soil mineral weathering: a field experiment. Mineral Mag 72:33–36

Carter KN (2018) The effects of Bioaccumulation on the ecosystem. https://sciencing.com/effects-bioaccumulation-ecosystem-13721.html

Chen W, Brühlmann F, Richard RD, Mulchandani A (1999) Engineering of improved microbes and enzymes for bioremediation. Curr Opin Biotechnol 10(2):137–141

Coleman DC, Wall DH (2015) Soil fauna: occurrence, biodiversity, and roles in ecosystem function. Soil Microbiol Ecol Biochem 4:111–149

Curry JP, Byrne D, Boyle KE (1995) The earthworm population of a winter cereal field and its effects on soil and nitrogen turnover. Biol Fertil Soils 19(2–3):166–172

Davison J (2005) Risk mitigation of genetically modified bacteria and plants designed for bioremediation. J Ind Microbiol Biotechnol 12:639–650

Edwards CA, Bohlen PJ (1996) Biology and ecology of earthworms. Springer, Berlin

Elliott ET (1997) Rationale for developing bioindicators of soil health. Agriculture 2:49–78

Emamverdian A, Ding Y, Mokhberdoran F, Xie Y (2015) Heavy metal stress and some mechanisms of plant defense response. Sci World J 2015:756120. https://doi.org/10.1155/2015/756120

Ernst W (1974) Schwermetallvegetation der Erde. Agriculture 11:163–179

Fulekar MH, Singh A, Bhaduri AM (2009) Genetic engineering strategies for enhancing phytoremediation of heavy metals. Afr J Biotechnol 8(4):529–535

Garbisu C, Alkorta I (1999) Utilization of genetically engineered microorganisms (GEMs) for bioremediation. J Chem Technol Biotechnol: Int Res Process Environ Clean Technol 74 (7):599–606

Goody C (2018) 7 classification of earthworms. https://sciencing.com/7-classifications-earthworms-8233433.html
Grill E, Winnacker EL, Zenk MH (1985) Phytochelatins: the principal heavy-metal complexing peptides of higher plants. Science 230(4726):674–676
Gupta SK, Tewari A, Srivastava R, Murthy RC, Chandra S (2005) Potential of Eisenia foetida for sustainable and efficient vermicomposting of fly ash. Water Air Soil Pollut 163(1–4):293–302
Ha SB, Smith AP, Howden R, Dietrich WM, Bugg S, O'Connell MJ, Goldsbrough PB, Cobbett CS (1999) Phytochelatin synthase genes from Arabidopsis and the yeast *Schizosaccharomyces pombe*. Plant Cell 11(6):1153–1163
Harnly M, Seidel S, Rojas P, Fornes R, Flessel P, Smith D, Kreutzer R, Goldman L (1997) Biological monitoring for mercury within a community with soil and fish contamination. Environ Health Perspect 105(4):424–429
Hassani AH, Nouri J, Mehregan I, Moattar F, Sadeghi Benis MR (2015) Phytoremediation of soils contaminated with heavy metals resulting from acidic sludge of Eshtehard industrial town using native pasture plants. J Environ Earth Sci 5(2):87–93
Hirano T, Tamae K (2011) Earthworms and soil pollutants. Sensors 11(12):11157–11167
Horn MA, Schramm A, Drake HL (2003) The earthworm gut: an ideal habitat for ingested N_2O-producing microorganisms. Appl Environ Microbiol 69(3):1662–1669
Hrywna Y, Tsoi TV, Maltseva OV, Quensen JF, Tiedje JM (1999) Construction and characterization of two recombinant bacteria that grow on ortho-and para-substituted chlorobiphenyls. Appl Environ Microbiol 65(5):2163–2169
Jafari M, Danesh YR, Goltapeh EM, Varma A (2013) Bioremediation and genetically modified organisms. In: Fungi as bioremediators. Springer, Berlin, pp 433–451
Jai B (2015) 5 best plants for phytoremediation. https://land8.com/5-best-plants-for-phytoremediation/
Jaskulak M, Rorat A, Grobelak A, Kacprzak M (2018) Antioxidative enzymes and expression of rbcL gene as tools to monitor heavy metal-related stress in plants. J Environ Manage 218:71–78
Joutey NT, Bahafid W, Sayel H, El Ghachtouli N (2013) Biodegradation: involved microorganisms and genetically engineered microorganisms. In: Chamy R, Rosenkranz F (eds) Biodegradation-life of science. Intechopen, London, pp 289–320
Kapagunta C (2017) Genetic engineering of plants can contribute to bioremediation efforts. Project Guru. Available at: https://www.projectguru.in/genetic-engineering-bioremediation/. Accessed 4 Sep 2020
Lange CC, Wackett LP, Minton KW, Daly MJ (1998) Engineering a recombinant Deinococcus radiodurans for organopollutant degradation in radioactive mixed waste environments. Nat Biotechnol 16(10):929–933
Lavelle P, Lattaud C, Trigo D, Barois I (1995) Mutualism and biodiversity in soils. In: Collins HP, Robertson GP, Klug MJ (eds) The significance and regulation of soil biodiversity. Developments in plant and soil sciences. Springer, Dordrecht
Lee KE (1985) Earthworms: their ecology and relationships with soils and land use. Academic Press, Sydney
Levinton JS, Suatoni E, Wallace W, Junkins R, Kelaher B, Allen BJ (2003) Rapid loss of genetically based resistance to metals after the cleanup of a superfund site. Proc Natl Acad Sci 100(17):9889–9891
Loredo-Osti C, López-Reyes L, Espinosa-Victoria D (2004) Bacterias promotoras del crecimiento vegetal asociadas con gramíneas: Una revisión. Terra Latinoamericana 22(2):225–239
McGrath SP, Zhao FJ (2003) Phytoextraction of metals and metalloids from contaminated soils. Curr Opin Biotechnol 14(3):277–282
Meyer JM, Grobbelaar N, Vleggaar R, Louw AI (1992) Fluoroacetyl-coenzyme a hydrolase-like activity in *Dichapetalum cymosum*. J Plant Physiol 139(3):369–372
Nahmani J, Hodson ME, Black S (2007) A review of studies performed to assess metal uptake by earthworms. Environ Pollut 145(2):402–424

Ow DW (1996) Heavy metal tolerance genes: prospective tools for bioremediation. Resour Conserv Recycl 1-4:135–149
Parle JN (1963) A microbiological study of earthworm casts. Microbiology 31(1):13–22
Peterson PJ, Butler GW (1967) Significance of selenocystathionine in an Australian selenium-accumulating plant, Neptunia amplexicaulis. Nature 213:599–600
Rastgoo L, Alemzadeh A (2011) Biochemical responses of Gouan (*Aeluropus littoralis*) to heavy metals stress. Aust J Crop Sci 5(4):375
Reineke W (1998) Development of hybrid strains for the mineralization of chloroaromatics by patchwork assembly. Annu Rev Microbiol 52(1):287–331
Romero EM (2001) Poblaciones de rhizobia nativas de México. Acta Zool Mex 1:29–38
Sasi K (2011) Phytoremediation—applications, advantages and limitations. Biotech Articles
Satchell J (2012) Earthworm ecology: from Darwin to vermiculture. Springer, Berlin
Siekierska E, Urbańska-Jasik D (2002) Cadmium effect on the ovarian structure in earthworm *Dendrobaena veneta* (Rosa). Environ Pollut 120(2):289–297
Singh SK, Sahoo JP, Swain E (2018) A review on gene stacking in crop plant. J Pharmacogn Phytochem 7(4):1862–1865
Song WY, Martinoia E, Lee J, Kim D, Kim DY, Vogt E, Shim D, Choi KS, Hwang I, Lee Y (2004) A novel family of cys-rich membrane proteins mediates cadmium resistance in *Arabidopsis*. Plant Physiol 135(2):1027–1039
Spurgeon DJ, Hopkin SP (1995) Extrapolation of the laboratory-based OECD earthworm toxicity test to metal-contaminated field sites. Ecotoxicology 4(3):190–205
Spurgeon DJ, Hopkin SP, Jones DT (1994) Effects of cadmium, copper, lead and zinc on growth, reproduction and survival of the earthworm *Eisenia fetida* (Savigny): assessing the environmental impact of point-source metal contamination in terrestrial ecosystems. Environ Pollut 84 (2):123–130
Stehouwer RC, Butler KL, Webber KA, Baetsen AM (2014) Introductory soil science laboratory. Springer, Berlin
Thakuria D, Schmidt O, Finan D, Egan D, Doohan FM (2010) Gut wall bacteria of earthworms: a natural selection process. ISME J 4(3):357–366
Thomine S, Wang R, Ward JM, Crawford NM, Schroeder JI (2000) Cadmium and iron transport by members of a plant metal transporter family in *Arabidopsis* with homology to Nramp genes. Proc Natl Acad Sci 97(9):4991–4996
Usmani Z, Kumar V (2015) Earthworms: the unheralded Soldiers' standing steadfast against. Res J Environ Sci 9(2):48–65
Verbruggen N, LeDuc D, Vanek T (2009) Potential of plant genetic engineering for phytoremediation of toxic trace elements. Phytotechnologies solutions for sustainable land management. EOLSS Publishers, pp 1–24
Yasmin S, D'Souza D (2010) Effects of pesticides on the growth and reproduction of earthworm: a review. Appl Environ Soil Sci 2010:1–9
Yee DC, Maynard JA, Wood TK (1998) Rhizoremediation of trichloroethylene by a recombinant, root-colonizing *Pseudomonas fluorescens* strain expressing toluene ortho-monooxygenase constitutively. Appl Environ Microbiol 64(1):112–118
Zeb A, Li S, Wu J, Lian J, Liu W, Sun Y (2020) Insights into the mechanisms underlying the remediation potential of earthworms in contaminated soil: a critical review of research progress and prospects. Sci Total Environ 740:140–145

Mitigation of Hazardous Contaminants: A Phyto-Microbiome Approach

16

Sandra Pérez Álvarez, Eduardo Fidel Héctor Ardisana, Sergio Guerrero Morales, and Abdon Palacios Monarez

Abstract

The elimination of toxic waste in soils, water, and in general in all types of environmental scenarios has become a goal for scientists and environmental organizations, due to the devastating effects it causes on health, biodiversity, soils, and sources of water. The pollutants are divided for study according to their chemical composition in hydrocarbons and their derivatives, heavy metals and pesticides. Intensive, traditional techniques for eliminating or attenuating the effects of toxic waste on ecosystems are very expensive and consume a great deal of time. Instead, the interactions that occur naturally between plants and microbes are being exploited for this purpose, as it has been shown that numerous species of both types of organisms have the ability to act on various types of pollutants through various detoxification mechanisms, and that plants and microorganisms can act in this direction together. This chapter analyzes the applications of these interactions in reducing pollution by the three groups of toxic products, both through the use of plants and microbes in their natural state and through the use of genetically modified organisms.

Keywords

Heavy metals · Hydrocarbons · Pesticides · Plants · Microorganisms

S. P. Álvarez (✉) · S. G. Morales · A. P. Monarez
Facultad de Ciencias Agrícolas y Forestales, Universidad Autónoma de Chihuahua, Delicias, Chihuahua, Mexico

E. F. H. Ardisana
Instituto de Posgrado, Universidad Técnica de Manabí, Portoviejo, Ecuador

© The Author(s), under exclusive licence to Springer Nature Singapore Pte Ltd. 2021

V. Kumar et al. (eds.), *Rhizobiont in Bioremediation of Hazardous Waste*,
https://doi.org/10.1007/978-981-16-0602-1_16

16.1 Introduction

Ecosystem contamination as a result of toxic waste dumping is a direct consequence of anthropic activity. Thousands of tons of waste are deposited in the soil and water every year, including hydrocarbons and their derivatives, heavy metals, pesticides, and many other products. The consequences of incorporating these substances into the environment are catastrophic, since their permanence in the soil or water is very long. For example, it is estimated that the decomposition time of plastic bottles should be about 1000 years, but of course this is no more than an estimate, since the time elapsed since its invention is much shorter and does not allow this assumption to be confirmed. In many cases, in addition to causing toxic effects on plants, animals, and humans, pollutants mix with other substances, forming new compounds; for example, excess aluminum tends to be associated with useful elements such as nitrogen and phosphorus, making it difficult for plants to absorb them.

Pollutants that can be detoxified from the soil by plants are divided into two large groups for study: inorganic (which includes heavy metals) and organic (including hydrocarbons, derivatives and pesticides) (Kuiper et al. 2004).

The main inorganic pollutants are heavy metals (lead, mercury, cadmium, arsenic, and chromium, among others) that come directly from industrial activity and mining. As they are not directly degraded by biological or chemical routes, once released into the environment they can remain in it for many years, which is why they have been the main subject of phytoremediation (Tangahu et al. 2011).

Polycyclic aromatic hydrocarbons (PAH) accumulate in soils as a result of some natural processes (such as forest fires and volcanic eruptions) and anthropogenic activity (partial combustion of organic substances, oil spills, and other industrial activities) (Chauhan et al. 2008). They are classified into two groups: low molecular weight compounds, such as naphthalene and anthracene, which have three or less rings, and high molecular weight, such as pyrene and benzo(a) pyrene, which contain four or more rings (Fig. 16.1). The hydrophobicity of these substances increases with their molecular mass, which increases their ability to be adsorbed by soil particles and makes their elimination difficult.

The term total petroleum hydrocarbons (TPH) (Divya and Kumar 2011) is used to name a mixture of different hydrocarbons that can be found in crude oil. In practice, due to the heterogeneity of the polluting sources and the degree of decomposition of these, it is very common to find mixtures of TPH and PAH in contaminated soils.

One of the strategies used to reduce the presence of toxic wastes in ecosystems is phytoremediation. Although the etymology of the term links it to the use of plants for that purpose, it actually includes not only plants, but also the microbial communities associated with them, the amendments and other agronomic practices tending to destroy, remove, or stabilize environmental pollutants (Yateem et al. 2000; Kumar et al. 2017).

Undoubtedly, plants are able to extract a wide range of contaminants from the soil. However, phytoremediation also suffers from limitations, which have been pointed out by Glick (2003): soil contamination causes stress that reduces the

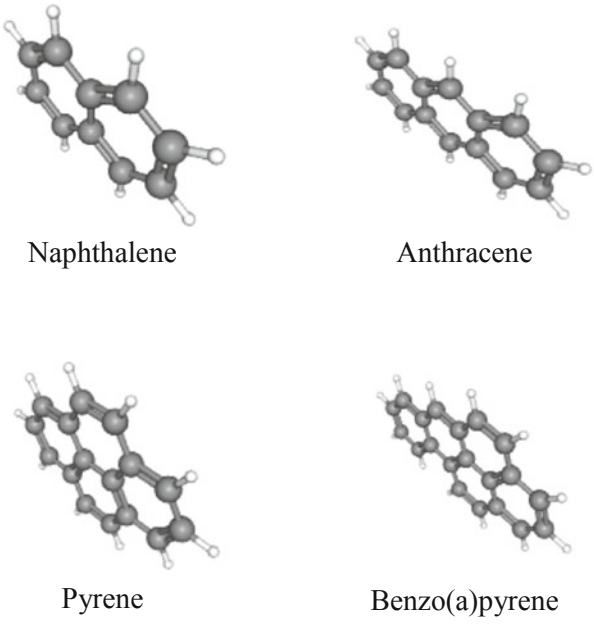


Fig. 16.1 Some polycyclic aromatic hydrocarbons (PAH) usually present in soils

germination of the plants used for this process, as well as reductions in growth and development, which leads to lower biomass and finally to low effectiveness in phytoremediation. On the other hand, most plants used in phytoremediation do not completely degrade contaminants, but accumulate them in vacuoles or apoplast (Eapen et al. 2007).

The presence of microorganisms in the rhizosphere allows plant–microbe interaction, whose usefulness has been demonstrated in the removal of toxic compounds, in particular insecticides and herbicides (Walton and Anderson 1990). For this reason, rhizoremediation is referred to the contribution that these rhizosphere microbes make to the degradation of pollutants (Schwab and Banks 1994). It is known that an important part of the degradation of pollutants is due to the action of microorganisms that live in the vicinity of plant roots.

The action of microorganisms in remediation can occur, according to Kuiper et al. (2004) through several mechanisms:

- Natural attenuation: The appearance of pollutants at a site leads to the microbes capable of using these compounds as a source of nutrients to prevail over other microorganisms, resulting in degradation of a part of pollutants.
- Bioaugmentation: It is based on the inoculation to the soil of microbes capable of degrading specific xenobiotic compounds. This allows to increase the degradation of the contaminants.
- PAH degradation: Polycyclic aromatic hydrocarbons (PAH) are a wide range of polluting compounds. Since the beginning of the twentieth century, the ability of

a variety of bacteria, fungi, and algae to degrade these compounds has been known.

This chapter analyzes the interaction between plants and microbes (rhizoremediation) in the degradation of hydrocarbons, heavy metals, and pesticides.

16.2 Plant–Microbe Interactions for the Remediation of Hydrocarbons as Environment Pollutants

The degradation of hydrocarbons and their derivatives by microorganisms can be carried out in two ways: aerobic or anaerobic (Chauhan et al. 2008). The degradation pathway depends on the conditions of the environment (generally in the soils the aerobic pathway and in the anaerobic aquifer spaces) and the bacterial genera present.

Numerous genera of bacteria capable of degrading PAH in interaction with various plant species have been identified. Kuiper et al. (2001) demonstrated the degradation of naphthalene by *Pseudomonas putida* in the rhizosphere of *Lolium perennial* L. Yateem et al. (2007) identified several PAH degrading microorganisms in the rhizosphere of *Paspalum vaginatum* Sw. and *Zoysia tenuifolia* Willd. Ex Thiele, among which the fungus *Fusarium solani* and the bacterium *Pseudomonas boreopolis* were the most effective. Several bacteria (*Alpha proteobacterium*, *Aspergillus versicolor*, *Bacillus licheniformis*, *Bacillus mojavensis*, *Rhodococcus equi*, *Arthrobacter globiformis*, *Mycobacterium fortuitum*) and a fungus (*Fusarium oxysporium*) degrade hydrocarbons in the rhizosphere of *Ficus infectious* Willd. and *Conocarpus lancifolius* Engl. trees (Yateem et al. 2008).

The association between microorganisms and plants plays an important role in the effectiveness of PAH degradation in soils. Degradation is usually more effective in the rhizosphere area (rhizoremediation). Plant roots exude substances that contribute to microbial survival, and the penetration of the radical system into the soil contributes to the spread of microbes (Gentry et al. 2004). On the other hand, the microorganisms that live in the rhizosphere provide the plant with various compounds, including vitamins, siderophores, and growth regulators (Kuiper et al. 2004; Kumar et al. 2018).

Legumes are plants that tend to form bacterial nodules, particularly with *Rhizobium* sp. Yateem et al. (2000) demonstrated the phytoremediation potential of *Vicia faba* L. and *Medicago sativa* L. in soils contaminated with 1% oil, observing that these species are capable of degrading oil by 36.6% and 35.8%, respectively, in contrast to the 24% reduction obtained in soils planted with *Lolium perenne* L. In addition, the presence of legumes increased the colonization of the rhizosphere by bacteria tenfold compared to that observed in the rhizosphere of the ryegrass. In contrast, Guo et al. (2017) found that the presence of *Lolium perenne* L. increased the degradation of PAH by *Mycobacterium* sp.

However, legumes are not the only plants with the capacity to participate in plant–microbial associations for the rhizoremediation of hydrocarbons and their

derivatives in soils. In a study conducted by Sangabriel et al. (2006) in Colombia, it was observed that, although *Phaseolus coccineus* L. showed the highest tolerance to fuel oil and the largest microbial population in its rhizosphere, the greatest total degradation of fuel oil occurred in the rhizosphere of *Brachiaria brizantha* (Hochst. Ex A Rich) and *Panicum maximum* Jacq., two grass species. Ying et al. (2011) found that the species *Atriplex centralasiatica* Iljin (Amaranthaceae), *Scorzonera mongolica* Maxim. (Asteraceae), and *Limonium bicolor* (Bunge) Kuntze (Plumbaginaceae) were able to reduce between 5 and 8 times the concentration of TPH in their rhizosphere, while in the soil not close to the roots of the plant, the concentration of TPH was only reduced 1.6 times. Some plant species such as the poplar (*Populus* sp.) and the willow (*Salix* sp.) that have an aerenchyma in their roots—and are therefore capable of carrying oxygen to the soil at considerable depths—are frequently used in the rhizoremediation of contaminated soils (Zalesny et al. 2005).

In addition to the associated plant species, the degree of self-degradation of pollutants resulting from weathering apparently also influences the degradation activity of microbes (Prakash et al. 2014). Maldonado et al. (2010) investigated the degradation of TPH in soils contaminated with new and weathered oil for 25 years. Inoculation of a consortium formed by bacteria (*Pseudomonas* sp. and *Serratia marcescens*) and fungi (*Aspergillus* sp. and *Trichoderma* sp.) produced greater degradation in new oil when the plant species was the legume *Leucaena leucocephala* (Lam.) De Wit, but when the oil was weathered, the greatest results were obtained with the grass *Brachiaria mutica* (Forssk.).

Pantoea sp. is a genus of bacteria that includes about 20 species, among which some have proven to have beneficial effects on vegetables. Yousaf et al. (2010) showed that two strains of *Pantoea* sp. in combination with compost favor the growth of *Lolium multiflorum* Lam. and *Lotus corniculatus* L. These two bacterial lines, in addition to achieving degradation rates of hydrocarbons higher than *Pseudomonas* sp., a genus known to possess this property, managed to colonize both the rhizosphere and the endosphere of both plant species.

Bacteria and fungi such as *Pseudomonas* sp., *Agrobacterium* sp., *Trichoderma* sp., *Aspergillus* sp., and *Mucor* sp. are capable of degrading oil hydrocarbons. Hernández et al. (2003) managed to isolate these species from soils contaminated with petroleum; subsequently they were inoculated in soils contaminated with oil in which beans (*Phaseolus vulgaris* L.) and corn (*Zea mays* L.) plants were living. The greatest degradation of hydrocarbons was obtained in the combination bacteria + fungi + corn, possibly due to its extensive fibrous and radical system.

Siciliano et al. (2001) were the first to observe that the endophyte microbes of plants that grew in soils contaminated with hydrocarbons could degrade polluting organic compounds. Based on this result and the possibilities of microbial consortia in rhizoremediation, the path has been opened to a more efficient approach that includes plants, bacteria and soil fungi and endophytic bacteria (Juwarkar et al. 2010; Singh 2011; Abhilash et al. 2012). In this integral system, bacteria and soil fungi degrade part of the contaminants in the rhizosphere; other xenobiotics penetrate the inner space of plants, and there they are degraded by endophytic bacteria

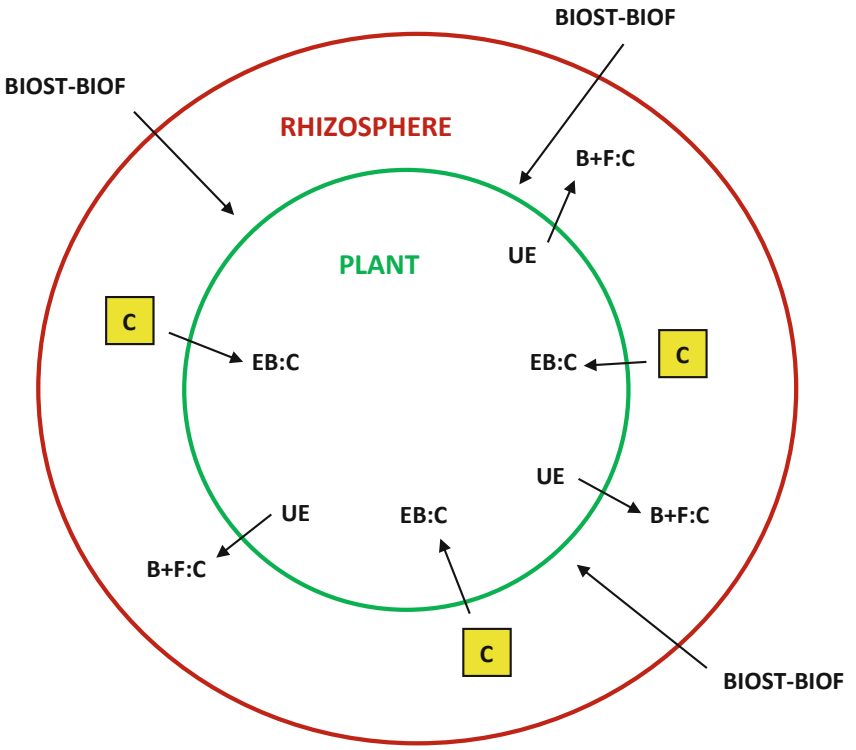


Fig. 16.2 Integrated strategy for rhizoremediation. B-bacteria; F-fungi; EB-endophytic bacteria. UE → B + F:C plant provides useful exudates to bacteria and fungi from rhizosphere which degrade contaminants. C → EB:C some contaminants enter the plant, where are degraded by endophytic bacteria. BIOST-BIOF → biostimulants and biofertilizers are provided in order to enhance plant growth and development

that have been selectively introduced. The system could be complemented with the addition of biofertilizers and biostimulants (Fig. 16.2). Additionally, it has been found that good tillage practices, such as proper cultivation and good soil drainage, favor the degradation of PAH by microorganisms (Mmom and Deekor 2010).

In general, the increase in the efficiency of rhizoremediation involves the acquisition of deeper knowledge about the signals emitted in the plant–microbe association that regulate the process. The clarification of these signals and their role in the activation of degrading mechanisms is essential, since it is known that the presence of a certain bacterial strain in the rhizosphere does not imply that it is metabolically active (Kiely et al. 2006).

Once the presence of a microorganism with PAH degrading activity is confirmed, a possible task would be to use it as a source of genes to enhance the activity of other microbes, through genetic engineering. The search for genes encoding the degradation of PAH is directly related to the activity of the catalytic enzymes involved,

which are mainly oxygenases, dehydrogenases, phosphatases, and lignolytic enzymes (Bisht et al. 2015).

An important advance in the understanding of plant–microbe interactions for survival in environments contaminated by hydrocarbons has been achieved from the work of Oliveira et al. (2014a, b) made in saline estuaries. In these sites, the presence of certain plant species (*Halimione portulacoides* L. and *Sarcocornia perennis* Mill.) is associated with the colonization of the rhizosphere by certain microbial genera (among which *Pseudomonas* sp. predominates). These genera, which appear particularly in areas where pollution is most severe, carry PAH-dioxygenase genes involved in the degradation of PAHs, which allow them to survive in these harsh conditions. In turn, the plants with which they are associated favor them by the vital space that their roots and radical exudates give them (Oliveira et al. 2012). In parallel, Fatima et al. (2016) revealed that the activity of a consortium of two degrading bacteria of crude oil (*Acinetobacter* sp. strain BRSI56 and *Pseudomonas aeruginosa* strain BRRI54) works better in *Brachiaria mutica* (Forrsk.) than *in Leptochloa fusca* L.

From the identification of the genes involved, it is possible to undertake genetic engineering projects to improve the efficiency of rhizoremediation. The two main lines of work would be the transformation of plants to stimulate population growth and the activity of microorganisms, and the transformation of microorganisms to increase their ability to live in contaminated environments and degrade xenobiotics.

A variant to increase the effectiveness of rhizoremediation would be to obtain transgenic plants in which the absorption of pollutants or their transport is increased (Doty 2008). Although numerous transgenic plants have been designed for almost two decades to fulfill these purposes in the detoxification of heavy metals, pesticides, and other organic compounds (Cherian and Oliveira 2005) there are no reports on obtaining transgenic plants for PAH remediation.

Genetic engineering can be useful in harnessing the natural potential of bacteria to build genetically modified lines capable of acting in rhizoremediation; however, the main results have been applicable mainly in laboratories (Wasilkowski et al. 2012). There are no abundant results in the genetic engineering of bacteria useful in the rhizoremediation of hydrocarbons and their derivatives, but some progress has been made in obtaining genetically engineered bacteria capable of degrading naphthalene (Sayler and Ripp 2000; Filonov et al. 2005) and oil (Jussila et al. 2007).

Not always the bacterial strains that carry genes for the degradation of hydrocarbons also have genes that stimulate plant growth, and vice versa. The genetic transformation to obtain bacteria that carry both types of genes would give them an additional advantage over other microorganisms (Iqbal et al. 2018) and would make them ideal candidates for use in rhizoremediation. An example of this type of gene construction is to obtain a recombinant bacterium capable of stimulating the growth of *Zea mays* L. and degrading phenol, from *Pseudomonas aeruginosa* SZH16 (phenol degrader) and *Pseudomonas fluorescens* (growth promoter) (Yang et al. 2011).

The difficulties in obtaining genetically modified organisms and achieving character expression are joined by legal restrictions for the introduction of transgenic

organisms (Ghosal et al. 2016), and the low survival of individuals introduced in areas where levels of contamination are truly problematic (Kuppusamy et al. 2016; Ite and Ibok 2019). However, the increase in the use of these technologies in the immediate future can be taken for granted.

16.3 Plant–Microbe Interactions for the Remediation of Heavy Metals as Environment Pollutants

Heavy metals are pollutants that cannot be biodegraded; they accumulate in soils and in living organisms causing several damage because of their toxicity (Singh et al. 2011). Numerous methods are used such as biological, chemical, and physical but they are expensive, long time is needed, and they can damage the environment (Jadia and Fulekar 2009; Danh et al. 2009; Ahmadpour et al. 2012; Kumar et al. 2017). Phytoremediation is a method that use green plants to degrade, stabilize pollutants such as heavy metals from soils, waters, etc. (Paz-Ferreiro et al. 2014; Elekes 2014) and bioremediation use plants and microbes for decontamination (Rayu et al. 2012). Both processes are most effective and less cost.

Green plant for phytoremediation is used according to the development of their root system, the contaminant to be treated, the soil and the temperature of the region (U.S. EPA 2001). Different types of plants are used for this purpose depending on the soils structure, contaminant nature (which is the principal factor for plant selection), soil fertility, and so on (Pivetz 2001). On this regard, for example, grasses can clean approximately <3 ft, shrubs <10 ft, and <20 ft for deep rooting trees (Sharma and Reddy 2004).

Grasses are the most recommended plants for phytoremediation because they grow rapidly, have a lot of biomass, are very resistant to biotic and abiotic stresses, and they have the capacity to remediate different types of soils (Elekes 2014).

16.4 Where Heavy Metals Come From?

Heavy metals are elements with metallic characteristics, natural components of the earth crust, with a density superior to 5 g cm^{-3}, atomic number >20, and natural constituents in soil (Alloway and Ayres 1997; Lasat 2000; Adriano 2001; Jadia and Fulekar 2008; Ismail et al. 2013). Some of them are necessary for plant growth [zinc (Zn), copper (Cu), manganese (Mn), nickel (Ni), and cobalt (Co)] and the most dangerous do not have a biological function [(cadmium (Cd), lead (Pb), and mercury (Hg)] (Gaur and Adholeya 2004).

The contamination of water, soil, sediments, and some living organisms by heavy metals comes mainly from industries and mining activities, and began between nineteenth and twentieth centuries (Benavides et al. 2005). According to Zhen-Guo et al. (2002), some other sources of heavy metals are fuel production, smelting processes, military operations, agricultural chemicals (fertilizers, pesticides),

small-scale industries (including battery production, metal products, metal smelting, and cable coating industries), brick kilns, and coal combustion.

Mining activities produce some particles named tailings that are discharged mainly in wetlands, resulting in higher concentrations of heavy metals (DeVolder et al. 2003). These activities also produce elevate quantities of Pb and Zn that contaminate soils resulting in risk to humans and ecological health.

The disposal of municipal wastage in some countries is an important source of soil contamination because they can be accumulated in landfills and the leachates usually are incorporated to soils or water for irrigation; most of these wastes contain carcinogens. Another cause of heavy metals increases in soils is the indiscriminate use of pesticides, fungicides, and fertilizers in agricultural activities (Zhen-Guo et al. 2002).

The use of wastewater dates back 400 years ago and at present has become a common practice in many countries (Reed et al. 1995). In 2007 approximately 20 million hectares of agricultural soil were irrigated with wastewater and in many Asian and African cities the vegetables supply for urban areas depends in a 50% of wastewater (Bjuhr 2007).

Fertilizers are necessary for the growth of plants as macro (N, P, K, S, Ca, and Mg) and micronutrients (Zn, Cu, Mn, and others) (Lasat 2000). Several fertilizers are used intensively to apply NPK to the soil so that plants can take them, but usually fertilizers contain small amounts of heavy metals such as Cd and Pb whose concentrations increase considerably (Jones and Jarvis 1981).

According to Atafar et al. (2010) concentrations of Cd, Pb, and As (arsenic) have increased in the soils cultivated with wheat (*Triticum sp.*) and the statistical analysis indicates that Pb and As concentrations increased dramatically compared to Cd concentration. The high concentrations of Pb, As, and Cd found were because an over application of fertilizers as well as the pesticides that are used to control plant pests, herbs, and rats. Another research in China showed that after the analysis of 177 organic fertilizers the concentrations of trace metals varied widely and the standard limits were exceeded by 0.85% for Cr (chrome), 5.98% for As, 1.71% for Cd, and 4.27% for Pb (Gong et al. 2019).

In India, not only fertilizers and pesticides applications increased heavy metals concentrations in soils, also industrial waste, wastewater irrigation, and corrosion of sewerage pipes (Mapanda et al. 2005; Sharma et al. 2007).

Ikem et al. (2008) reported in southeastern Missouri (USA), that the concentration of heavy metals, increased by 2–31%, where the lowest concentrations was for Mn and the highest for Pb, mostly produced by the use of chemical fertilizers and sewage sludge.

According to Raven et al. (1998), some fertilizers with phosphorus (phosphatic) indirectly add certain heavy metals such as Cd, Hg, and Pb. Also, Fan et al. (2012) found that the high concentration of heavy metals in the finer fractions of soil aggregates is because of fertilization.

The increase of Zn and Cd in soils is also because of the excessive application of low-quality fertilizers, pesticides, and sewage irrigation, among several causes (Tang et al. 2010; Wei and Yang 2010).

The contamination of soils by heavy metals is an important topic because a lot of land extension has become dangerous and non-useful for animals and humans. Today it is uncommon to find soils without traces of these elements, and they become more toxic with the time because the anthropogenic or natural activities are still increasing (Turan and Esringu 2007).

16.5 Bioremediation as Technologies to Clean up the Environment of Heavy Metals

The conventional methods used for the remediation of heavy metals in soil and water are expensive, need a lot of time and exhaustive work that induces the mobilization of contaminants and damages the soil by destroying the biotic and structure, so they are not recommended for large contaminated areas (Baccio et al. 2003). Examples of those methods are ex situ excavation, landfill of the top contaminated soils (Zhou and Song 2004), detoxification (Ghosh and Singh 2005), and physico-chemical remediation (Danh et al. 2009).

Bioremediation is a heavy metal remediation technique that uses microorganisms to degrade them into a low toxic level (Vidali 2001) and they use some mechanism such as (Jan et al. 2014):

1. Proteins such as metallothioneins (MT), phytochelatins, and compounds like siderophores produced by bacteria and fungi (hydroxamate siderophores) which can sequestrate toxic metals;
2. Change or variation of some biochemical pathways with the aim of block metal uptake;
3. Enzymes that can transform toxic metals into harmless forms;
4. Concentration of metals that can be dangerous can be reduced by the use of precise efflux systems.

Several microorganisms are related to heavy metal remediation, and in this cases bacteria that live in plant rhizosphere are important, because they can change metal bioavailability by the alteration of soil pH, generation of chelators (organic acids, siderophores), and oxidation/reduction reactions (Khan et al. 2009; Wenzel 2009; Ma et al. 2011). Also, mycorrhizal fungi have been reported in metals remediation (Zarei et al. 2010; Miransari 2011).

Isolation of 15 strains of Pb-solubilizing bacteria from mine soils contaminated with heavy metals was done and they were proved in a solid medium containing PbO or $PbCO_3$ where they solubilized Pb and dissolved the Pb minerals in a liquid medium. The molecular study (16S rRNA gene) showed that the strains are from the genera *Bacillus*, *Paenibacillus*, *Brevibacterium*, and *Staphylococcus* (Yahaghi et al. 2018).

A research was done by testing *Pseudomonas fluorescens* and *P. aeruginosa* for the remediation of heavy metals where the concentrations of Fe^{2+}, Zn^{2+}, Pb^{2+}, Mn^{2+}, and Cu^2 were near to 100 mg L^{-1} and the elimination percentage was 86 and 74 after

using them. The examination of metal percentage was realized in an atomic adsorption spectrophotometer (Perkin-Elmer) at 0.01 ppm sensitivity level after dilution of the samples (Paranthaman and Karthikeyan 2015).

Two bacterial strains (PB-5 and RSA-4) were identified from mangrove sediments by Priyalaxmi et al. (2014) and they were described as Cd resistant, but only the strain RSA-4 was useful for remediation purpose. The study was done under several pH levels (pH 5, 6, 7, 8, and 9) and two concentrations of Cd (40 and 60 ppm); percentages of Cd reduction and absorption were 83.5, 39% and 98.10, 92% for 40 and 60 ppm of cadmium, respectively, at pH 7. The strain was identified as *Bacillus safensis* accession JX126862.

Several Pb resistant bacterial isolates (*Salmonella choleraesuis* strain 4A, *Proteus penneri* strain GM10, *Bacillus subtilis* strain GM02, *Pseudomonas aeruginosa* strain 4EA, *Proteus penneri* strain GM03, and *Providencia rettgeri* strain GM04) from soil polluted with car battery waste in India were quarantined to be used for remediation. By PCR (Polymerase Chain Reaction) analysis (amplification of smtAB genes encoding bacterial metallothionein) was demonstrated that *Salmonella choleraesuis* strain 4A and *Proteus penneri* strain GM10 express the smtA gene for occurrence of metal-binding metallothionein (SmtA), responsible for the resistance towards Pb (Naik et al. 2012).

According to Machuca et al. (2007) some ectomycorrhizal fungi (EMF) (*Scleroderma verrucosum*, *Suillus luteus*, and *Rhizopogon luteolus*) isolated from *Pinus radiata* (tree species belonging to the family of the Pinaceae) can produce siderophores (catecholates and hydroxamates) in a soil with iron deficient condition.

Cellular toxicity induced by Cd can be reduced by *Pseudomonas putida* expressing EC20 (metal-binding peptide) which was demonstrated in sunflower (*Helianthus annuus* L.). When the plant roots were inoculated with the bacteria the Cd phytotoxicity was reduced and the accumulation of this metal increased in the roots (40%) (Wu et al. (2006).

In the case of fungi, several examples illustrate the application in bioremediation. Oladipo et al. (2018) studied several filamentous fungi isolated from gold and gemstone mine site according to their tolerance to several toxic metals like Cd, Cu, Pb, As, and Fe. Using PCR technique (internal transcribed spacer 1 and 2 (ITS 1 and ITS 2) regions) the strains were identified as *Fomitopsis meliae*, *Trichoderma ghanense* and *Rhizopus microspores* and they were grown in malt extract agar with 0-100 mg kg^{-1} of Cd, 0-1000 mg kg^{-1} of Cu, 0-400 mg kg^{-1} of Pb, 0–500 mg kg^{-1} of As, and 0-800 mg kg^{-1} of Fe. The results showed that all tested fungi had tolerance to Cu, Pb, and Fe in all the concentrations and specifically *T. ghanense* and *R. microspores* had a great capacity for Cd and As concentrations.

Gohre and Paszkowski (2006) pointed out the importance of arbuscular mycorrhizal fungi (AMF) to reduce the metals uptake in plants so the effect of these fungi were study on wheat plants (*Triticum aestivum* L.) cultivated with Zn concentrations of 0, 100, 300, and 900 mg kg^{-1}. Results showed that plants with AMF association had a better growth and Zn content on those plants was lower in the aerial part than in the roots, also the phosphorous (P) content was higher in plants with AMF association that in the control (Kanwal et al. 2016).

Massaccesi et al. (2002) isolated several fungi (*Aspergillus terreus*, *Cladosporium cladosporioides*, *Fusarium oxysporum*, *Gliocladium roseum*, *Penicillium* spp., *Talaromyces helicus*, and *Trichoderma* koningii) from industrial contaminated soils in La Plata, Argentina, and after that they were cultivated in cadmium-basal medium where they developed 5–53% of biomass.

16.6 Phytoremediation as Technologies to Clean Up the Environment of Heavy Metals

Plants can be used to clean up contaminated sites through a technology called phytoremediation. This technology does not need a lot of money, is environmentally friendly, immobilized/stabilized metals pesticides, hydrocarbons, and chlorinated solvents (Zhao et al. 2003; Jadia and Fulekar 2008). Phytoremediation can be used not only to decontaminate soils but also water (U.S. EPA 2001).

This technology emerged more than 300 years ago and is based on natural processes ago (Lasat 2000). The plants used for decontamination process can accumulate great quantities of toxic heavy metals ($\geq$100 times) (Ghosh and Singh 2005) and they are classified as hyperaccumulator plants (Barceló and Poschenrieder 2002).

16.7 Phytoremediation Can Be Classified into Different Applications (Jadia and Fulekar 2009) Such as

16.7.1 Phytofiltration or Rhizofiltration

This process is similar to phytoextraction with the difference that plant roots are used to absorb or adsorb pollutants (metals) from liquid environment (groundwater and aqueous waste streams) (Garbisu and Alkorta 2001). Metals are either adsorbed on the root surface or are absorbed by the plant roots. These plants are first adapted to a polluted water (they are hydroponically cultivated with clean water until the roots are well developed and later the clean water is changed by polluted one) and then they are planted in situ (Scragg 2006).

16.7.2 Phytostabilization

Through this process soil sediment and sludge are immobilized by plants that are capable to decrease water infiltrating, avoid direct contact with the contaminate soil by acting as a barrier and prevent soil erosion (Raskin and Ensley 2000). This technique is valuable for the cleaning of several heavy metals such as Pb, As, Cd, Cr, Cu, and Zn (Jadia and Fulekar 2009).

16.7.3 Phytovolatilization

Through this process plants absorb contaminants and then these contaminants are volatilized to the atmosphere (complex organic molecules are degraded into simple ones) so heavy metals are present in groundwater, soils, sediments, and sludges medium (Prasad and De Oliveira 2003).

16.7.4 Phytodegradation

In this process contaminants that were absorbed by plants are degraded through metabolic process inside the plant, or external contaminants decomposition is achieved through the effect of several compounds produced by the plant (Prasad and De Oliveira 2003).

16.7.5 Phytoextraction

In this process the plant roots take the heavy metals from the soil and they are translocated to the upper tissues. The plants that realize this process should be tolerant to heavy metals concentration, grow rapidly with a lot of biomass per hectare to be able to accumulate these metals in the foliar part, and they also need a well-developed root system with a high bioaccumulation factor (Ghosh and Singh 2005; Scragg 2006; Jadia and Fulekar 2008).

Some examples of phytoremediation are soil improvement with organic compounds; thermophilic compost, vermicompost, and coconut coir were tested for the bioavailability of trace heavy metals of Zn, Cd, Pb, Co, and Ni under laboratory conditions, and results showed that the organic compounds used decreased the amount of bioavailable metals in the soils and increased soil pH, electrical conductivity (EC), and soil nutrient content. The conditions of switchgrass were also evaluated and shoot and biomass were higher in the soils where the organic compounds were used (Shrestha et al. 2019). Another example is the use of *Brassica juncea* L. to remove heavy metals from urban soil amended with cow dung: Pb uptake by this plant was better than for other heavy metals; finally, this plant was classified as hyperaccumulator according to the Translocation Factor (Gayatri et al. 2019).

Some species (*Macrotyloma uniflorum* (Lam.) Verdc., *Vigna radiata* (L.) R. Wilczek, and *H. annuus*) were used to evaluate their potential for metal extraction in contaminated soil. The higher remediation potential for three metals (Cr 74%, Cd 42.2%, and Pb 62%) was displayed by *H. annuus*, while the other two species remediated chromium more than the other two metals (Reddy et al. 2019).

H. annuus was used for the phytoextraction of Cd and Pb from contaminated soil in pots and the decrease in fresh and dry weights of the plants was clear when heavy metals concentrations increased (up to 200 mg kg^{-1} of both metals). The roots of the plant showed higher accumulation of Cd (Alaboudi 2018).

Some plants species are classified as they accumulate metals mainly in roots because they have a translocation factor (TF) <1 and a bioconcentration factor (BCF) >1; these plants are *Cyperus involucratus* Rottb. (accumulates Cu in roots), *Ipomoea pescaprae* (L.) R. Br. (accumulates Zn in roots), *Typha angustifolia* L. (accumulates Mn in roots), and *Phragmites karka* (Retz.) Trin. ex Steud (accumulates Pb in roots) (Kaewtubtim et al. 2016). According to Prapagdee and Khonsue (2015) plants of *Ocimum gratissimum* L. growing for 2 months in soil contaminated with Cd can accumulate this metal in association with a bacterium (*Arthrobacter* sp.) in roots, above-ground tissues, and whole plant.

An hyperaccumulator plant (*Micranthemum umbrosum* (J.F. Gmel.) S.F. Blake) was reported than can remove 79.3–89.5% of As compared to Cd (60–73.1%) (Islam et al. 2013).

16.8 Plant–Microbe Interactions for the Remediation of Pesticides as Environment Pollutants

Pesticides can be defined as different types of chemicals such as insecticides, fungicides, herbicides, and rodenticides (Singhvi et al. 1994). The uses of pesticides varied over time (according to Singhvi et al. 1994; U.S. EPA 2000):

- In the middle of 1940s the production and application of synthetic organic pesticides increased;
- Until 1991 the US Environmental Protection Agency (EPA) registered about 23,400 pesticides;
- In 1997, 1.2 billion pounds of pesticides were used;
- The distribution of this product use is: in the agriculture sector 77% of pesticides are used, while 12% are used by industrial, commercial, and government organizations and the other 11% is used by private houses.

There are organizations that regulate the production and application of pesticides such as The Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA), and Environmental Protection Agency (EPA) which regulate the registration of the product taking into an account the risk to human health and the environment. The persistence of the compounds is determined in the soil according to aerobic and anaerobic soil metabolism and photolysis, for example, the re-registration fact sheet for metolachlor estimates a half-life between 7 and 292 days in soil surface (U.S. EPA 1995).

Due to biological stability of pesticides and higher degree of lipophilicity in food they have a great effect on human and animal health (Tayade et al. 2013). It is also important to know that the continuous use of them induces their accumulation in soils and water. The reason why they are widely used is because of the necessity of increasing the yield of crops (Bag 2000).

Bag (2000) also points out that the continuous use of pesticides causes several health and environmental problems such as poisoning of farmers, miscarriages,

cardiopulmonary diseases, fetal deformities, neurological and skin disorders, low sperm count of applicators—as human health problems—and soil and water contamination, damage to insects and microorganisms, as environmental problems (Singh et al. 2014). One of the most dangerous and problematic pesticides used are organochlorines (Odukkathil and Vasudevan 2013). Chlororganic compounds (aldrin, heptachlor, endosulfan, DDT) are of deep concern, due to these pesticides can accumulate in living tissues inducing several diseases in humans (Das and Chandran 2011).

According to Ahmad and Ahmad (2015) pesticides can be classified by their chemical nature in the following major groups:

- *Organochlorines*: These synthetic organic pesticides are chlorinated hydrocarbons used extensively from the 1940s through the 1960s in agriculture and mosquito control. They have low toxicity level and long residual effects with stable chemical structure; thus, these pesticides are difficult to breakdown in nature and this leads to environmental pollution. Examples of these pesticides are DDT, methoxychlor, dieldrin, chlordane, toxaphene, mirex, kepone, lindane, and benzene hexachloride.
- *Organophosphates*: These pesticides can control a wide variety of pests and they are potent nerve agents, functioning by inhibiting the action of acetylcholinesterase (AChE) in nerve cells. They are one of the most common causes of poisoning worldwide, and are frequently intentionally used in suicides in agricultural areas. In the environment they are biodegradable, so the pollution caused by their use is minimum. Examples of these pesticides are:
  - Insecticides: malathion, parathion, diazinon, fenthion, dichlorvos, chlorpyrifos, ethion;
  - Ophthalmic agents: echothiophate, isoflurophate;
  - Antihelmintics: erichlorfon;
  - Herbicides: tribufos (DEF), merphos.
- *Carbamates*: The principle of the action of these pesticides is the same of organophosphates, that means they affect signals transmitted by nerves so the pest die by poisoning. These pesticides are also fumigants, stomach and contact poisons. In the environment they are biodegradable so the pollution caused by their use is minimum. Examples of these pesticides are: aldicarb, carbofuran, carbaryl, ethienocarb, fenobucarb, oxamyl, methomyl.
- *Synthetic pyrethroids*: These are pesticides derived from naturally occurring pyrethrins, taken from pyrethrum of dried Chrysanthemum flowers. They are very toxic with the property of lower break down times and are formulated with synergists increasing potency and compromising the body's ability to detoxify the pesticide. The extensive use of pyrethroids is a main problem because they pollute the agricultural soils and water resources and affect non-target organisms and humans. Examples of these pesticides are allethrin, permethrin, cypermethrin, deltamethrin, bifenthrin, cyfluthrin.

16.9 Bioremediation as Technologies to Clean Up the Environment of Pesticides

Microorganism like bacteria, fungi, and algae can be used to clean up the environment. In 1973 was isolated the first microorganism that degraded organophosphorus compounds identified as *Flavobacterium sp*. Some strains of Pseudomonas have been informed to mineralize organophosphorous pesticides and fungicides (*Pseudomonas sp.*) and *Pseudomonas fluorescens* SM1 strain was reported as a bacterium that could remediate sites polluted with pesticides in India. Table 16.1 summarizes published results on these topics in the last 10 years.

The mechanism that fungi use to bioremediate soils contaminated with pesticides is through introducing minor structural changes, making the pesticide nontoxic and susceptible to additional biodegradation by bacteria (Gianfreda and Rao 2004). Several pesticide groups such as phenylurea, phenylamide, chlorinated and organophosphorus compounds can be degraded by fungi like *Hypholoma fasciculare,*

Table 16.1 Recent studies on some pesticides degrading and/or detoxifying microbes published during 2010–2019

Pesticides	Microorganisms	References
Organochlorine		
Aldrin	Bacteria: *Pseudomonas fluorescens* and *Bacillus polymyxa*	Doolotkeldieva et al. (2018)
Lidane, hexachlorocyclohexane, DDT, pentachlorophenol	Bacterium: *Pseudomonas sp*.	Kurashvili et al. (2016)
Endosulfan	Bacteria genera: Klebsiella, Acinetobacter, Alcaligenes, Flavobacterium, and Bacillus; and fungi *Pleurotus ostreatus*	Kadilzadeh et al. (2015), Sadiq et al. (2019)
Lindane	Fungus: *Fusarium verticillioides*	Guillen-Jimenez et al. (2012)
Tetrachlorvinphos (TCV)	Consortium of bacteria: *Stenotrophomonas maltophilia, Proteus vulgaris, Vibrio metschnikovii, Serratia ficaria, Serratia* spp. and *Yersinia enterocolitica*	Ortiz-Hernández and Sánchez-Salinas (2010)
Organophosphate		
Monocrotophos	Bacteria: *Enterobacter sp* and *Pseudomonas aeruginosa*	Jaramillo et al. (2016)
Methamidophos	Fungus: *Penicillium oxalicum*	Zhao et al. (2010)
Herbicide		
Linuron, metribuzin, and chlorpyrifos	Fungi: *Pleurotus ostreatus, Pycnoporus coccineus, Phlebiopsis gigantea* and *Trametes versicolor*	Gouma et al. (2019)
Chlorsulfuron	Fungi: *Alternaria alternata*, *Metacordyceps chlamydosporia*, *Stachybotrys chartarum*, *Penicillium simplicissimum*	Ergüven (2017)

Pleurotus ostreatus, *Coriolus versicolor*, *Avatha discolor*, and some others (Bending et al. 2002).

Ectomycorrhizal fungi have been used for degradation of DDT pesticide using a media with 5 mg L^{-1} of the DDT and the fungi used (*Laccaria bicolor*, *Boletus edulis*, *Leccinum scabrum*, and *Gomphidius viscidus*) degraded all the pesticide in 15 days of exposition (Huang et al. 2007).

Several white rot fungi from basidiomycete orders were investigated by Boyle et al. (1998) with the aim to analyze the degradation of mono-aromatic pesticides (diuron, atrazine, terbuthylazine, metalaxyl). Authors found that *Coriolus versicolor*, *Hypholoma fasciculare*, and *Stereum hirsutum* at 42 days degraded diuron, atrazine, and terbuthylazine until 86% and for metalaxyl not more than 44%. Proteases are enzymes involved in ligninolytic activities regulation in cultures of *T. versicolor* under nutrient limitation (Staszczak et al. 2000) and naphthalene (aromatic hydrocarbon) has a positive influence on protease (Margesin et al. 2000).

In the case of bacteria, they use hydrolytic enzymes as degrading mechanism breaking down some herbicides such as atrazine; examples are *Pseudomonas sp.* and *Klebsiella pneumoniae*. Other enzymes like oxygenases, hydroxylases, hydrolases, and isomerases that can degrade herbicide 2, 4-D; bacteria having these enzymes are *Pseudomonas* and *Alcaligenes* sp. The mainly reported genera of bacteria than can degrade pesticides are *Flavobacterium, Arthrobacter, Azotobacter, Burkholderia, and Pseudomonas* (Mulbry and Kearney 1991).

In Kyrgyzstan, a research to study the microorganisms that can live in soils from dumping zones contaminated with pesticides identified bacteria from *Micrococcus* genus in some of these soils, also authors identified bacteria from the genus *Pseudomonas* and *Bacillus* species. *Pseudomonas fluorescens* and *Bacillus polymyxa* population were selected for Aldrin (organochlorine insecticide) (Doolotkeldieva et al. 2018).

Kurashvili et al. (2016) investigated growth of several strains of Pseudomonas with organochlorine pesticides. The pesticides used were lindane (hexachlorocyclohexane), DDT and PCP in concentrations of 0.01, 0.1, and 1 mM and they found that after bacteria cultivation with DDT, several strains from genera Pseudomonas (35) grow better with glucose, while 15 strains had a superior growth with DDT. Respect to lindane 14 strains had a better growth with glucose and 13 strains with lindane than with glucose. About PCP, 14 strains from genera Pseudomonas revealed best growth with glucose and 4 strains were grown better with PCP. Finally, respect to DDT 11 strains of Pseudomonas that showed best grown with glucose were selected; for lindane and PCP, 11 and 10 strains, respectively, of Pseudomonas that revealed best grown with glucose were selected (Kurashvili et al. 2016).

16.10 Phytoremediation as a Technology to Clean Up the Environment of Pesticides

Plants can use different mechanisms to eliminate or degrade contaminants from the environment; some of the mechanisms are via root uptake, detoxification or conjugation, and some others (Van Eerd et al. 2003; Wilson et al. 2000).

Trees can be used also for phytoremediation because they have a lot of biomass (stems and branches, 95%). In this sense polychlorinated biphenyls (PCBs) can accumulate in bark of black walnut and white oak (*Quercus alba*) and poplar trees (Meredith and Hites 1987).

The degradation of atrazine (herbicide of the triazine class) was studied by Anderson and Coats (1995). The research was made in the rhizosphere of 15 plant species and they found higher mineralization in rhizopshere soil from several of the species under study, such as kochia (*Kochia scoparia*), common lambsquarters *(Chenopodium album*), witchgrass (*Panicum capillare*), and some others. Another study of atrazine was done with poplar (*Populus deltoides x nigra)*; this plant can transform the herbicide into dealkylates (Burken and Schnoor 1996; Burken and Schnoor 1997).

Another research was made with atrazine, metolachlor, and cyanazine where bromegrass strip (*Bromus inermis* L.) retained atrazine (11–100%) and the three herbicides were retained by the grass because of infiltration process (Arora et al. 1996).

Wilson et al. (2000) reported use of *Typha latifolia* to remove simazine (herbicide of the triazine class) from contaminated water.

Schnabel and White (2001) reported that balsam poplar (*Populus balsamifera*) is tolerant to aldrin because of uptake and metabolism, and Baz and Fernandez (2002) reported several plants that can be tolerant or sensitive to some pesticides like: Virginia sweetspire (*Itea virginica* L.), white willow (*Salix alba* L.), black pussywillow (*S. gracilistyla*).

After harvest of crops in a field, phytoremediation technology can stop leaching of contaminants to groundwater (field without crops) (Wilson et al. 2000; Coleman et al. 2002).

Several grasses (*Andropogon gerardii* Vitman; *Sorghastrum nutans* L., and *Panicum virgatum* L.) were studied referred to atrazine and metolachlor degradation by Zhao et al. (2003). The grasses mentioned were grown in soil with atrazine (100 μg g^{-1} of dry soil) and metolachlor (25 μg g^{-1} of dry soil); the use of mixed grasses increased the degradation of atrazine in soil without microorganism, also metolachlor concentration was reduced with the mixture.

Soils cultivated with *Pennisetum clandestinum* can be cleaned up of atrazine and simazine due to the high rates of removal of this plant (Singh et al. 2004).

Lunney et al. (2004) investigated the ability of five plant varieties (zucchini, tall fescue, alfalfa, rye grass, and pumpkin) for the mobilization and translocation of DDT used in soil at concentrations of 3700 ng g^{-1} (high concentration) and 150 ng g^{-1} (low concentration). Results showed that *Cucurbita pepo* species (pumpkin and zucchini) had the highest translocation and bioaccumulation factors.

Xia and Ma (2006) studied the phytoremediation capacity of *Eichhornia crassipes*, an aquatic plant known as water hyacinth with long pendant roots, rhizomes, and stolons. This plant was used with the aim to decontaminate polluted water of malathion and ethion and as results *E. crassipes* degraded about 56% of 10 ppm of malathion in 250 mL and the accumulated ethion in this plant decreased in different parts of the plants like in shoots (55–91%) and roots (74–81%) after the plant growing for 1 week in ethion free culture solutions.

At present there are several examples of genetically modified plants for pesticide degradation: *A. thaliana*, *Solanum lycopersicum* L., *Nicotiana tabacum* L. and *Glycine max* L. plants can express glyphosate oxidase, cytochrome P450 enzymes, a Rieske non-heme monooxygenase that converts dicamba to 3,6-dichlorosalicyclic acid (Behrens et al. 2007); corn can express aryloxyalkanoate dioxygenase enzymes (TfdA) useful for the degradation of 2,4-D and pyridyloxyacetate herbicides (Scott et al. 2008).

Ricinus communis L. was used for the degradation of several persistent organic pollutants (POPs), in a 66-day period. The results showed that hydrophobicity of the organic compound and its molecular constitution interacted with soil or root matrix and increased its tendency to concentrate in root tissues hexachlorocyclohexane (HCHs) < diclofop-methyl < chlorpyrifos < methoxychlor < heptachlor epoxide < endrin < o,p′-DDE < heptachlor < dieldrin < aldrin < o,p′-DDT < p,p′-DDT. The plant removed 25–70% of pollutant, proving that *R. communis* can be used for the phytoremediation of such compounds. The greatest results were found for the remediation of HCHs (65.07–68.33%), chlorpyrifos (46.34–69.01%), diclofop-methyl (53.66–54.98%), and trans-chlordane (44.17–49%) (Rissato et al. 2015).

Five plants (alfalfa, oat, ryegrass, Indian mustard, sunflower, tall fescue, and switch grass) were grown under greenhouse conditions to phytoremediate soil contaminated with mixed metal-PAH-pesticide (DDT as model). The results revealed that sunflower and Indian mustard were the most tolerant plants to the studied mixed contaminants; also, sunflower removed metals and PAH at the same time. In the case of oat, it was inappropriate for phytoremediation of metal-PAH contaminated soil (Ndubueze 2018).

Aioub et al. (2019) used *Plantago major* (perennial herb) and some surfactants [liquid silicon dioxide (SiO_2, 750 mg L^{-1}), 2-hydroxypropyl-beta-cyclodextrin (HPßCD, 1%), humic acid (HA, 10 mg L^{-1}) and Tween 80 (Tw80, 9.2 mg L^{-1})] for reducing soil contamination with cypermethrin (CYP, 10 μg g^{-1}) (pyrethroid insecticides). Soil improvement with *P. major* together with SiO_2 significantly decreased the quantity of CYP and increased the concentration of the insecticide in *P. major* roots and leaves.

16.11 Conclusions

Interactions between plants and microorganisms begin to bear fruit in the elimination of toxic waste from the environment. In contrast to the indiscriminate dumping of waste, which is increasing every day due to the increase in population and anthropic

activities, solutions have begun to appear that contribute to the reduction of the impact of these actions. In reducing pollutants, the combined possibilities of plants, bacteria, and fungi are used, which, through different mechanisms, hydrolyze the pollutants or a part of them, transform them into nontoxic substances or accumulate them in the plant organs, removing them from the soil and the water.

Plant–microbe interactions have been useful in the detoxification of hydrocarbons and their derivatives, heavy metals, and pesticides. The genetic engineering of plants and microbes is also providing results in this regard (mainly in the remediation of heavy metals and herbicides) although it stumbles upon the laws that in many countries regulate the introduction of genetically modified organisms. However, due to the demonstrated ability to enhance the capacities of natural organisms, genetically modified plants and microorganisms are expected to participate in environmental detoxification in a much larger proportion in the future.

References

Abhilash PC, Powell JR, Singh HB, Singh BJ (2012) Plant-microbe interactions: novel applications for exploitation in multipurpose remediation technologies. Trends Biotechnol 30(8):416–420

Adriano DC (2001) Trace elements in terrestrial environments: biochemistry, bioavailability and risks of metals, 2nd edn. Springer, New York, p 796

Ahmad M, Ahmad I (2015) Bioremediation of pesticides. Australas Biotechnol 11:125–165

Ahmadpour P, Ahmadpour F, Mahmud TMM, Abdu A, Soleimani M, Hosseini FT (2012) Phytoremediation of heavy metals: a green technology. African J Biotech 11:14036–14043

Aioub AAA, Li Y, Qie X, Zhang X, Hu Z (2019) Reduction of soil contamination by cypermethrin residues using phytoremediation with *Plantago major* and some surfactants. Environ Sci Eur 31 (26):1–12

Alaboudi KA, Ahmeda B, Brodie G (2018) Phytoremediation of Pb and cd contaminated soils by using sunflower (*Helianthus annuus*) plant. Ann Agri Sci 63:123–127

Alloway BJ, Ayres DC (1997) Chemical principles of environmental pollution. Blackie Academic, London, pp 168–176

Anderson TA, Coats JR (1995) Screening rhizosphere soil samples for the ability to mineralize elevated concentrations of atrazine and metolachlor. J Environ Sci Health B 30:473–484

Arora K, Mickelson SK, Baker JL, Tierney DP (1996) Herbicide retention by vegetative buffer strips from runoff under natural rainfall. Trans ASAE 39(6):2155–2162

Atafar Z, Mesdaghinia A, Nouri J, Homaee M, Yunesian M, Ahmadimoghaddam M, Hossein AM (2010) Effect of fertilizer application on soil heavy metal concentration. Environ Monit Assess 160:83–89

Baccio D, Tognetti R, Sebastiani L, Vitagliano C (2003) Responses of *Populus deltoides*× *Populus nigra* (Populus× euramericana) clone I-214 to high zinc concentrations. New Phytol 159 (2):443–452

Bag D (2000) Pesticides and health risks. Eco Pol Weekly 6(16):20–21

Barceló J, Poschenrieder C (2002) Fast root growth responses, root exudates, and internal detoxification as clues to the mechanisms of aluminium toxicity and resistance: a review. Environ Exp Bot 48(1):75–92

Baz M, Fernandez RT (2002) Evaluating woody ornamentals for use in herbicide phytoremediation. J Am Soc Hort Sci 127(6):991–997

Behrens M, Mutlu N, Chakraborty S, Dumitru R, Zhi WJ, Lavallee BJ, Herman PL, Clemente TE, Weeks DP (2007) Dicamba resistance: enlarging and preserving biotechnology-based weed management strategies. Forensic Sci 316(5828):1185–1188

Benavides MP, Gallego SM, Tomaro ML (2005) Cadmium toxicity in plants. Braz J Plant Physiol 17:21–34

Bending G, Friloux DM, Walker A (2002) Degradation of contrasting pesticides by white rot fungi and its relationship with ligninolytic potential. FEMS Microbiol Lett 212:59–63

Bisht S, Pandey P, Kumar V, Bhargava B, Sharma S, Sharma KD (2015) Bioremediation of polyaromatic hydrocarbons (PAHs) using rhizosphere technology. Braz J Microbiol 46(1):7–21

Bjuhr J (2007) Trace metals in soils irrigated with waste water in a periurban area downstream Hanoi City. Vietnam, Seminar paper, Institutionen för markvetenskap, Sveriges Lantbruksuniversitet (SLU), Uppsala, Sweden, p 50

Boyle D, Wiesner C, Richardson A (1998) Factors affecting the degradation of polyaromatic hydrocarbons in soil by white-rot fungi. Soil Biol Biochem 30:873–882

Burken JG, Schnoor JL (1996) Phytoremediation: plant uptake of atrazine and role of root exudates. J Environ Eng 122:958–963

Burken JG, Schnoor JL (1997) Uptake and metabolism of atrazine by poplar trees. Environ Sci Technol 31:1399–1406

Chauhan A, Fazlurrahman JG, Oakeshott RKJ (2008) Bacterial metabolism of polycyclic aromatic hydrocarbons: strategies for bioremediation. Indian J Microbiol 48:95–113

Cherian S, Oliveira MM (2005) Transgenic plants in phytoremediation: recent advances and new possibilities. Environ Sci Technol 39(24):9377–9390

Coleman JOD, Frova C, Schroder P, Tissut M (2002) Exploiting plant metabolism for the phytoremediation of persistent herbicides. Environ Sci Pollut Res 9:18–28

Danh LT, Truong P, Mammucari R, Tran T, Foster N (2009) Vetiver grass, *Vetiveria zizanioides*: a choice plant for phytoremediation of heavy metals and organic wastes. Int J Phytoremediation 11:664–691

Das N, Chandran P (2011) Microbial degradation of petroleum hydrocarbon contaminants: an overview. Biotechnol Res Int 2011:1–13

DeVolder PS, Brown SL, Hesterberg D, Pandya K (2003) Metal bioavailability and speciation in a wetland tailings repository amended with biosolids compost, wood ash, and sulfate. J Environ Qual 32(3):851–864

Divya B, Kumar MD (2011) Plant-microbe interaction with enhanced bioremediation. Res J Biotech 6(4):72–79

Doolotkeldieva T, Konurbaeva M, Bobusheva S (2018) Microbial communities in pesticide-contaminated soils in Kyrgyzstan and bioremediation possibilities. Environ Sci Pollut Res Int 25(32):31848–31862

Doty SL (2008) Enhancing phytoremediation through the use of transgenics and endophytes. New Phytol 179:318–333

Eapen S, Singh S, D'Souza SF (2007) Advances in development of transgenic plants for remediation of xenobiotic pollutants. Biotechnol Adv 25:442–451

Elekes CC (2014) Eco-technological solutions for the remediation of polluted soil and heavy metal recovery. In: Hernández-Soriano MC (ed) Environmental risk assessment of soil contamination. InTech, Rijeka, pp 309–335

Ergüven OG (2017) Role of some selected fungi cultures on bioremediation of herbicide chlorsulfuron. J Tekirdag Agric Faculty 14(02):110–118

Fan JL, Ding WX, Chen ZM, Ziadi N (2012) Thirty-year amendment of horse manure and chemical fertilizer on the availability of micronutrients at the aggregate scale in black soil. Environ Sci Pollut Res 19:2745–2754

Fatima K, Imran A, Amin I, Khan QM, Afzal M (2016) Plant species affect colonization patterns and metabolic activity of associated endophytes during phytoremediation of crude oil-contaminated soil. Environ Sci Pollut Res 23(7):6188–6196

Filonov AE, Akhmetov LI, Puntus IF, Esikova TZ, Gafarov AB, Izmalkova TV, Sokolov SL, Kosheleva IA, Boronin AM (2005) The construction and monitoring of genetically tagged, plasmid-containing, naphthalene-degrading strains in soil. Microbiology 74(4):526–532

Garbisu C, Alkorta I (2001) Phytoextraction: a cost-effective plant-based technology for the removal of metals from the environment. Bioresour Technol 77(3):229–236
Gaur A, Adholeya A (2004) Prospects of arbuscular mycorrhizal fungi in phytoremediation of heavy metal contaminated soils. Curr Sci 86(4):528–534
Gayatri N, Sailesh AR, Srinivas N (2019) Phytoremediation potential of Brassica junceafor removal of selected heavy metals in urbansoil amended with cow dung. J Mater Environ Sci 10 (5):463–469
Gentry TJ, Rensing C, Pepper IL (2004) New approaches for bioaugmentation as a remediation technology. Crit Rev Environ Sci Technol 34:447–494
Ghosal D, Ghosh S, Dutta TK, Ahn Y (2016) Current state of knowledge in microbial degradation of polycyclic aromatic hydrocarbons (PAHs): a review. Front Microbiol 7:1369. https://doi.org/10.3389/fmicb.2016.01369
Ghosh M, Singh SP (2005) A review on phytoremediation of heavy metals and utilization of its byproducts. Appl Ecol Env Res 3(1):1–18
Gianfreda L, Rao M (2004) Potential of extra cellular enzymes in remediation of polluted soils: a review. Enzyme Microb Technol 35:339–354
Glick BR (2003) Phytoremediation: synergistic use of plants and bacteria to clean up the environment. Biotechnol Adv 21:383–393
Gohre V, Paszkowski U (2006) Contribution of the arbuscular mycorrhizal symbiosis to heavy metal phytoremediation. Planta 223(6):1115–1122
Gong Q, Chen P, Shi R, Gao Y, Xu Y, Shao C, Zheng X (2019) Health assessment of trace metal concentrations in organic fertilizer in northern China. Int J Environ Res Public Health 16:1–22
Gouma S, Papadaki AA, Markakis G, Magan N, Goumas D (2019) Studies on pesticides mixture degradation by white rot fungi. J Ecol Eng 20(2):16–26
Guillen-Jimenez FDM, Cristiani-Urbina E, Cancino-Díaz JC, Flores-Moreno JL, Barragán-Huerta BE (2012) Lindane biodegradation by the *Fusarium verticillioides* AT-100 strain, isolated from *Agave tequilana* leaves: kinetic study and identification of metabolites. Int Biodeter Biodegr 74:36–47
Guo M, Gong Z, Miao R, Rookes J, Cahill D, Zhuang J (2017) Microbial mechanisms controlling the rhizosphere effect of ryegrass on degradation of polycyclic aromatic hydrocarbons in an aged-contaminated agricultural soil. Soil Biol Biochem 113:140–142
Hernández E, Ferrera R, Gutiérrez MC, Rodríguez R, Rubiños JE, Fernández L (2003) Bacterias y hongos hidrocarbonoclastas de rizósfera frijol y maíz, en un suelo contaminado con petróleo. Terra Latinoamericana 21(4):493–502
Huang Y, Zhao X, Luan S (2007) Uptake and biodegradation of DDT by 4 ectomycorrhizal fungi. Sci Total Environ 385:235–241
Ikem A, Campbell N, Nyirakabibi I, Garth J (2008) Baseline concentrations of trace elements in residential soils from southeastern Missouri. Environ Monit Assess 140:69–81
Iqbal A, Arshad M, Ahmed I (2018) Plant-microbe association for bioremediation of hydrocarbon substrates. In: Kumar V et al (eds) Microbial action on hydrocarbons. Springer, Singapore
Islam MS, Ueno Y, Sikder MT, Kurasaki M (2013) Phytofiltration of arsenic and cadmium from the water environment using *Micranthemum umbrosum* (jf GMEL) sf blake as a hyperaccumulator. Int J Phytoremediation 15:1010–1021
Ismail S, Khan F, Zafar MI (2013) Phytoremediation: assessing tolerance of tree species against heavy metal (PB and CD) toxicity. Pak J Bot 45:2181–2186
Ite AE, Ibok UJ (2019) Role of plants and microbes in bioremediation of petroleum hydrocarbons contaminated soils. Int J Env Biorem Biodegr 7(1):1–19
Jadia CD, Fulekar MH (2008) Phytoremediation: the application of vermicompost to remove zinc, cadmium, copper, nickel and lead by sunflower plant. Environ Eng Manag J 7:547–558
Jadia CD, Fulekar FH (2009) Phytoremediation of heavy metals: recent techniques. Afr J Biotechnol 8(6):921–928
Jan AT, Azam M, Ali A, Haq QMR (2014) Prospects for exploiting bacteria for bioremediation of metal pollution. Crit Rev Environ Sci Technol 44:519–560

Jaramillo BE, Bermúdez AT, Tirado IB (2016) Organophosphorus pesticides degrading bacteria pres-ent in contaminated soils. Rev Cienc Téc Agrop 25(3):13–22
Jones LHP, Jarvis SC (1981) The fate of heavy metals. In: Greenland DJ, Hayes MHB (eds) The chemistry of soil processes. Wiley, New York, p 593
Jussila MM, Zhao J, Suominen L, Lindström K (2007) TOL plasmid transfer during bacterial conjugation *in vitro* and rhizoremediation of oil compounds *in vivo*. Environ Pollut 146 (2):510–524
Juwarkar AA, Singh SK, Mudhoo A (2010) A comprehensive overview of elements in bioremediation. Rev Environ Sci Biotechnol 9(3):215–288
Kadilzadeh F, Ebrahimnezhad M, Tahery Y (2015) Isolation and identification of Endosulfan-degrading bacteria and evaluation of their bioremediation in Kor River. Iran Osong Public Health Res Perspect 6(1):39–46
Kaewtubtim P, Meeinkuirt W, Seepom S, Pichtel J (2016) Heavy metal phytoremediation potential of plant species in a mangrove ecosystem in Pattani Bay, Thailand. Appl Ecol Env Res 14 (1):367–382
Kanwal S, Bano A, Malik RN (2016) Role of arbuscular mycorrhizal fungi in phytoremediation of heavy metals and effects on growth and biochemical activities of wheat (*Triticum aestivum* L.) plants in Zn contaminated soils. Afr J Biotechnol 15(20):872–883
Khan MS, Zaidi A, Wani PA, Oves M (2009) Role of plant growth promoting rhizobacteria in the remediation of metal contaminated soils. Environ Chem Lett 7:1–19
Kiely PD, Haynes JM, Higgins CH, Franks A, Mark GL, Morrissey JP, O'Gara F (2006) Exploiting new systems-based strategies to elucidate plant-bacterial interactions in the rhizosphere. Microb Ecol 51:257–266
Kuiper I, Bloemberg GV, Lugtengerg BJJ (2001) Selection of a plant-bacterium pair as an oval tool for rhizostimulation of polycyclic aromatic hydrocarbon-degrading bacteria. MPMI 14:1197–1205
Kuiper I, Lagendijk EL, Bloemberg GV, Lugtenberg BJJ (2004) Rhizoremediation: a beneficial plant-microbe interaction. MPMI 17(1):6–15
Kumar V, Kumar M, Sharma S, Prasad R (2017) Probiotics in agroecosystem. Springer, Singapore
Kumar V, Kumar M, Prasad R (2018) Microbial action on hydrocarbons. Springer, Singapore
Kuppusamy S, Lee YB, Thavamani P, Venkateswarlu K, Naidu R, Megharaj M (2016) Remediation approaches for polycyclic aromatic hydrocarbons (PAHs) contaminated soils: technological constraints, emerging trends and future directions. Chemosphere 168:944–968
Kurashvili MV, Adamia GS, Amiranashvili LL, Ananiasvili TI, Varazi TG, Pruidze MV, Gordeziani MS, Khatisashvili GA (2016) Targeting of detoxification potential of microorganisms and plants for cleaning environment polluted by organochlorine pesticides. Ann Agrar Sci 14:222–226
Lasat MM (2000) Phytoextraction of metals from contaminated soil: a review of plant/soil/metal interaction and assessment of pertinent agronomic issues. J Hazard Substance Res 2(5):1–25
Lunney AI, Zeeb BA, Reimer KJ (2004) Uptake of weathered DDT in vascular plants: potential for phytoremediation. Environ Sci Technol 38(22):6147–6154
Ma Y, Prasad MNV, Rajkumar M, Freitas H (2011) Plant growth promoting rhizobacteria and endophytes accelerate phytoremediation of metalliferous soils. Biotechnol Adv 29:248–258
Machuca A, Pereira G, Aguiar A, Milagres AMF (2007) Metal-chelating compounds produced by ectomycorrhizal fungi collected from pine plantations. Lett Appl Microbiol 44:7–12
Maldonado E, Rivera MC, Izquierdo F, Palma DJ (2010) Efectos de rizosfera, microorganismos y fertilización en la biorremediación y fitorremediación de suelos con petróleos crudo nuevo e intemperizado. Universidad y Ciencia 26(2):121–136
Mapanda F, Mangwayana EN, Nyamangara J, Giller KE (2005) The effect of long-term irrigation using wastewater on heavy metal contents of soils under vegetables in Harare, Zimbabwe. Agric Ecosyst Environ 107:151–165

Margesin R, Walder G, Schinner F (2000) The impact of hydrocarbon remediation (diesel oil and polycyclic aromatic hydrocarbons) on enzyme activities and microbial properties of soil. Acta Biotechnol 20:313–333

Massaccesi G, Romero MC, Cazau MC, Bucsinszky AM (2002) Cadmium removal capacities of filamentous soil fungi isolated from industrially polluted sediments, in La Plata (Argentina). World J Microbiol Biotechnol 18(9):817–820

Meredith ML, Hites RA (1987) Polychlorinated biphenyl accumulation in tree bark and wood growth rings. Environ Sci Technol 21:709–712

Miransari M (2011) Hyperaccumulators, arbuscular mycorrhizal fungi and stress of heavy metals. Biotechnol Adv 29:645–653

Mmom PC, Deekor T (2010) Assessing the effectiveness of land farming in the remediation of hydrocarbon polluted soils in the Niger Delta. Nigeria Res J Appl Sci Eng Technol 2 (7):654–660

Mulbry W, Kearney CK (1991) Degradation of pesticides by micro-organisms and the potential for genetic manipulation. Crop Prot 10(5):334–346

Naik MM, Shamim K, Dubey SK (2012) Biological characterization of lead resistant bacteria to explore role of bacterial metallothionein in lead resistance. Curr Sci 103:426–429

Ndubueze EU (2018) Potential of five plant species for phytoremediation of metal-PAH-pesticide contaminated soil. Electronic thesis and dissertation repository, pp 1–132

Odukkathil G, Vasudevan N (2013) Toxicity and bioremediation of pesticides in agricultural soil. Rev Environ Sci Biol 12(4):421–444

Oladipo OG, Awotoye OO, Olayinka A, Bezuidenhout CC, Maboeta MS (2018) Heavy metal tolerance traits of filamentous fungi isolated from gold and gemstone mining sites. Braz J Microbiol 49:29–37

Oliveira V, Santos AL, Aguiar C, Santos L, Salvador AC, Gomes NCM, Silva H, Rocha SM, Almeida A, Cunha A (2012) Prokaryotes in salt marsh sediments of Ria de Aveiro: effects of halophyte vegetation on abundance and diversity. Estuar Coast Shelf Sci 110:61–68

Oliveira V, Gomes NCM, Almeida A, Silva AMS, Silva H, Cunha A (2014a) Microbe-assisted phytoremediation of hydrocarbons in estuarine environments. Microb Ecol 69(1):1–12

Oliveira V, Gomes NCM, Almeida A, Silva AMS, Simões MMQ, Smalla K, Cunha A (2014b) Hydrocarbon contamination and plant species determine the phylogenetic and functional diversity of endophytic degrading bacteria. Mol Ecol 23:1392–1404

Ortiz-Hernández ML, Sánchez-Salinas E (2010) Biodegradation of the organophosphate pesticide tetrachlorvinphos by bacteria isolated from agricultural soils in México. Rev Int Contam Ambient 26(1):27–38

Paranthaman SR, Karthikeyan B (2015) Bioremediation of heavy metal in paper mill effluent using *Pseudomonas spp*. Int J Microbiol 1:1–5

Paz-Ferreiro J, Lu H, Fu S, Mendez A, Gasco G (2014) Use of phytoremediation and biochar to remediate heavy metal polluted soils: a review. Solid Earth 5:65–75

Pivetz P (2001) Phytoremediation of contaminated soil and ground water at hazardous waste sites. EPA/540/S-01/500, United States Environmental Protection Agency (EPA), Washington, DC, p 36

Prakash A, Bisht S, Singh J, Teotia P, Kela R, Kumar V (2014) Biodegradation potential of petroleum hydrocarbons (PHCs) by bacteria and mixed bacterial consortium isolated from contaminated sites. Turkish J Eng Env Sci 38(1):31–40

Prapagdee B, Khonsue N (2015) Bacterial-assisted cadmium phytoremediation by *Ocimum gratissimum* L. in polluted agricultural soil: a field trial experiment. Int J Environ Sci Technol 12:3843–3852

Prasad MNV, De Oliveira HM (2003) Metal hyperaccumulation in plants-biodiversity prospecting for phytoremediation technology. Electron J Biotechnol 6(3):110–146

Priyalaxmi R, Murugan A, Raja P, Raj KD (2014) Bioremediation of cadmium by *Bacillus safensis* (JX126862), a marine bacterium isolated from mangrove sediments. Int J Current Microbio App Sci 3:326–335

Raskin I, Ensley BD (2000) Phytoremediation of toxic metals: using plants to clean up the environment. Wiley, New York, p 304

Raven PH, Berg LR, Johnson GB (1998) Environment, 2nd edn. Saunders College Publishing, New York, p 640

Rayu S, Karpouzas DG, Singh BK (2012) Emerging technologies in bioremediation: constraints and opportunities. Biodegradation 23:917–926

Reed SC, Crites RW, Middlebrooks EJ (1995) Natural systems for waste management and treatment, 2nd edn. McGraw-Hill, New York, p 433

Reddy O, Muppuru K, Kumar SD (2019) Pilot study on phytoremediation of contaminated soils with different plant species. J Hazard Toxic Radioact Waste 23(4):753–764

Rissato SR, Galhiane MS, Fernandes JR, Gerenutti M, Gomes HM, Ribeiro R, de Almeida MV (2015) Evaluation of *Ricinus communis* L. for the phytoremediation of polluted soil with organochlorine pesticides. BioMed Res Inter 2015:1–8

Sadiq S, Hassan MM, Ahad K, Ishtiaq M (2019) Bioremediation of Endosulfan under solid-state and submerged fermentation of Pleurotus ostreatus and its correlation with lignolytic enzyme activities. Pol J Environ Stud 28(6):4529–4536

Sangabriel W, Ferrera R, Trejo D, Mendoza MR, Cruz JS, López C, Delgadillo J, Alarcón A (2006) Tolerancia y capacidad de fitorremediación de combustóleo en el suelo por seis especies vegetales. Rev Int Contam Amb 22(2):63–73

Sayler GS, Ripp S (2000) Field applications of genetically engineered micro-organisms for bioremediation processes. Curr Opin Biotechnol 11(3):286–289

Schnabel WE, White DM (2001) The effect of mycorrhizal fungi on the fate of aldrin: phytoremediation potential. Int J Phytoremediation 3(2):221–241

Schwab AP, Banks MK (1994) Biologically mediated dissipation of polyaromatic hydrocarbons in the root zone. In: Anderson TA, Coats JR (eds) Bioremediation through rhizosphere technology. American Chemical Society, Washington DC

Scott C, Pandey G, Hartley CJ, Jackson CJ, Cheesman MJ, Taylor MC, Pandey R, Khurana JL, Teese M, Coppin W, Weir KM, Jain RK, Lal R, Russell RJ, Oakeshott JG (2008) The enzymatic basis for pesticide bioremediation. Indian J Microbiol 48:65–79

Scragg A (2006) Environmental biotechnology, 2nd edn. Oxford University Press, Oxford, p 456

Sharma HD, Reddy KR (2004) Geoenvironmental engineering: site remediation, waste containment and emerging waste management technologies. Wiley, New York, p 992

Sharma RK, Agrawal M, Marshall F (2007) Heavy metal contamination of soil and vegetables in suburban areas of Varanasi, India. Ecotoxicol Environ Saf 66(2):258–266

Shrestha P, Bellitürk K, Görres JH (2019) Phytoremediation of heavy metal-contaminated soil by switchgrass: a comparative study utilizing different composts and coir fiber on pollution remediation, plant productivity, and nutrient leaching. Int J Environ Res Public Health 16:1–16

Siciliano SD, Fortin N, Mihoc A, Wisse G, Labelle S, Beaumier D, Ouellette D, Roy R, Whyte LG, Banks MK, Schwab AP, Lee K, Greer CW (2001) Selection of specific endophytic bacterial genotypes by plants in response to soil contamination. Appl Environ Microbiol 67:2469–2475

Singh BK (2011) Emerging and genomic approaches in bioremediation. In: Proceeding of the 4th international cont site remote conference, CRC-CARE, pp 75–76

Singh N, Megharaj M, Kookana RS, Naidu R, Sethunathan N (2004) Atrazine and simazine degradation in *Pennisetum* rhizosphere. Chemosphere 56:257–263

Singh R, Gautam N, Mishra A, Gupta R (2011) Heavy metals and living systems: an overview. Indian J Pharm 43(3):246–253

Singh R, Singh P, Sharma R (2014) Microorganism as a tool of bioremediation technology for cleaning environment: a review. Proc Int Acad Ecol Environ Sci 4(1):1–6

Singhvi R, Koustas RN, Mohn M (1994) Contaminants and remediation options at pesticide sites. EPA/600/R-94/202. US EPA Office of Research and Development, Risk Reduction Engineering Laboratory, Cincinnati, p 130

Staszczak M, Zdunek E, Leonowicz A (2000) Studies on the role of proteases in the white-rot fungus *Trametes versicolor*: effect of PMSF and chloroquine on ligninolytic enzymes activity. J Basic Microbiol 1:51–53

Tang WZ, Shan BQ, Zhang H, Mao ZP (2010) Heavy metal sources and associated risk in response to agricultural intensification in the estuarine sediments of Chaohu Lake Valley. East China J Hazard Mater 176(13):945–951

Tangahu BV, Abdullah SRS, Basri H, Idris M, Anuar N, Mukhlisin M (2011) A review on heavy metals (As, Pb, and Hg) uptake by plants through phytoremediation. Int J Chem Eng 2011:939161. https://doi.org/10.1155/2011/939161

Tayade S, Patel ZP, Mutkule DS, Kakde AM (2013) Pesticide contamination in food: a review. IOSR J Agri Vet Sci 6(1):7–11

Turan M, Esringu A (2007) Phytoremediation based on canola (Brassica napus L.) and Indian mustard (*Brassica juncea* L.) planted on spiked soil by aliquot amount of Cd, Cu, Pb, and Zn. Plant Soil Environ 53(1):7–15

U.S. EPA (1995) R.E.D. facts: metolachlor. EPA/738/F-95/007. Prevention, pesticides and toxic substances. Washington, DC, p 14

U.S. EPA (2000) Pesticides industry sales and usage: 1996 and 1997 market estimates. Office of Pesticide Programs. www.epa.gov/oppbead1/pestsales/97pestsales/table3.htm, p 46

U.S. EPA (2001) Brownfields technology primer: selecting and using phytoremediation for site cleanup. USEPA, Washington DC, p 46

Van Eerd LL, Hoagland RE, Hall JC (2003) Pesticide metabolism in plants and microorganisms. Weed Sci 51:472–495

Vidali M (2001) Bioremediation. An overview. Pure Appl Chem 73(7):1163–1172

Walton BT, Anderson TA (1990) Microbial degradation of trichloroethylene in the rhizosphere: potential application to biological remediation of waste sites. Appl Environ Microbiol 56:1012–1016

Wasilkowski D, Swędzioł Z, Mrozik A (2012) The applicability of genetically modified microorganisms in bioremediation of contaminated environments. CHEMIK 66(8):817–826

Wei BG, Yang LS (2010) A review of heavy metal contaminations in urban soils, urban road dusts and agricultural soils from China. Microchem J 94(2):99–107

Wenzel WW (2009) Rhizosphere processes and management in plant-assisted bioremediation (phytoremediation) of soils. Plant and Soil 321:385–408

Wilson PC, Whitwell T, Klaine SJ (2000) Metalaxyl and simazine toxicity to and uptake by *Typha latifolia*. Arch Environ Contam Toxicol 39:282–288

Wu CH, Wood TK, Mulchandani A, Chen W (2006) Engineering plant–microbe symbiosis for rhizoremediation of heavy metals. Appl Environ Microbiol 72:1129–1134

Xia H, Ma X (2006) Phytoremediation of ethion by water hyacinth (*Eichhornia crassipes*) from water. Bioresour Technol 97(8):1050–1054

Yahaghi Z, Shirvani M, Nourbakhsh F, de la Peña TC, Pueyo JJ, Taleb M (2018) Isolation and characterization of Pb-solubilizing bacteria and their effects on Pb uptake by *Brassica juncea*: implications for microbe- assisted phytoremediation. J Microbiol Biotechnol 28(7):1156–1167

Yang L, Wang Y, Song J, Zhao W, He X, Chen J, Xiao M (2011) Promotion of plant growth and *in situ* degradation of phenol by an engineered *Pseudomonas fluorescens* strain in different contaminated environments. Soil Biol Biochem 43(5):915–922

Yateem A, Balba MT, El-Nawawy AS, Al-Awadhi N (2000) Plants-associated microflora and the remediation of oil-contaminated soil. Int J Phytoremediation 2(3):183–191

Yateem A, Al-Sharrah T, Bin-Haji A (2007) Investigation of microbes in the rhizosphere of selected grasses for rhizoremediation of hydrocarbon-contaminated soils. Soil Sed Contam 16 (3):269–280

Yateem A, Al-Sharrah T, Bin-Haji A (2008) Investigation of microbes in the rhizosphere of selected trees for the rhizoremediation of hydrocarbon-contaminated soils. Int J Phytoremediation 10:311–324

Ying X, Dongmei G, Judong L, Zhenyyu W (2011) Plant-microbe interactions to improve crude oil degradation. Energy Procedia 5:844–848

Yousaf S, Ripka K, Reichenauer TG, Andria V, Afzal M, Sessitsch A (2010) Hydrocarbon degradation and plant colonization by selected bacterial strains isolated from Italian ryegrass and birdsfoot trefoil. J Appl Microbiol 109:1389–1401

Zalesny RS, Bauer EO, Hall RB, Zalesny JA, Kunzman J, Rog CJ, Riemenschneider D (2005) Clonal variation in survival and growth of hybrid poplar and willow in an in situ trial on soils heavily contaminated with petroleum hydrocarbons. Int J Phytoremediation 7:177–197

Zarei M, Wubet T, Schäfer SH, Savaghebi GR, Jouzani GS, Nekouei MK, Buscot F (2010) Molecular diversity of arbuscular mycorrhizal fungi in relation to soil chemical properties and heavy metal contamination. Environ Pollut 158:2757–2765

Zhao S, Arthur EL, Coats JR (2003) The use of native prairie grasses to degrade atrazine and metolachlor in soil. In: Coats JR, Yamamoto H (eds) Environmental fate and effects of pesticides. ACS, Washington, DC, pp 157–167ACS Symposium Series 853

Zhao RB, Bao HY, Liu YX (2010) Isolation and characterization of *Penicillium oxalicum* ZHJ6 for biodegradation of methamidophos. Agric Sci China 9(5):695–703

Zhen-Guo S, Xian-Dong L, Chun-Chun W, Huai-Man C, Hong Ch C (2002) Lead Phytoextraction from contaminated soil with highbiomass plant species. J Environ Qual 31:1893–1900

Zhou QX, Song YF (2004) Principles and methods of contaminated soil remediation. Science Press, Beijing, p 568

Microbes: A Potential Tool for Bioremediation

17

Nilesh Sonune

Abstract

Environmental pollution has become a universal problem because of the fast growth of population, civilization and industrialization. It leads to the accumulation of contaminants in the environment that has an adverse effect on human health and ecosystem. Bioremediation is a most efficient, eco-friendly and cost effective technology for the transformation of contaminates. Culturable microorganisms have been exploited efficiently in biodegradation of contaminants but, inefficient in exploitation of unculturable microorganisms. The successful implementation of technology needs a detailed knowledge of microbial metabolism, growth and function of native microbial population at polluted site. This could be overcome by exploitation of recent innovative tools such as nanobioremediation, biosurfactant, cell immobilization, genetically modified organism, chemotaxis, metagenomics and proteomics. These tools have provided crucial insights of microbial communities and their mechanisms in bioremediation of environmental contaminants. These tools provide important information of microorganism along with their mechanisms for restoration of contaminants. This chapter focuses on the overview of important techniques of bioremediation as well as recent advances used for the bioremediation of environment.

Keywords

Bioaugmentation · Bioremediation · Chemotaxis · Genomics · Nanoremediation

N. Sonune (✉)
Adarsha Science, J.B. Arts and Birla Commerce Mahavidyalaya, Dhamangaon Railway, Maharashtra, India

© The Author(s), under exclusive licence to Springer Nature Singapore Pte Ltd. 2021

V. Kumar et al. (eds.), *Rhizobiont in Bioremediation of Hazardous Waste*,
https://doi.org/10.1007/978-981-16-0602-1_17

17.1 Introduction

In the last couple of decades, due to explosive rise in industrialization, urbanization and human population, the utilization of the natural resources has increased enormously. This has led to high stress on agricultural and industrial production. However, it reults in the production of huge quantity of different organic and inorganic products such as chemicals, pesticides, fertilizers and industrial waste. The release of such waste into the environment, leads to the pollution of the habitats like soil, water and air (Bharagava et al. 2019; Sonune and Garode 2015).

The release of these contaminants can occur either accidentally or because of anthropogenic activities into the environment that ultimately results in environmental pollution, leading to many health hazards. These pollutants or chemicals come into the different food chains from the atmosphere. The chemicals flow occurs from one tropical level to others resulting in bioaccumulation that imparts risks to the ecosystem (Das et al. 2014). Because of these, nature is constantly evolving, posing new difficulties and making consistent requirement to develop new and more suitable technology (Juwarkar et al. 2014).

There is a need of efficient, cheap, long lasting and effective treatment for waste generated in the environment. To meet the challenges, there are several conventional techniques available such as physico-chemical methods to treat these chemicals or waste. Although these methods are not cost effective, unsuccessful to eliminate contaminants completely and the final product is also again lethal. Therefore, development of eco-friendly and cost effective techniques is necessary. Hence, currently, microbial treatment process has become popular and accepted globally which overcome the problems associated with traditional techniques (Sonune and Garode 2018; Kumar et al. 2018).

Nowadays, biotechnology is being considered as emerging science and has tremendous potential of protection and management of the environment. It involves the exploitation of microbes for biological treatment of environmental pollutants (Azadi and Ho 2010; Pandey and Fulekar 2012). Bioremediation is a green technology for the treatment of the harmful chemicals and a popular alternative to traditional methods for degradation of contaminants because it uses natural activities of different types of microbial consortia (Juwarkar et al. 2014).

17.2 Bioremediation

Bioremediation is a process by which living organisms are stimulated to rapidly degrade harmful organic contaminants to environmentally safe levels in the environment (Sasikumar and Papinazath 2003), which may be aquatic, terrestrial or both. In bioremediation mainly microorganisms have been exploited because of their miscellaneous metabolic capacities to transform toxic pollutants to non-toxic compounds through mineralization, carbon dioxide and water production (Singh et al. 2017).

The efficiency of bioremediation needs the presence of precise types of microbes, their proper quantity, combination and suitable environmental conditions.

Microorganisms that are already present at polluted environments are frequently well adapted to live in the presence of existing pollutants, pH, temperature and oxidation/reduction potential of the site (Pandey and Fulekar 2012).

17.3 Microbial Bioremediation

Microbes are extensively scattered in nature because of their diverse metabolism, thrive in a broad range of environmental conditions and versatility in nutrients. Therefore, they can be utilized for bioremediation of contaminants. The basis of the bioremediation is capability of certain microbes to transform and utilize contaminates to acquire energy for their growth (Prakash et al. 2014; Abatenh et al. 2017). Microorganisms are well-known to be the most important agents for bioremediation, which transform and clean up the complex lipophilic organic molecules, to the simple water soluble molecules. The biological agents used for bioremediation are mainly microorganisms includes bacteria, fungi and algae for removal of contaminants from polluted areas (Strong and Burgess 2008; Kumar et al. 2018). When selective microbial population are exposed to the specific or structurally related contaminants, they first attack on this by enzymatic process. These contaminants if present in the environment may act as inducer or repressor for the enzymatic function of microorganisms. Primary or secondary groups of microorganisms typically attacked on these water soluble intermediates and convert them into the inorganic end product by complete degradation. The microorganisms involved in this process may be indigenous or exogenous to polluted location. Polluted substances are altered by metabolic processes of the microorganisms. Generally, multiple microorganisms are involved in biodegradation of a compound (Gupta and Mahapatra 2003).

17.4 Bioremediation Organisms

Bioremediation is the method of eco-friendly waste management that utilizes the inherent ability of microorganisms which includes bacteria, algae and fungi to eliminate or transform the contaminants from the environment (Saxena and Bharagava 2015; Bharagava et al. 2017). Such microbes have potential to obtain energy from almost all compounds by using different electron acceptors in aerobic or anaerobic environment.

17.4.1 Bacteria

Numerous types of bacteria are reported that involved in the transformations or degradation of pollutants includes genera of *Achromobacter, Alcaligenes, Arthrobacter, Acinetobacter, Flavobacterium, Micrococcus, Bacillus, Escherichia, Pseudomonas, Gordonia, Moraxella, Pandoraea, Streptomyces, Rhodococcus,*

Nocardia, Sphingobium, Desulfotomaculum, Azoarcus, Clostridium, Methanospirillum, Sphingomonas, Desulfovibrio, Methanococcus, Geobacter, Methanosaeta, Syntrophobacter, Pelotomaculum, Syntrophus, Xanthomonas, Thauera, etc. (Lopez et al. 2002; Kim et al. 2007; Hasin et al. 2010; Weelink et al. 2010; Liu et al. 2011; Jayashree et al. 2012; Garode and Sonune 2014; Sonune and Garode 2018).

17.4.2 Fungi

Many fungal genera have been isolated and identified for bioremediation of contaminates. These fungal genera include: *Aspergillus, Cladosporium, Mucor, Fusarium, Phanerochaete, Trichoderma, Rhizopus, Penicillium, Agaricus, Pleurotus, Hansenula, Rhodotorula, Coprinellus, Gloeophyllum, Candida, Saccharomyces,* etc. (Tigini et al. 2010; Aranda et al. 2010; Karigar and Rao 2011; Pereira et al. 2014; Safiyanu et al. 2015; Burghal et al. 2016).

17.4.3 Algae

Phycoremediation is application of algae for bioremediation and is effective for removal of contaminants (Wang et al. 2016). Many algal species are involved in bioremediation that includes genera of *Spirulina, Selenastrum, Portieria, Chlorella*, *Agmenellum, Monoraphidium, Chlorococcum, Scenedesmus, Oscillatoria, Caepidium, Chlamydomonas*, *Monoraphidium, Anabaena,* etc. (Terry and Stone 2002; Boshoff et al. 2004; Wang et al. 2011; Newete and Byrne 2016; Bwapwa et al. 2017).

17.5 Methods for Bioremediation

On the basis of transport and removal of contaminants, bioremediation has been categorized into two types- ex situ and in situ bioremediation (Fig. 17.1). Both methods are essentially depending on the metabolism of microorganisms. Among them, in situ method is preferred than ex situ method for bioremediation of polluted site. However, the selection of particular technology is based on many factors such as native microbial population, conditions of site, and quantity, type and toxicity of contaminants present (Jorgensen 2007).

17.5.1 In Situ Bioremediation

In this technique, the treatment of polluted substances is done at the site of pollution. This technique does not require excavation of contaminated materials such as soil and water to achieve the remediation process. In this process, aqueous solution

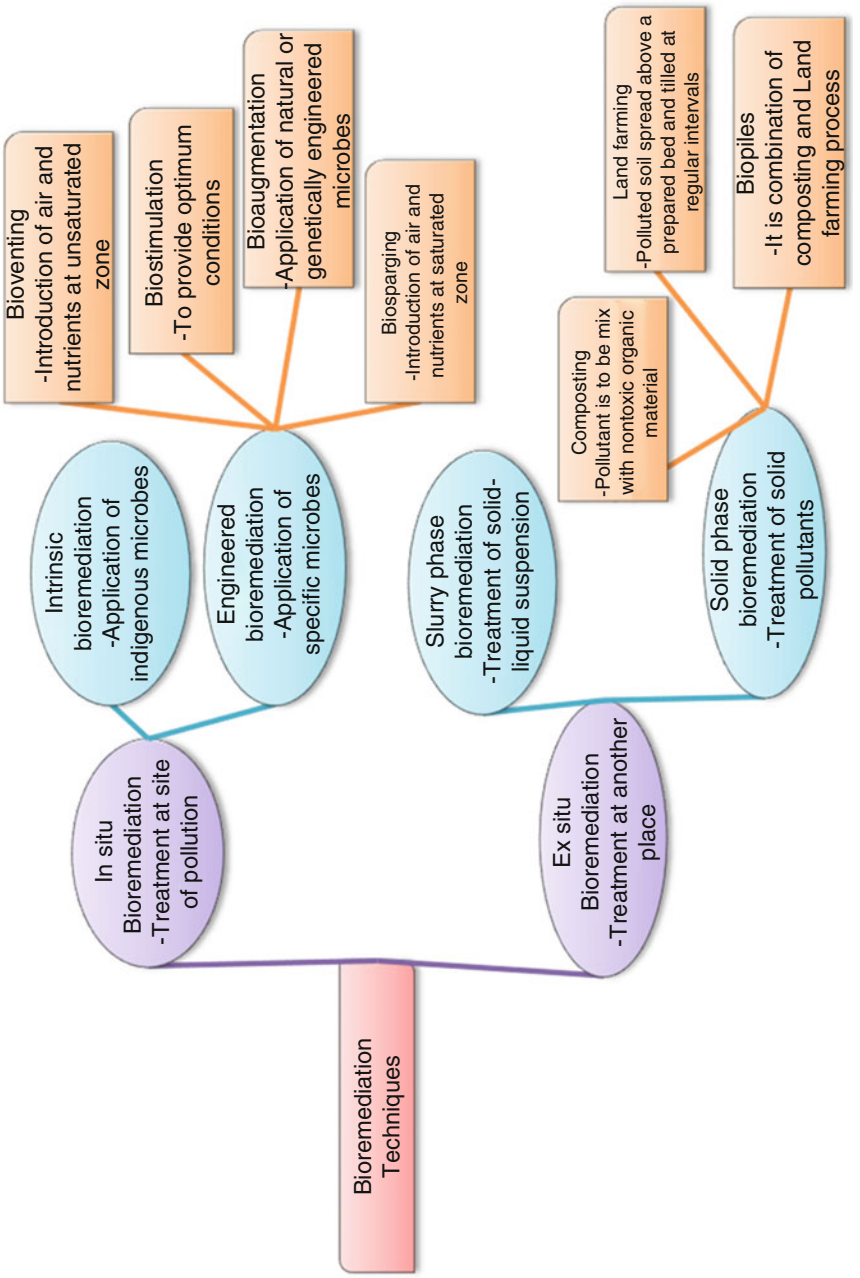


Fig. 17.1 Various bioremediation techniques

containing nutrients and oxygen is circulated through contaminated soil to increase the activity of the indigenous microbial community to degrade toxic organic pollutants (Folch et al. 2013; Frascari et al. 2015). These techniques are less costly compared to the ex situ techniques because extra costs are not needed for the excavation processes. Similarly, it uses native harmless microbial organisms for degradation of pollutants, and has potential to treat large amount of contaminant. Based upon the origin of microorganisms applied, there are two types of in situ bioremediation, i.e. Intrinsic and Engineered bioremediation (Kim et al. 2014; Roy et al. 2015).

17.5.2 Intrinsic In Situ Bioremediation

It is also referred as natural attenuation or bioattenuation. In this method, natural processes are employed to degrade contaminants or to decrease the quantity of contaminants at polluted sites by stimulating the activity of indigenous microorganisms by providing stimulants such as oxygen and nutrients (Philp and Atlas 2005). For the success, intrinsic remediation depends on various factors such as adequate biodegradable microbial population, sufficient nutrients availability and suitable environment at the contaminated site (i.e., pH, oxygen, temperature) and appropriate time for degradation (NRC 2000).

17.5.3 Engineered In Situ Bioremediation

With this approach, bioremediation achieved through the introduction of specific microbes to a polluted site. This approach speed up the degradation of contaminants by providing proper physic-chemical conditions to supports the microbial growth. For this purpose, sufficient quantity of oxygen and nutrients is to be provided to promote microbial growth and enhance the remediation process. Some methods of this approach include biostimulation, bioventing, bioaugmentation and biosparging (Sardrood et al. 2013).

17.5.3.1 Bioventing

This method is one of the most widely recognized *in situ* methods for the bioremediation. In this, air and nutrients are delivered to the unsaturated zone of contaminated soil through wells to stimulate the indigenous microorganisms. This approach provides optimum quantity of oxygen required for the degradation with minimize the volatilization that discharges it into the environment. Bioventing works for hydrocarbon as well as those contaminants which are deep beneath the surface (Vidali 2001; Philp and Atlas 2005).

17.5.3.2 Biostimulation

Biostimulation is another strategy for bioremediation in which native microbial activity in ground water and/or soil is enhanced by adjusting pH, optimum nutrient

and oxygen in order to speed up the bioremediation. This technology is designed mainly for the treatment of groundwater and soil contaminated by fuels, herbicides and pesticides. It needs the presence of native microorganisms which are capable of degradation of particular pollutants (Li and Li 2011; Azad et al. 2014).

17.5.3.3 Bioaugmentation

Bioaugmentation is a process where the natural or genetically engineered microbial culture with potential of transformation or degradation of contaminants is to be added at contaminated environment (Azad et al. 2014). Two factors that limit the use of addition of microbial cultures in a land treatment unit, i.e. competition of non-indigenous microbes with an indigenous microbial population for their survival and the soil which have long-term exposure to the contaminants has native microbes which are highly efficient for degradation (Vidali 2001).

17.5.3.4 Biosparging

Biosparging method is very much related to bioventing where in both air is to be introduced into the soil subsurface for enhancement of microbial activities for remediation of contaminants from sites. However, in bioventing approach, air is introduced at unsaturated zone that causes movement of volatile compounds at upward direction in to the saturated zone to help biodegradation. However, the efficacy of this method depends on pollutant biodegradability and the permeability of the soil. Biosparging has been extensively exploited for the treatment of aquifers polluted with petroleum products (Philp and Atlas 2005; Azubuike et al. 2016).

17.6 Ex Situ Bioremediation

Ex situ method have need to dig polluted materials to assist degradation process. This method has many drawbacks than the advantages. Here, cost can be high as it required for the excavation process of the contaminated samples and its transportation for remediation treatment. Based on the state of the pollutant to be removed for bioremediation, ex situ bioremediation methods are classified into two systems, i.e. slurry phase and solid phase bioremediation (Hashmi et al. 2017).

17.6.1 Slurry Phase Bioremediation

This method includes treatment of the solid-liquid suspensions. It is comparatively fast treatment compared to the other methods. In this method, degradation is accomplished in bioreactor in which polluted soil is combines with the water, native microbes, appropriate nutrients and oxygen to provide optimal condition. After completion of the treatment, the liquid part is separated from the solid and is properly disposed of. The remaining solid wastes material is disposed of or subjected to other processes for further decontamination (Sardrood et al. 2013).

17.6.2 Solid Phase Bioremediation

This method involves treatments of various solid pollutants includes agricultural wastes, industrial wastes, municipal solid wastes and sewage sludge. This process is simple to manage; however, requires more space and time for degradation compare to the slurry phase process. Principle of this process is based on the mechanical breakdown of contaminated soil by abrasion and intensive mixing in an enclosed vessel. This treatment process includes composting, land farming and biopiles techniques (Sardrood et al. 2013).

17.6.2.1 Composting

Composting is an aerobic and the thermophilic surface treatment process used to transform contaminants. In composting, polluted is to be mixed with non-toxic organic amendments, i.e. agricultural waste or manure (Kumar and Singh 2001). This process enhances the development of robust microbial communities that speed up the composting. A composting process occurs at elevated temperatures ranging from 55 to 65 °C. This temperature range achieved as a result of heat production by microbial activity during organic material degradation present in the waste (Vidali 2001).

17.6.2.2 Land Farming

In land farming process, polluted soil is excavated, spread above a prepared bed and tilled at regular intervals up to contaminants are degraded. The main objective of this process is to stimulate indigenous microorganisms that are capable of biodegradation. However, this treatment process limited for uppermost surface of soil generally up to 10–35 cm. This approach received much attention as a disposal option of waste material because of low monitoring and maintenance cost (Margesin and Schinner 1999; Vidali 2001).

17.6.2.3 Biopiles

Biopiles techniques are the combination of composting and land farming bioremediation methods. This method reduces physical losses of the pollutants which take place due to volatilization and leaching (Kastner and Mahro 1996). Biopiles give a favourable environment for native microbes involved in degradation. Generally, this method is a refined version of land farming and applied for treatment of the surface contaminated with petroleum hydrocarbons (Whelan et al. 2015).

17.7 Emerging Approaches in Bioremediation

In recent year, a number of new tools and techniques are developed that overcome some of the limitations of traditional processes and helps to speed up the process, improve reliability, cost efficiency of bioremediation (Fig. 17.2). A brief overview of such important processes involved is discussed as follow:

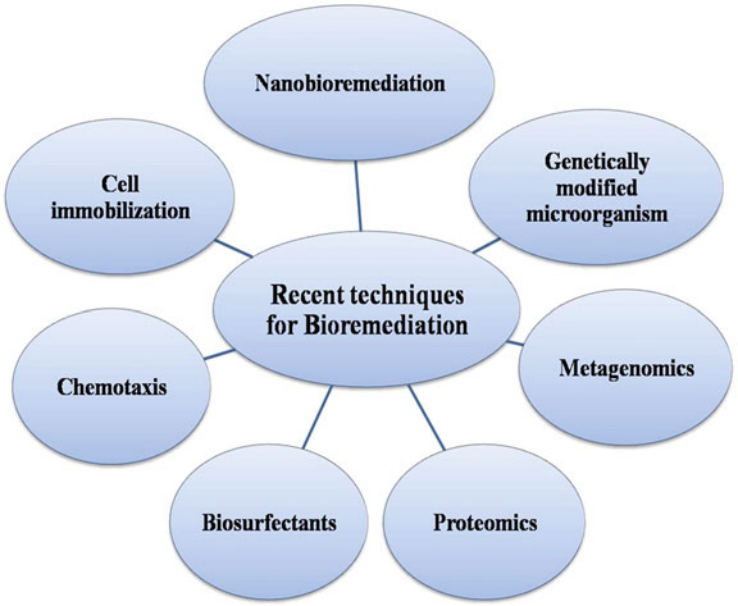


Fig. 17.2 Recent bioremediation techniques

17.7.1 Biosurfactants

Biosurfactants are surface active molecules produced by living cells particularly microorganisms. Application of biosurfactants is an excellent option to enhance the bioremediation of contaminated site that would enhance the effectiveness of efficient microorganisms for bioremediation potential. The availability of targeted pollutants to degradative microbes is one of the major problems in the bioremediation process because of the hydrophobic nature of the contaminants. This problem can be overcome with the help of biosurfactants that facilitate direct contact between contaminants and the microbes (Banat et al. 2000). Biosurfactants reduce the hydrophobic nature of pollutants and make it readily accessible to the microorganism for their degradation. Microbial surfactants are non-toxic, biodegradable, non-hazardous and cheap, and cost effective, hence they have been using for bioremediation (Ron and Rosenberg 2002). The most common biosurfactants are glycolipids, lipoproteins, lipopeptides and heteropolysaccharides (Dua et al. 2002). The application of biosurfactants has been progressively rising in recent year because of their environment friendly nature, selectivity, diversity, production in large scale and performance under extreme conditions (Banat et al. 2000). Use of the biosufactants is mainly involved in the bioremediation of hydrocarbons and heavy metals contaminated sites, to enhance oil recovery, management of oil spill and oil recovery from the sludge (Dua et al. 2002). Considerable studies were done on the biosurfactant production by a variety of microbial strains (Chen et al. 2011; Imura et al. 2014; Anaukwu et al. 2015; Kuyukina et al. 2015).

17.7.2 Cell Immobilization

In recent times, applications of cell immobilization methods in bioremediation of contaminants are increased significantly. Immobilization means restricting the movement of microorganisms or their enzymes without disturbing their catalytic functions and viability (Guzik et al. 2014; Kourkoutas et al. 2004; Dzionek et al. 2016). Immobilization process has many benefits in bioremediation process like multiple use of biocatalysts, reduced costs as reuse of cells, higher efficiency of pollutant degradation, resistance to the shear forces in bioreactors and other adverse environmental conditions, reduced risk of genetic mutations and increased tolerance to high pollutant concentrations (Rivelli et al. 2013; Bayat et al. 2015). For microbial cells immobilization, carriers are essential for surface binding. The carriers used may be rather organic or inorganic in nature. Carrier selection is important aspects in bioremediation as on its surface microbes is to be attached. In immobilization, total five techniques are there. However, adsorption is the most frequent method employed in bioremediation because of the simplicity. Considerable work has been done on microbial cell immobilization (Angelim et al. 2013; Bhatnagar et al. 2015; Dzionek et al. 2016).

17.7.3 Nanobioremediation

Application of nanoparticle for bioremediation of contaminated sites is also known as nanobioremediation. Nanotechnology is a recent and promising branch of science that attracted the attention of researchers interested in different subjects because of its small size and efficient outcomes towards issues such as environmental pollution. Nanobioremediation involves the use of nanomaterials for the treatment of contaminants either by using in situ or ex situ method. In the recent year, nanotechnology has significantly contributed in bioremediation of the pollutants from soil, water and air into non-toxic and eco-friendly compounds. Along with bioremediation, it also plays important role in pollution monitoring, detection and prevention (Rajan 2011; Carata et al. 2017). Various types of microorganisms such as bacteria, actinomycetes, fungi and algae are used for biological synthesis of metal nanoparticles. Various types of metals have been used for the preparation of biological nanoparticles for bioremediation includes nickel, iron, silver, gold and palladium (Thome et al. 2015). The role of nanoparticles in bioremediation is to sequester or degrade pollutants like the herbicides, pesticides, insecticides and heavy metals from contaminated atmosphere (Sakulchaicharoen et al. 2010). It is cost effective and potential technique for bioremediation. It facilitates chemical reduction as well as catalysis to mitigate the contaminants of the concern. Because of their innovative surface coatings and tiny size, they are capable to permeate the subsurface in very small spaces and stay suspended in the groundwater. This allows them to move fast than large sized particles and achieve wider distribution (Kanatzidis and Poeppelmeier 2007).

17.7.4 Genetic Engineered Microorganisms

Degradation of xenobiotic compounds remains a serious issue of environmental pollution. In recent years, the interests have been increased on bioremediation of such compounds. The common use and lack of biodegradation of xenobiotic compounds leads to their widespread occurrence and persistence in the environment. Investigations on the microbial biodegradation pathways on these compounds shown that recalcitrance is a factor that causes biochemical blockage which result in dysfunctional catabolic routes. This factor has raised interest to construct genetically engineered microorganisms with superior catabolic activities (Janssen and Stucki 2020). Genetic engineering technologies have been used on many occasions to improve the rate of biodegradation of particularly recalcitrant organic pollutants. The exploitation of genetically engineered microorganisms for restoration purpose is cost effective and eco-friendly method for removal of pollutants in contaminated sites (Panz and Miksch 2012). To remediate heavy metals from polluted sites is difficult by natural bacteria, however, this can be overcome by the use of genetically engineered bacteria. For the remediation of different types of heavy metals like Ni, Hg, Cd, Cu, Fe and As, genetically engineered microbes have been used (Bruschi and Goulhen 2006). Several kinds of genetically engineered microorganisms have been developed through recombinant technologies and applied for remediation of sites polluted with heavy metals and other toxic materials (Azad et al. 2014). Some studies reported remediation of metals and recalcitrant chlorinated chemicals from different polluted sites by different microorganisms (Murtaza et al. 2002; Furukawa 2003; Cases and de Lorenzo 2005; Bondarenko et al. 2008; Gong et al. 2017).

17.7.5 Chemotaxis

Chemotaxis is an important feature of some motile microorganisms. It is a movement of microbes under the influence of the chemical. This movement helps them to search the most favourable environment for their survival and growth (Ford and Harvey 2007). It has been observed that chemotaxis is a selective advantage for bacteria to sense and locate the environmental contaminants. Chemotaxis has the ability to significantly improve in situ bioremediation processes (Paul et al. 2006). Though, this feature has not received much attention, even though certain microorganisms have capability of chemotatic movement towards various xenobiotic compounds (Bhushan et al. 2000). Some reports are available on the isolation and characterization of chemotactic microorganisms towards various xenobiotic compounds (Parales and Harwood 2002). In several cases, chemoattractant is a compound that serves as a source of carbon and energy, whereas chemorepellent is toxic to bacteria. Recently, number of microbes with chemotactic activity towards diverse environmental contaminants have been reported (Pandey and Jain 2002; Parales and Harwood 2002; Ford and Harvey 2007). The several studies reported direct or indirect correlation between chemotaxis and bioremediation of

contaminated ground water and soil (Samanta et al. 2000; Parales and Harwood 2002; Bhushan et al. 2000).

17.7.6 Metagenomics

Metagenomics is the study of metagenome which recovered directly from the environmental samples. It is an emerging approach which can be used for the characterization of microbial population, gives detail information of the genomes of uncultured microorganisms and degradation of contaminants at the contaminated site (Uhlik et al. 2013; Bharagava et al. 2019). This approach is helpful to find out the efficient microbes for degradation of a particular contaminants or catabolic gene that is responsible for degradation or detoxification of the particular contaminants. The accessibility of entire genome sequences from many environmental microbes is an important step for bioremediation. This technique is valuable in assessing the gene pool of the enzymes which involved in pollutants the degradation (Galvao et al. 2005; Desai et al. 2010). In recent years, methods focused on metagenomics have been useful in evaluating novel gene families as well as microorganisms involved in remediation of xenobiotic compounds. Nowadays, DNA microarray has been used to track microbial communities, to characterize contaminants, biodegrading microorganisms and to identify novel pathway for biodegradation (Bae and Park 2006). The construction and screening of metagenomic libraries for identification of genes involved in bioremediation has been documented in several studies (Jennings et al. 2009; Wang et al. 2012; Ma et al. 2015; Sul et al. 2016; Hong et al. 2017).

17.7.7 Proteomics

Investigation of proteins, termed as proteomics, is recently being used as a technique in bioremediation. It involved identification and quantification of proteins of the microorganisms (Aslam et al. 2017). Expression of proteins in the microorganisms depends on the various environmental conditions which are responsible for their adaption as well as physiological changes. Proteomics approach is helpful for the examination of protein components and detection of key proteins that are involved in the physiological state of the microorganism in the presence of particular contaminants. Because of the proteomics approach, novel pathway for biodegradation of contaminants are uncovered that provides an idea for detection of novel proteins (Santos et al. 2004; Kim et al. 2006).

17.8 Conclusion

Bioremediation is one of the green, eco-friendly and inexpensive technology for degradation or removal of toxic contaminates from the environment. Various approaches of bioremediation efficiently involved in the removal of contaminants,

however, certain factors such as recalcitrant and high toxicity of contaminates remain a challenge for this approaches. This can be overcome by implementing the recent tools and techniques. Recent tools help for bioremediation by many ways such as selection of microorganism with suitable traits for degradation of particular compound, provide detail information of the genomes of uncultured microbes, type of condition at contaminated sites and uncovered new pathway for biodegradation of toxic wastes.

References

Abatenh E, Gizaw B, Tsegaye Z, Wassie M (2017) The role of microorganisms in bioremediation—a review. Open J Environ Biol 1:38–46

Anaukwu CG, Ekwealor AI, Ezemba CC, Anakwenze VN, Okafor UC, Archibong EJ (2015) Pseudomonas monteilii and Citrobacter murliniae, biosurfactant-producing bacteria isolated from Nigerian soil. Br Microbiol Res J 10:1–9

Angelim AL, Costa SP, Farias BCS, Aquino LF, Melo VMM (2013) An innovative bioremediation strategy using a bacterial consortium entrapped in chitosan beads. J Environ Manage 127:10–17

Aranda E, Ullrich R, Hofrichter M (2010) Conversion of polycyclic aromatic hydrocarbons, methyl naphthalenes and dibenzofuran by two fungal peroxygenases. Biodegradation 21:267–281

Aslam B, Basit M, Nisar MA, Khurshid M, Rasool MH (2017) Proteomics: technologies and their applications. J Chromatogr Sci 55:182–196

Azad MAK, Amin L, Sidik NM (2014) Genetically engineered organisms for bioremediation of pollutants in contaminated sites. Chin Sci Bull 59:703–714

Azadi H, Ho P (2010) Genetically modified and organic crops in developing countries: a review of options for food security. Biotechnol Adv 28:160–168

Azubuike CC, Chikere CB, Okpokwasili GC (2016) Bioremediation techniques-classification based on site of application: principles, advantages, limitations and prospects. World J Microbiol Biotechnol 32:180

Bae JW, Park YH (2006) Homogeneous versus heterogeneous probes for microbial ecological microarrays. Trends Biotechnol 24:318–323

Banat IM, Makkar RS, Cameotra SS (2000) Potential commercial applications of microbial surfactants. Appl Microbiol Biotechnol 53:495–508

Bayat Z, Hassanshahian M, Cappello S (2015) Immobilization of microbes for bioremediation of crude oil polluted environments: a mini review. Open Microbiol J 9:48–54

Bharagava RN, Chowdhary P, Saxena G (2017) Bioremediation, an ecosustainable green technology: its applications and limitations. In: Bharagava RN (ed) Environmental pollutants and their bioremediation approaches. CRC Press, Taylor & Francis Group, Boca Raton, pp 1–22

Bharagava RN, Purchase D, Saxena G, Sikandar IM (2019) Applications of metagenomics in microbial bioremediation of pollutants: from genomics to environmental cleanup. In: Das S, Dash HR (eds) Microbial diversity in the genomic era. Elsevier/Academic Press, Oxford, pp 459–477

Bhatnagar Y, Singh GB, Mathur A, Srivastava S, Gupta S, Gupta N (2015) Biodegradation of carbazole by Pseudomonas sp. GBS. 5 immobilized in polyvinyl alcohol beads. J Biochem Technol 6:1003–1007

Bhushan B, Samanta SK, Chauhan A, Chakraborti AK, Jain RK (2000) Chemotaxis and biodegradation of 3-methyl- 4-nitrophenol by Ralstonia sp. SJ98. Biochem Biophys Res Commun 275:129–133

Bondarenko O, Rolova T, Kahru A, Ivask A (2008) Bioavailability of Cd, Zn and Hg in soil to nine recombinant luminescent metal sensor bacteria. Sensors 8:6899–6923

Boshoff G, Duncan J, Rose PD (2004) The use of micro-algal biomass as a carbon source for biological sulphate reducing systems. Water Res 38:2659–2666

Bruschi M, Goulhen F (2006) New bioremediation technologies to remove heavy metals and radionuclides using Fe(III)-sulfate and sulfur reducing bacteria. In: Singh SN, Tripathi RD (eds) Environmental bioremediation technologies. Springer, New York, pp 35–55

Burghal AA, Abu-Mejdad NMJA, Tamimi WHA (2016) Mycodegradation of crude oil by fungal species isolated from petroleum contaminated soil. Int J Innovat Res Sci Eng Technol 5:1517–1524

Bwapwa JK, Jaiyeola AT, Chetty R (2017) Bioremediation of acid mine drainage using algae strains: a review. South African J Chem Eng 24:62–70

Carata E, Panzarini E, Dini L (2017) Environmental nanoremediation and electron microscopies. In: Nanotechnologies for environmental remediation. Springer, Cham, pp 115–150

Cases I, de Lorenzo V (2005) Genetically modified organisms for the environment: stories of success and failure and what we have learned from them. Int Microbiol 8:213–222

Chen S, Yang L, Hu M, Liu J (2011) Biodegradation of fenvalerate and 3-phenoxybenzoic acid by a novel *Stenotrophomonas* sp. strain ZS-S-01 and its use in bioremediation of contaminated soils. Appl Microbiol Biotechnol 90:755–767

Das S, Raj R, Mangwani N, Dash HR, Chakraborty J (2014) Heavy metals and hydrocarbons: adverse effects and mechanism of toxicity. In: Das S (ed) Microbial biodegradation and bioremediation. Elsevier, Amsterdam, pp 23–54

Desai C, Pathak H, Madamwar D (2010) Advances in molecular and "-omics" technologies to gauge microbial communities and bioremediation at xenobiotic/anthropogen contaminated sites. Bioresour Technol 101:1558–1569

Dua M, Singh A, Sethunathan N, Johri A (2002) Biotechnology and bioremediation: successes and limitations. Appl Microbiol Biotechnol 59:143–152

Dzionek A, Wojcieszynska D, Guzik U (2016) Natural carriers in bioremediation: a review. Electron J Biotechnol 23:28–36. https://doi.org/10.1016/j.ejbt.2016.07.003

Folch A, Vilaplana M, Amado L, Vicent R, Caminal G (2013) Fungal permeable reactive barrier to remediate groundwater in an artificial aquifer. J Hazard Mater 262:554–560

Ford RM, Harvey RW (2007) Role of chemotaxis in the transport of bacteria through saturated porous media. Adv Water Resour 30:1608–1617

Frascari D, Zanaroli G, Danko AS (2015) In situ aerobic cometabolism of chlorinated solvents: a review. J Hazard Mater 283:382–399

Furukawa K (2003) Super bugs for bioremediation. Trends Biotechnol 21:187–190

Galvao TC, Mohn WW, Lorenzo V (2005) Exploring the microbial biodegradation and biotransformation gene pool. Trends Biotechnol 23:497–506

Garode AM, Sonune NA (2014) Screening and identification of lipase producing bacteria from domestic wastewater. Int J Pharm Bio Sci 5:265–268

Gong T, Xu X, Che Y, Liu R, Gao W, Zhao F, Yu H, Liang J, Xu P, Song C, Yang C (2017) Combinatorial metabolic engineering of *Pseudomonas putida* KT2440 for efficient mineralization of 1,2,3-trichloropropane. Sci Rep 7:7064

Gupta R, Mahapatra H (2003) Microbial biomass: an economical alternative for removal of heavy metals from waste water. Indian J Exp Biol 41:945–966

Guzik U, Hupert-Kocurek K, Krysiak M, Wojcieszyńska D (2014) Degradation potential of protocatechuate 3,4-dioxygenase from crude extract of *Stenotrophomonas maltophilia* strain KB2 immobilized in calcium alginate hydrogels and on glyoxyl agarose. Biomed Res Int 2014:138768

Hashmi MZ, Kumar V, Verma A (2017) Xenobiotics in the soil environment: monitoring. In: Toxicity and management. Springer, Cham. https://doi.org/10.1007/978-3-319-47744-2

Hasin AA, Gurman SJ, Murphy LM, Perry A, Smith TJ, Gardiner PH (2010) Remediation of chromium (VI) by a methane-oxidizing bacterium. Environ Sci Technol 44:400–405

Hong YH, Ye CC, Zhou QZ, Wu XY, Yuan JP, Peng J, Deng H, Wang JH (2017) Genome sequencing reveals the potential of *Achromobacter* sp. HZ01 for bioremediation. Front Microbiol 8:1507

Imura T, Morita T, Fukuoka T, Ryu M, Igarashi K, Hirata Y, Kitamoto D (2014) Spontaneous vesicle formation from sodium salt of acidic sophorolipid and its application as a skin penetration enhancer. J Oleo Sci 63:141–147

Janssen DB, Stucki G (2020) Perspectives of genetically engineered microbes for groundwater bioremediation. Environ Sci Process Impacts 22:487–499

Jayashree R, Nithya SE, Rajesh PP, Krishnaraju M (2012) Biodegradation capability of bacterial species isolated from oil contaminated soil. J Academia Indust Res 1:127–135

Jennings LK, Chartrand MM, Lacrampe-Couloume G, Lollar BS, Spain JC, Gossett JM (2009) Proteomic and transcriptomic analyses reveal genes upregulated by cis-dichloroethene in *Polaromonas* JS666. Appl Environ Microbiol 11:3733–3744

Jorgensen KS (2007) In situ bioremediation. Adv Appl Microbiol 61:285–305

Juwarkar AA, Misra RR, Sharma JK (2014) Recent trends in bioremediation. In: Geomicrobiology and biogeochemistry. Springer, Berlin, Heidelberg, pp 81–100

Kanatzidis MG, Poeppelmeier KR (2007) Report from the third workshop on future directions of solid-state chemistry: the status of solid-state chemistry and its impact in the physical sciences. Prog Solid State Chem 36:1–133

Karigar CS, Rao SS (2011) Role of microbial enzymes in the bioremediation of pollutants: a review. Enzyme Res 1:1–11

Kastner M, Mahro B (1996) Microbial degradation of polycyclic aromatic hydrocarbons in soils affected by the organic matrix of compost. Appl Microbiol Biotechnol 44:668–675

Kim YH, Cho K, Yun SH, Kim JY, Kwon KH, Yoo JS, Kim SI (2006) Analysis of aromatic catabolic pathways in pseudomonas putida KT 2440 using a combined proteomic approach: 2DE/MS and cleavable isotope-coded affinity tag analysis. Proteomics 6:1301–1318

Kim SU, Cheong YH, Seo DC, Hu JS, Heo JS, Cho JS (2007) Characterization of heavy metal tolerance and biosorption capacity of bacterium strains CPB4 (*Bacillus* Sp.). Water Sci Technol 55:105–111

Kim S, Krajmalnik-Brown R, Kim JO, Chung J (2014) Remediation of petroleum hydrocarbon-contaminated sites by DNA diagnosis-based bioslurping technology. Sci Total Environ 497:250–259

Kourkoutas Y, Bekatorou A, Banat IM, Marchant R, Koutinas AA (2004) Immobilization technologies and support materials suitable in alcohol beverages production: a review. Food Microbiol 21:377–397

Kumar V, Singh KP (2001) Enriching vermicompost by nitrogen fixing and phosphate solubilizing bacteria. Bioresour Technol 76:173–175

Kumar V, Kumar M, Prasad R (2018) Microbial action on hydrocarbons. Springer, Singapore

Kuyukina MS, Ivshina IB, Baeva TA, Kochina OA, Gein SV, Chereshnev VA (2015) Trehalolipid biosurfactants from nonpathogenic *Rhodococcus actinobacteria* with diverse immunomodulatory activities. N Biotechnol 32:559–568

Li Y, Li B (2011) Study on fungi–bacteria consortium bioremediation of petroleum contaminated mangrove sediments amended with mixed biosurfactants. Adv Mat Res 183:1163–1167

Liu S, Zhang F, Chen J, Guo-Xin S (2011) Arsenic removal from contaminated soil via biovolatilization by genetically engineered bacteria under laboratory conditions. J Environ Sci 23:1544–1550

Lopez A, Lazaro N, Morales S, Marques A (2002) Nickel biosorption by free and immobilized cells of Pseudomonas fluorescens 4F39: a comparative study. Water Air Soil Pollut 135:157–172

Ma Q, Qu Y, Shen W, Zhang Z, Wang J, Liu Z, Li D, Li H, Zhou J (2015) Bacterial community compositions of coking wastewater treatment plants in steel industry revealed by Illumina high-throughput sequencing. Bioresour Technol 179:436–443

Margesin R, Schinner F (1999) Biological decontamination of oil spills in cold environments. J Chem Technol Biotechnol 74:381–389

Murtaza I, Dutt A, Ali A (2002) Biomolecular engineering of Escherichia coli organomercurial lyase gene and its expression. Indian J Biotechnol 1:117–120
Newete SW, Byrne MJ (2016) The capacity of aquatic macrophytes for phytoremediation and their disposal with specific reference to water hyacinth. Environ Sci Pollut Res 23:10630–10643
NRC (2000) Natural attenuation for groundwater remediation, committee on intrinsic remediation. National Academy Press, Washington, DC, p 2000
Pandey B, Fulekar MH (2012) Bioremediation technology: a new horizon for environmental clean-up. Biol Med 4:51–59
Pandey G, Jain RK (2002) Bacterial chemotaxis toward environmental pollutants: role in bioremediation. Appl Environ Microbiol 68:5789–5795
Panz K, Miksch K (2012) Phytoremediation of explosive (TNT, RDX, HMX) by wild-type and transgenic plants. J Environ Manage 113:85–92
Parales RE, Harwood CS (2002) Bacterial chemotaxis to pollutants and plant-derived aromatic molecules. Curr Opin Microbiol 5:266–273
Paul D, Singh R, Jain RK (2006) Chemotaxis of Ralstonia sp. SJ98 towards p-nitrophenol in soil. Environ Microbiol 8:1797–1804
Pereira P, Enguita FJ, Ferreira J, Leitao AL (2014) DNA damage induced by hydroquinone can be prevented by fungal detoxification. Toxicol Rep 1:1096–1105
Philp JC, Atlas RM (2005) Bioremediation of contaminated soils and aquifers. In: Atlas RM, Philp JC (eds) Bioremediation: applied microbial solutions for real-world environmental clean-up. American Society for Microbiology Press, Washington, pp 139–236
Prakash A, Bisht S, Singh J, Teotia P, Kela R, Kumar V (2014) Biodegradation potential of petroleum hydrocarbons (PHCs) by bacteria and mixed bacterial consortium isolated from contaminated sites. Turkish J Eng Env Sci 38(1):31–40
Rajan S (2011) Nanotechnology in groundwater remediation. Int J Environ Sci Dev 2:182–187
Rivelli V, Franzetti A, Gandolfi I, Cordoni S, Bestetti G (2013) Persistence and degrading activity of free and immobilised allochthonous bacteria during bioremediation of hydrocarbon-contaminated soils. Biodegradation 24:1–11
Ron EZ, Rosenberg E (2002) Biosurfactants and oil bioremediation. Curr Opin Biotechnol 13:249–252
Roy M, Giri AK, Dutta S, Mukherjee P (2015) Integrated phytobial remediation for sustainable management of arsenic in soil and water. Environ Int 75:180–198
Safiyanu I, Abdulwahid Isah A, Abubakar US, Rita Singh M (2015) Review on comparative study on bioremediation for oil spills using microbes. Res J Pharma Biol Chem Sci 6:783–790
Sakulchaicharoen N, O'Carroll DM, Herrera JE (2010) Enhanced stability and dechlorination activity of pre-synthesis stabilized nanoscale FePd particles. J Contam Hydrol 118:117–127
Samanta SK, Bhushan B, Chauhan A, Jain RK (2000) Chemotaxis of a *Ralstonia* sp. SJ98 toward different nitroaromatic compounds and their degradation. Biochem Biophys Res Commun 269:117–123
Santos PM, Benndorf D, Sa-Correia I (2004) Insights into Pseudomonas putida KT2440 response to phenol-induced stress by quantitative proteomics. Proteomics 4:2640–2652
Sardrood BP, Goltapeh EM, Varma A (2013) An introduction to bioremediation. In: Goltapeh E, Danesh Y, Varma A (eds) Fungi as bioremediators. Soil biology, vol 32. Springer, Berlin, Heidelberg
Sasikumar CS, Papinazath T (2003) Environmental management: bioremediation of polluted environment. In: Bunch MJ, Suresh VM, Kumaran TV (eds) Proceedings of the third international conference on environment and health. University of Madras and Faculty of Environmental Studies, York University, Chennai, pp 465–469
Saxena G, Bharagava RN (2015) Persistent organic pollutants and bacterial communities present during the treatment of tannery wastewater. In: Chandra R (ed) Environmental waste management. CRC Press, Taylor and Francis Group, Boca Raton, pp 217–247

Singh P, Jain R, Srivastava N, Borthakur A, Pal DB, Singh R, Madhav S, Srivastava P, Tiwary D, Mishra PK (2017) Current and emerging trends in bioremediation of petrochemical waste: a review. Crit Rev Environ Sci Technol 47:155–201

Sonune NA, Garode AM (2015) Bioremediation potential of bacterial isolates for muncipal wastewater treatment. Curr World Environ 10:619–625

Sonune N, Garode A (2018) Isolation, characterization and identification of extracellular enzyme producer *Bacillus licheniformis* from municipal wastewater and evaluation of their biodegradability. Biotechnol Res Innov 2:37–44

Strong PJ, Burgess JE (2008) Treatment methods for wine-related ad distillery wastewaters: a review. Biorem J 12:70–87

Sul WJ, Kim IS, Ekpeghere KI, Song B, Kim BS, Kim HG, Kim JT, Koh SC (2016) Metagenomic insight of nitrogen metabolism in a tannery wastewater treatment plant bioaugmented with the microbial consortium BM-S-1. J Environ Sci Health, Part A: Tox Hazard Subst Environ Eng 51:1164–1172

Terry PA, Stone W (2002) Biosorption of cadmium and copper contaminated water by Scenedesmus abundans. Chemosphere 47:249–255

Thome A, Reddy KR, Reginatto C, Cecchin I (2015) Review of nanotechnology forsoil and groundwater remediation: Brazilian perspectives. Water Air Soil Pollut 226:1–20

Tigini V, Prigione V, Giansanti P, Mangiavillano A, Pannocchia A, Varese GC (2010) Fungal biosorption, an innovative treatment for the decolourisation and detoxification of textile effluents. Water 2:550–565

Uhlik O, Leewis MC, Strejcek M, Musilova L, Mackova M, Leigh MB, Macek T (2013) Stable isotope probing in the metagenomics era: a bridge towards improved bioremediation. Biotechnol Adv 31:154–165

Vidali M (2001) Bioremediation: an overview. Pure Appl Chem 73(7):1163–1172

Wang Q, Zhang S, Li Y, Klassen W (2011) Potential approaches to improving biodegradation of hydrocarbons for bioremediation of crude oil pollution. J Environ Protection 2:47–55

Wang X, Hu M, Xia Y, Wen X, Ding K (2012) Pyrosequencing analysis of bacterial diversity in 14 wastewater treatment systems in China. Appl Environ Microbiol 78:7042–7047

Wang Y, Ho SH, Cheng CL, Guo WQ, Nagarajan D, Ren NQ, Lee DJ, Chang JS (2016) Perspectives on the feasibility of using microalgae for industrial wastewater treatment. Bioresour Technol 222:485–497

Weelink SAB, van Eekert MHA, Stams AJM (2010) Degradation of BTEX by anaerobic bacteria: physiology and application. Rev Environ Sci Biotechnol 9:359–385

Whelan MJ, Coulon F, Hince G, Rayner J, McWatters R, Spedding T, Snape I (2015) Fate and transport of petroleum hydrocarbons in engineered biopiles in polar regions. Chemosphere 131:232–240

Physical, Chemical, and Biological Remediation Techniques for Textile Effluents in Context with Developed and Developing Countries

18

Anum Mahmood, Barira Bilal, Zainab Naeem, and Shazia Iram

Abstract

There is an immense increase in the demand of colorful, sophisticated, and versatile garments produced by textile industry. Previously dyes were obtained from the natural sources but the quantity generated was very low and the color produced was not steady. In the present world natural dyes are widely replaced by synthetic dyes because of their stability, brightness, and cost effectiveness. Like every man-made product, synthetic dyes have their own set of disadvantages. Most prominently the dyes having chromophore groups are persistent, carcinogenic, and toxic to the aquatic environment in which they are released. This chapter focusses on the techniques adopted by developing and developed nations for the remediation of textile dyes. In a broader perspective these practices are divided into physical, chemical, and biological remediation techniques. Pros and cons of each method are discussed along with the recent developments in each method. To overcome the harsh effects of textile dyes effluent on the ecosystem,it is highly recommended to develop a combined approach that has benefit from all the remediation techniques.

Keywords

Biological remediation · Microbes · Mechanism · Textile effluents

A. Mahmood · B. Bilal · Z. Naeem · S. Iram (✉)
Department of Environmental Sciences, Fatima Jinnah Women University, Rawalpindi, Pakistan

© The Author(s), under exclusive licence to Springer Nature Singapore Pte Ltd. 2021

V. Kumar et al. (eds.), *Rhizobiont in Bioremediation of Hazardous Waste*,
https://doi.org/10.1007/978-981-16-0602-1_18

18.1 Introduction

Natural dyes are harnessed from the plants, insects, and shells of fish but provide a very short range of colors. The extract from all the natural sources was very limited thus making it highly expensive and short lived. The hard work for the development of such a dye that is long lasting and cost effective results in the formation of highly stable and inert organic structures now commonly known as textile dyes (Ziarani et al. 2018). The excessive usage of synthetic colors was noticed in the mid of the previous century. These dyes were designed to be resistant to color fading, UV radiations, chemical and biological degradation (Shahid et al. 2013). Synthetic dyes are not only toxic but if released as it is in the aquatic environment are potent to produce such by-products that can lead to the eutrophication and decrease sunlight penetration (Ahmed et al. 2018). The fabric industry is responsible for the most toxic effluent discharge as compared to rest of the production sectors due to high chemical oxygen demand, resistant dyes, raised pH, and low biodegradability (O'Neill et al. 1999; Vilaseca et al. 2010). The textile effluent poses serious threat to environment due to their complex mixture of various organic, inorganic, elemental, and polymeric pollutant substances (Choi et al. 2004). They have major environmental implication because 50% of initial dye used for coloring process remain in consumed bath as hydrolyzed entity which cannot be used again for dyeing the fabric (Laszlo 1995). Excessive employment of chemicals with in the textile processes leads to the release of huge amount of toxic effluents in fresh water resources. The major fraction of textile wastewater encompasses cancer causing dyes, noxious heavy metals, bleaching agents, and other such chemicals with sediments dissolved solids (Correia et al. 1994). The improper disposal of highly colored and toxic effluent when discharged into freshwater bodies stops re-oxygenation capacity and blocks sunlight that causes disturbance in the aquatic ecosystem (Nassar and Magdy 1997). Dyes having aromatic rings are known carcinogen. The presence of toxic aromatic compounds and their degraded forms in aqueous medium leads to severe ailments in humans' that resulted into irreversible impairment of various vital organs such as kidneys, liver, and all body systems (Ramachandran et al. 2013).

As the need of the hour many techniques have been developed and practiced by both developing and developed nations. These techniques can broadly be distinguished into physical, chemical, and biological remediation techniques. Physical as name suggests deals with the removal of pollutants without any permanent change, chemical involves use of chemical moieties that can undergo certain reactions for detoxification, whereas biological includes employment of living organisms (both plants and microorganisms) for the pollutant's removal from waste water.

18.2 Types of Textile Dyes

Dyes retain pigment because they absorb light in the range of 400–700 nm. All of them holds at minimum one chromophore group (Uday et al. 2016). Many dyes along with chromophores possess *auxochromes*. These are color helpers and can be

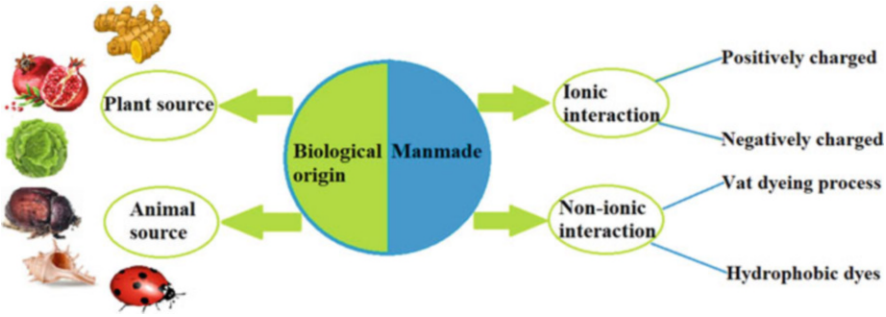


Fig. 18.1 General classification of dyes

composed of various acids (carboxylic, sulfonic) and polar groups (amino, hydroxyl) (IARC Working Group on the Evaluation of Carcinogenic Risk to Humans 2010). They do not impart any color but crucial for the dye solubility (Abrahart 1977).

There are two main categories of dyes, i.e. ionic and nonionic dyes (Ahmed et al. 2018). The ionic dyes can be alienated into cationic (positively charged) and anionic (negatively charged) dyes. The cationic dyes can further be classified as basic dyes (e.g. Basic Brown 1). Basic dyes form a cationic salt in water and are powerful coloring agents for acrylic fibers (Gupta and Suhas 2009). Anionic dyes can be classified into acidic (e.g. Acid yellow 36), reactive (e.g. reactive blue 5), and direct (e.g. Direct orange 26) dyes (Fig. 18.1). Dyes that are acidic have greater water solubility and are employed for dying the natural and synthetic fabric (Axelsson et al. 2006). Reactive dyes are most preferable in fabric business as they own high color intensity and reactivity towards cellulose (Khataee et al. 2013). Direct dyes are not readily dried up fast and are more specifically required for the dying of protein fibers (Royer and Cardoso 2009). Nonionic dyes are segregated into vat (e.g. Vat Blue 4) are insoluble in water used for coloring cellulosic fibers (Gutowska et al. 2006). Disperse dyes such as Red 4 is used for dyeing the polyster, nylon, cellulose and acrylic fibers (Tan et al. 2008).

18.3 Physical Remediation Techniques for Textile Effluents

Textile industry is a complex and labor intensive sector which is also a backbone of South Asian economies. This sector is a source of profit but at the cost of environmental degradation. Following section discuss some of the physical remediation methods which are being practiced by major textile producers of South Asia.

18.3.1 China

In South Asia, China is the principal exporter of yard goods and dyes and also the Chinese silk is in high demand globally. Moreover, China's textile sector share in

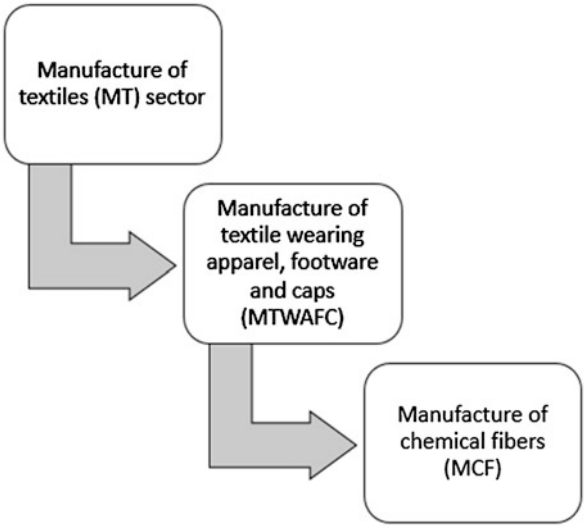


Fig. 18.2 Textile sector division as per China industrial classification for national economic activities (GB/T 4754–2011)

global economy is 34% and Fig. 18.2 shows division of Chinese textile sector (Jichao 2010). The main products from textile sector in China include cotton, silk, and man-made fibers produced via wet processing, spinning, and weaving including other processes. The major pollution is caused by waste water in China which is produced as a result of different processes involved in textile sector such as bleaching, scouring, salt bath, dyeing, desizing, and mercerizing (Peng et al. 2015). There are certain physical processes which are being used in Chinese textile industry for pre-treatment of sludge and waste water. One of the common physical methods is using screens and bars for treating waste water to remove suspended solids, fibers, and yarns. After screening, mechanical scrapper is used to scrap the floating particles and the remaining sludge is transferred to the equalization tank. This tank mixes the sludge to improve the flow and clear it from other impurities. Later, floatation ensures the separation of oil particles and fibers from the treated water through buoyancy caused by air introduced within the tank (Yang et al. 2019). Then this water is mixed slowly with paddles so that the smaller particles coagulate with heavier particles which can settle and can be removed as sludge. This method known as clariflocculation separates the colloids and adsorbs them into flocks which are easily removed (Wang et al. 2011). Then for secondary treatment, trickling filters are used which contain circular beds coated with either PVC or coal which curtail the microorganisms present in the sludge (Fig. 18.3). For tertiary treatment, electrolytic precipitation is practiced in China which uses an electric pulse which passes through the electrodes. This result in the combination of disbanded metallic ions with disseminated particulates thus developing heftier metallic ions that can be expelled via precipitation. In addition, some textile sectors in China also use reverse osmosis and electrodialysis techniques for the remediation of textile wastewater (Mostafa 2015).

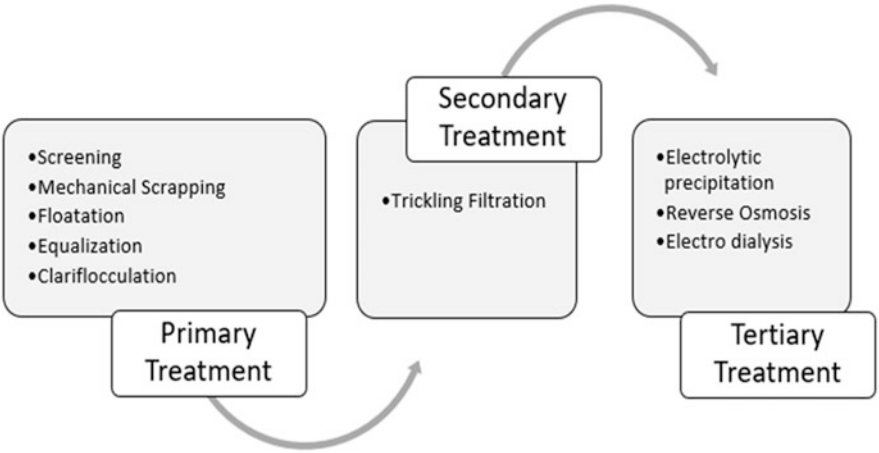


Fig. 18.3 Physical remediation methods used for treating effluents in textile industry of China

18.3.2 India

Globally, India is the subsequent major manufacturer of textile and is the third largest producer of cotton and like China; textile sector incorporates small and medium scale industry because of linkage with heritage and culture. India also produces 18% of the global silk making it second largest silk producing country (Sharma and Dhiman 2016). Though this sector is unorganized yet its diversity and products are globally competitive. It is the traditional industry of India and a backbone to the economy and is scattered in Mumbai, Chennai, Ahmedabad, Bangalore, and other parts of India (Jain 2010). However, this sector is also a major contributor to water pollution in India because 10–15% of untreated synthetic dyes are released in the water bodies (Hasanbeigi and Price 2012; Rani et al. 2014). For removal on synthetic dyes from effluents, adsorption method using bagasse is commonly applied (Desai and Kore 2011). Moreover, coagulation is also practiced in some parts of India for removing contaminants from industrial waste water. Another technique known as gamma radiation (by controlling radiation dose and oxygen supply) is also practiced by major textile finishing sector (Zahid et al. 2017).

In some cities of India, there are common effluent treatment plants established which can be used by textile based SMEs to treat the effluents before releasing in water bodies. Moreover, maximum pollution is produced from cotton weaving and polyester fiber production in the country (Raichurkar and Ramachandran 2015). Also, because of the diverse dye industry, gray fabric is purchased and even imported sometime to convert it into dyed finished fabric. So this is how value addition is practiced. Also, like Pakistan, Indian textile sector is based on fossil fuels. Commonly used methods of physical remediation of industrial waste water are described in Fig. 18.4.

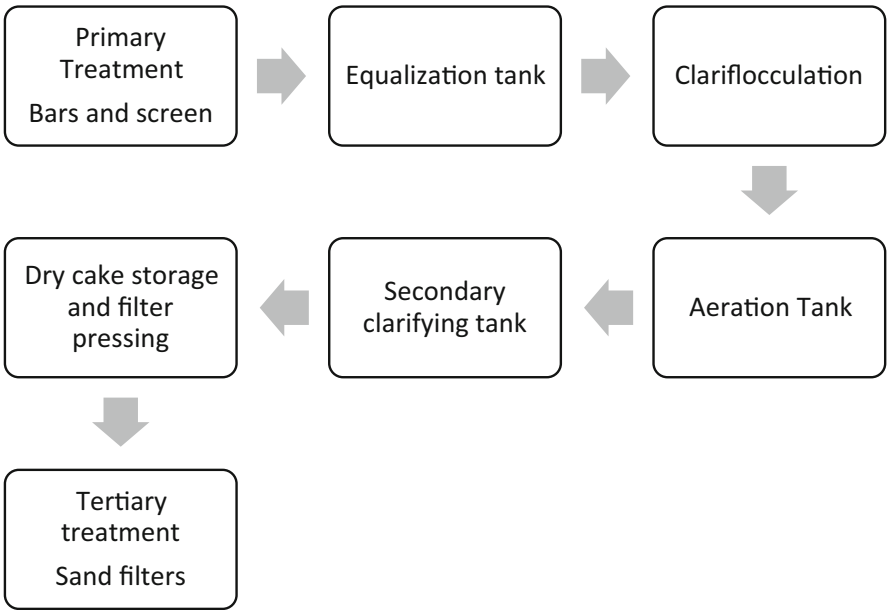


Fig. 18.4 Steps of physical remediation method of textile industrial waste water in India

18.3.3 Pakistan

Pakistan's share of textile exports to the world is accounted to be 65% as per the year 2011–12 (WB) and it is the 8th largest exporter of textile in Asia. Moreover, cotton fabric is the most widely produced and exported from Pakistan to the international market (Chequer et al. 2013). Currently, 700 textile industry units are operational in the country, however; the city of Faisalabad in Punjab is considered a hub of textile sector which produces maximum export quality textiles. The industry has suffered huge losses owing to the issues of electricity shortage and also the global recession (Khan and Khan 2010). Furthermore, this sector is contaminating the environment by discharging effluents without proper pre-treatment to the fresh water bodies. The main fresh water rivers like Ravi and Chenab are getting polluted due to the discharge from textile sector. Usually, azo and synthetic dyes are used and bleaching is also performed extensively. Hence waste water and effluents pose a serious threat owing to the textile industry because this sector generates waste water which is high in Biological Oxygen Demand (BOD), pH, temperature, Chemical Oxygen Demand (COD), color, and turbidity (Malik et al. 2010). Furthermore, dye fixing agents and retarders are cancer causing and pose a serious threat to the environment. Another cause of concern is the dust generated during fabric production and is released directly into the air, thus furthering air pollution (Ismail et al. 2019). Hence, one of the reasons why Faisalabad is considered to be one of the most polluted cities in the world (Asghar et al. 2018).

Some of the conventional pre-treatments are carried out in by some textile industrial units after regulations and check and balance by the Pakistan Environmental Protection Agency. This involves primary, secondary, and tertiary physical treatments for removal of contaminants. Such as in primary treatment, screens are used to separate fiber and yarn from the sludge which is then further treated chemically. Secondary treatment involves aerobic and anaerobic processes to treat sludge and in tertiary system, another physical remediation method of reverse osmosis is used commonly to treat the sludge. Only a few textile units practice electrolysis because it is costly (Kiran et al. 2019). Also, water heating is commonly used for dyeing process in Pakistan and since textile sector is run on fossil fuels, there is a need to consider solar heating for this purpose. The reason is because Pakistan has great potential for solar energy (Muneer et al. 2006). Although there is a demand for eco-friendly practices and there are certain cost effective methods which are being tested at pilot phase, still physical practices for removing contaminants needs to be encouraged.

18.4 Chemical Remediation Techniques for Dye Removal

Chemical methods involve the addition of certain chemicals including solvents for the removal of pollutants from any desired entity such as polluted water and soil. The aim of the chemical remediation techniques can either be to stabilize the pollutants or convert them into less toxic forms and making them safe for the consumption of all the living organisms including plants, animals, and human beings. The complete waste water remediation is hard to be achieved using physical and biological methods alone, so in many situations certain chemical reactions and entities are required for the restoration purposes (Choudhury et al. 2018). The materials generally employed for chemical degradation are carbon based, metallic oxides, clays, and sometimes of biological origin (Tara et al. 2020). Chemical methods are usually faster than the physical and biological processes but can be expensive or generate more toxic by-products (De Castro et al. 2018). So selection of appropriate method regarding the nature of pollutant is crucial in remediation process. The ongoing and recent research has revealed the potential of discussed below techniques for the remediation of coloring compounds from waste water (Fig. 18.5).

18.4.1 Adsorption of Dyes

Many processes and methods employing basic principles, i.e. physical interactions and permanent reactions have been practiced for the removal of natural/manmade dyes from effluents. Few of these processes involve removal via activated sludge, membrane separation and coagulation, etc. All of these techniques have their own certain advantages and disadvantages. The adsorption technique has a cutting edge over the rest of the methods because of its simple design, cost effectiveness, consistent results, and recovery of adsorbing material. These properties have made

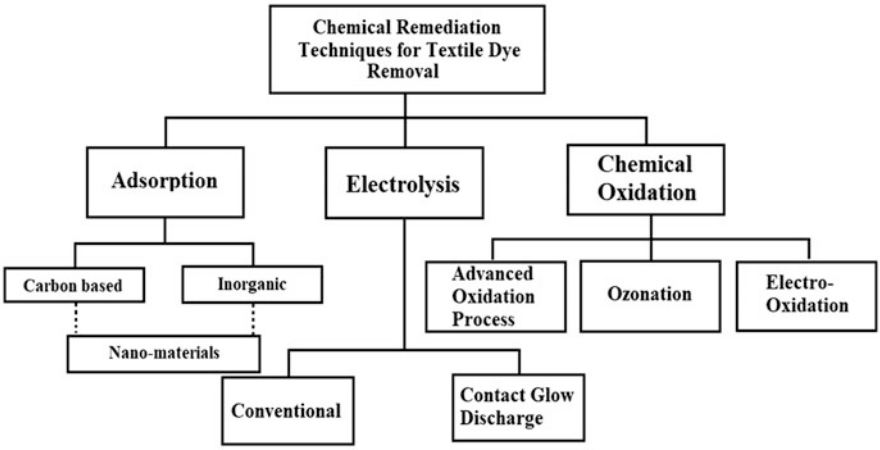


Fig. 18.5 Chemical remediation techniques for the removal of textile dyes

many researchers to discover the potential of various materials as adsorbents for the extraction of dying compounds from the textile waste effluents (Kausar et al. 2018). In process of adsorption the solute molecule gets attached to a solid substrate's surface either by physical or chemical bonding, sometimes both phenomena's can occur. The solute that gets adsorbed is known as adsorbate whereas the solid surface on which it gets attached is called adsorbent. The dyes have a chromogenic moiety that imparts a characteristic color to the dye (Nassar et al. 2017). In terms of adsorption these groups act as a suitable site for attachment on adsorbent. In the process of adsorption many factors are involved such as nature of bonding between the adsorbate-adsorbent, pH, contact time, and particulate size of the adsorbent. In order to prepare a good adsorbent optimization of all the parameters is important.

In literature many studies have been reported that had examined the adsorption potential of various adsorbents in terms of dye removal from textile effluents. In terms of adsorption two types of processes occur "chemisorption and physisorption." Chemisorption is considered to be irreversible because of the exchange of electrons between adsorbate and adsorbent molecules that results in the strong bond formation. In contrast physisorption is reversible because of the formation of weak van der Waals interactions among the molecules of adsorbent and adsorbate. Adsorbents such as activated carbon owned the properties such as high porosity, surface area, and restoration that makes it a very desirable adsorbent for variety of dyes. Many textile industries have been reported to use the saleable grade activated carbon for remediation of dye wastewater but it is not a cost effective option. Some studies have reported to employ coconut husk to synthesize activated carbon to generate a cost effective solution (Aljeboree et al. 2017).

Now a days among the class of carbon based adsorbents graphene oxide is the most well studied nano-material. Graphene owned superior adsorption properties because of the two factors; one it has a planar structure and secondly has a very high

surface area per layer. The graphene oxide is derived from the graphene that is basically a single sheet of graphite. The oxygen containing functional groups, i.e. hydroxyl, epoxy, and carboxylic group imparts hydrophilic character to the graphene oxide. Many researchers have reported adsorption of anionic and cationic dye using the nanosheets of graphene oxide. The ability of adsorption of graphene oxide can be attributed to the electrostatic interaction of oppositely charged adsorbate and adsorbent species (Xiao et al. 2016). In current scenario, immense work has been completed on synthesizing and employing nano-particles as adsorbents for the elimination of dyes from textile waste effluents because of their exceptional great surface area (Tara et al. 2020). Among carbon based nano-materials carbon nanotubes possess large surface area, hollow and layered structures. These properties make them efficient adsorbents and have shown the potential to be used as a potent dye removal from the textile effluents. Nano-materials have been vastly studied and employed in a variety of applications such as nanocoatings and electronic devices. The inorganic nano materials such as metal oxides owned the capability to decontaminate wastewaters due to high surface area, greater availability of active sites, and high stability. Among various inorganic nano materials, nano magnesium oxide (MgO) is cost effective, more chemically stable, non-toxic and easily producible having greater surface area. All these properties make MgO nano-particles an auspicious material for the exclusion of anionic dyes. MgO nano-particles can be produced via various methods, e.g. laser vaporization, chemical vapor deposition, and laser vaporization technique (Nassar et al. 2017). Recently it was discovered that simultaneous adsorption of two dyes "Reactive red 195" and "Reactive yellow 145" can be done using the nano-composite cobalt ferrite-alginate within 60 min and pH range of 3–6 and could be prepared via *polymerization*. The exceptional adsorption of this nano-composite can be attributed to the presence of various polar functional groups (amine, hydroxyl and carbonate) at the superficial side of the particles. This new composite material proposes a sustainable and cost effective adsorbent for the actual elimination of chromophore moiety from effluents. More interestingly, this adsorbent can be separated because of having magnetic properties and hence it is reusable (Jayalakshmi and Jeyanthi 2019).

18.4.2 Chemical Oxidation of Dyes

Remediation of textile dye effluent is a difficult task due to complex chemical structure of dyes, low biodegradability, strong color and greater organic and salt content in wastewater. Chemical oxidation derived techniques most notably "Advanced Oxidative Processes" (AOP) have expected to be potentially the most appropriate technique for the remediation of persistent and recalcitrant chemical moieties known as dyes (Baeissa 2016). AOP technique is a clean solution for the remediation of contaminated water either by mineralizing or decreasing the resistance of conjugated organic compounds. They possess the potential to decompose persistent compounds into inert substances such as carbon dioxide, water, and inorganic compounds (da Rocha Santana et al. 2019). AOP is centered on the

creation of highly reactive and strong oxidizing chemical moieties such as hydroxyl radicals ($^{\bullet}$OH). These radicals have the capability to oxidize any organic molecules up to the complete mineralization (Saeed et al. 2018). Out of many methods of AOP the photochemical one has the advantage over the rest because it is non-toxic, quick, and effective. In this process the hydroxyl ions (OH) are produced during the reaction and non-selectively attack the organic contaminants either by generation of atomic hydrogen or electrophilic addition via transfer of electrons (Mousset et al. 2018). The photochemical-assisted Fenton reaction is found to be very effective for oxidation of pollutant in an aqueous solution with a pH around 3. In this process the principal ferric iron species $Fe(OH)^{2+}$ appreciably absorbs the light in ultraviolet region that afterwards lead to the reduction of this species resulting in the creation of Fe^{2+} along with OH^{-} (depicted in Eq. 18.1). Fe^{2+} then reacts with H_2O_2 for the further generation of OH^{-} (as depicted in Eq. 18.2). The photolysis of H_2O_2 acts as a supporting source for the production of · OH (as depicted in Eq. 18.3). Whereas, the impact of photolysis of H_2O_2 is less significant as compared to reactions (18.1) and (18.2) as its absorption coefficient is low (Tarkwa et al. 2019)

$$Fe(OH)^{2+} + h\nu \rightarrow Fe^{2+} + OH \tag{18.1}$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe(OH)^{2+} + OH \tag{18.2}$$

$$H_2O_2 + h\nu \rightarrow 2^{\cdot}OH \tag{18.3}$$

The conditions required to achieve the optimal dissociation of chromophore is hinged on the acidity of solution (optimal at around 3), the quantity of H_2O_2 and ferric iron (as catalyst) along with wavelength of subjected light ($\lambda = 240$–300 nm) (Ameta et al. 2013). Many researches have achieved the Fenton-related successful degradation of chemical dyes in wastewater. One such study depicted the degradation mechanism of an Orange G dye via oxidation done through photo-Fenton (homogeneous photo catalysis) process (Fig.18.6).

The intermediate products that originate during the Photo-Fenton degradation of Orange G dye involved aromatic hydroxyl amines, nitroso and phenolic substituted compound. In the reaction high electron density azo bonds were the primary cites targeted by the OH radical as proposed in the literature (Brillas and Martínez-Huitle 2015). Afterwards the sulfonate groups were triggered and attacked to be released as sulfates. The major intermediates were subjected to oxidation that further leads to subsequent hydroxylation and results in the formation of hydroxylated aromatic intermediates. The aromatic's hydroxylation finally lead to the opening of ring and production of short-chain carboxylic acids. These acids further lead to the formation of inorganic species and complete mineralization of the dye (Tarkwa et al. 2019).

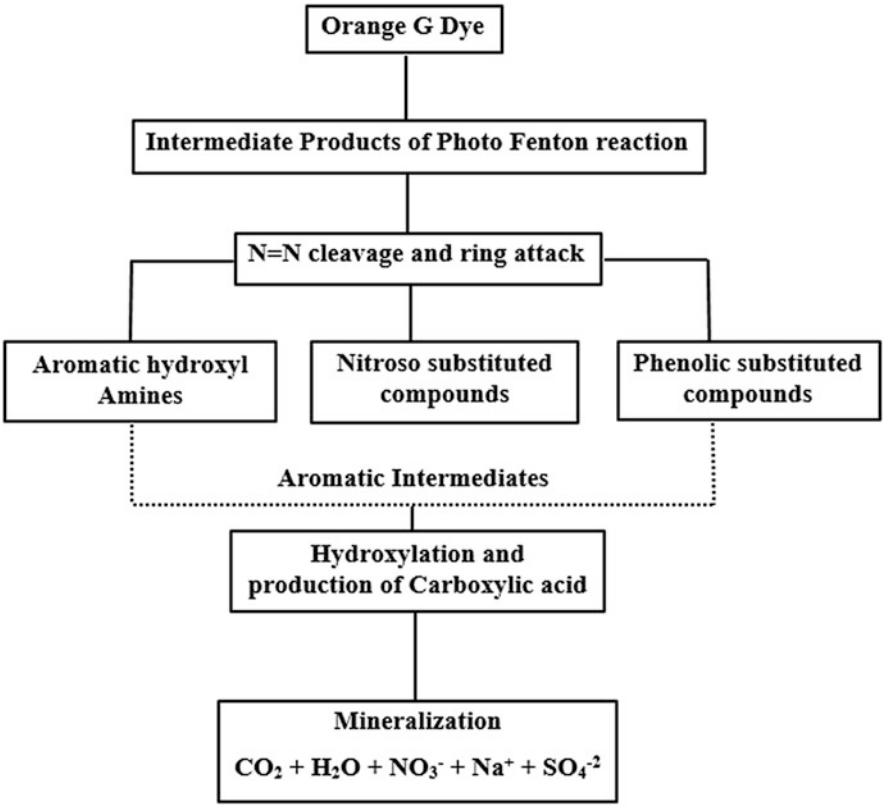


Fig. 18.6 Schematic representation of degradation of Orange G Dye by Photo-Fenton reaction

18.4.3 Ozonation

Ozone (O_3) is an extremely reactive gas which comprises of three oxygen atoms. It can be produced both naturally and by anthropogenic activities. Ozone is considered to be a very strong oxidizing agent in the presence of water and displays a rapid reactivity with more or less all of the organic moieties. This capability of ozone has made it a well-known and established technique for the removal of color imparting organics present in waste water especially dyes. The oxidation carried out by ozone mainly occurs either by a direct electrophilic reaction or through an indirect route that comprises of the generation of another powerful radical that in most cases is a hydroxyl radical (**.**OH) (El Hassani et al. 2019).

Studies have revealed that if only ozone is used for the waste water remediation, then an effective discoloration could occur but a complete mineralization would not be possible. This would lead to the buildup of biodegradable organic matter or inorganic compounds along with water. In order to overcome this issue ozonation

technique can be coupled with a solid catalyst thus naming the process as catalytic ozonation process (COP). It is an advanced oxidation process that makes the degradation process much better while enhancing the efficacy. To be precise in COP, the oxidation via ozone is increased because of the addition of a solid substance that acts as a catalyst and produce more reactive radicals. In comparison to the conventional ozonation, the radicals generated here enhance the mineralization rate thus reducing the reaction time that afterwards make the process cost effective. More over solid catalysts enhance the surface area that plays a vital role in the process of adsorption (El Hassani et al. 2019). Multiple solid catalysts have been investigated up to this date that involves metal oxides, zeolites, clay minerals, and activated carbon (Faria et al. 2008). According to the type of catalyst used, the COP can be distinguished into heterogeneous and homogeneous processes. Among all the types of solid catalysts the most notable are the (LDHs) layered double hydroxides. LDHs comprise of the synthetic clays that are anionic in nature having general formula $[M_{1-x}^{2+}M_x^{3+}(OH)_2]A_{x/m}^{m-}.nH_2O$, here M^{2+} depicts divalent metal, M^{3+} = trivalent metal, and A^{m-} represents an anion. The extensive selection of metal cations and the profusion of hydroxyl groups within the layered structure of LDH, makes it an outstanding material with superior catalytic abilities. LDH come under the heading of nano-materials and are used in heterogeneous catalysis systems speeding the various reactions such as electro catalysis, photo degradation, and decomposition reactions.

The LDHs compounds in a heterogeneous nano-catalyst system can be employed for the decomposition of Azo dye via the process of ozonation. Methyl orange (MO) is a type of an Azo dye regarded as a toxic entity. A variety of reaction mechanisms are possible to be going on during the breakdown of methyl orange under the effect of Ni-LDH catalyst assisted Ozonation. According to the literature adsorption of ozone molecules occurs on Ni-LDH catalyst via getting weakly bonded with hydroxyl groups oriented outside the layered structure of catalyst. The Ni with in the catalyst acts as an initiator site for the ozone decomposition and is oxidized to $Ni^{(II)}$ forming a reactive complex of $Ni^{(IV)}O(OH)_2$. This reaction is depicted as follows:

$$Ni^{(II)}(OH)_2 + O_3 \rightarrow Ni^{(IV)}\ O(OH)_2 + O_2$$

As the $Ni^{(IV)}$ is the peak oxidation state of Nickel so the complex will disintegrate and oxygen is released that results in the availability of active sites throughout the reaction (Stoyanova et al. 2006). Moreover, the $Ni^{(II)}$ and $Ni^{(III)}$ will be available on the surface of catalyst followed by ozone disintegration as depicted in the following reactions:

$$2Ni^{(IV)}\ O(OH)_2 \rightarrow 2Ni^{(II)}\ (OH)_2 + O_2$$

$$3Ni^{(IV)}O(OH)_2 \rightarrow Ni^{(II)}\ (OH)_2 + 2Ni^{(III)}\ O(OH)_2 + H_2O + O_2$$

Along with all the reactions going on, the molecules of methyl orange quite possibly get chemically or physically attached on the surface. Overall organic molecules and active complexes established by the catalyst will efficiently undergo the oxidation of the methyl orange dye at the boundary between solid and liquid phase. Along with the going on reactions, the disintegration of dye at pH $\sim$ 9 can also be associated to an indirect reaction carried by the active **.**OH radical formation which causes degradation of ozone. In that case the dye molecule is attacked at the azo group site which leads to the cleavage of chromophore group (N=N) that connects two aromatic rings of methyl orange molecule. This will result in the breakage of N-N bond. The literature suggests that at the termination of this remediation process, these molecules can further be decomposed into organic acids and inorganic species. The nitrogen in the parent dye moiety will be transformed to NO^{3-} ions whereas the sulfonyl group becomes harmless SO_4^{2-} ions (Devi et al. 2009).

18.4.4 Electro-Oxidation

Electro-oxidation (EO) methods employ electrons as the basic tool for the remediation of the waste water having synthetic dyes as impurities. As in this technique electrons are used so it is considered to be the most clean and green process of remediation. This method is divided into two main catagories, namely direct electro-oxidation and indirect electro-oxidation. In case of direct EO, hydroxyl radicals are generated on the anode surface, as **.**OH is a powerful oxidant it disintegrates dye structure (Fig. 18.7). In indirect EO, oxidizing agents (either oxygen or chlorine-based) are electrochemically generated in the solution. This process involves the generation of hydrogen peroxide (oxidizing agent) at the cathode and the generation of active chlorine species at the anode. In case of electro-fenton process the generated H_2O_2 in the availability of iron metal (Fe^{2+}) can produce the hydroxyl radicals (Ghanbari and Moradi 2016).

18.4.5 Electrolysis of Dyes

In early 90's electrolysis was opted for the remediation of textile effluents. Since then it have been proved to be an effective method for the elimination of undesired material from discharged water. This technique has many good aspects as compared to conventional methods such as it does not require any other chemical, no sludge is generated and complete conversion of toxic dyes into non-toxic is achievable. The remediation of dye is influenced by optimization of some parameters in order to achieve the maximum removal of certain pollutants. These parameters involve chemical nature of electrode, separation between the electrodes, density of applied current, concentration of dye, pH, and time given for the electrolysis (Fig. 18.8). A huge versatility is available in terms of material that is used to make electrodes. Mostly anode is easily corroded or dissolved while remediation. Due to this reason

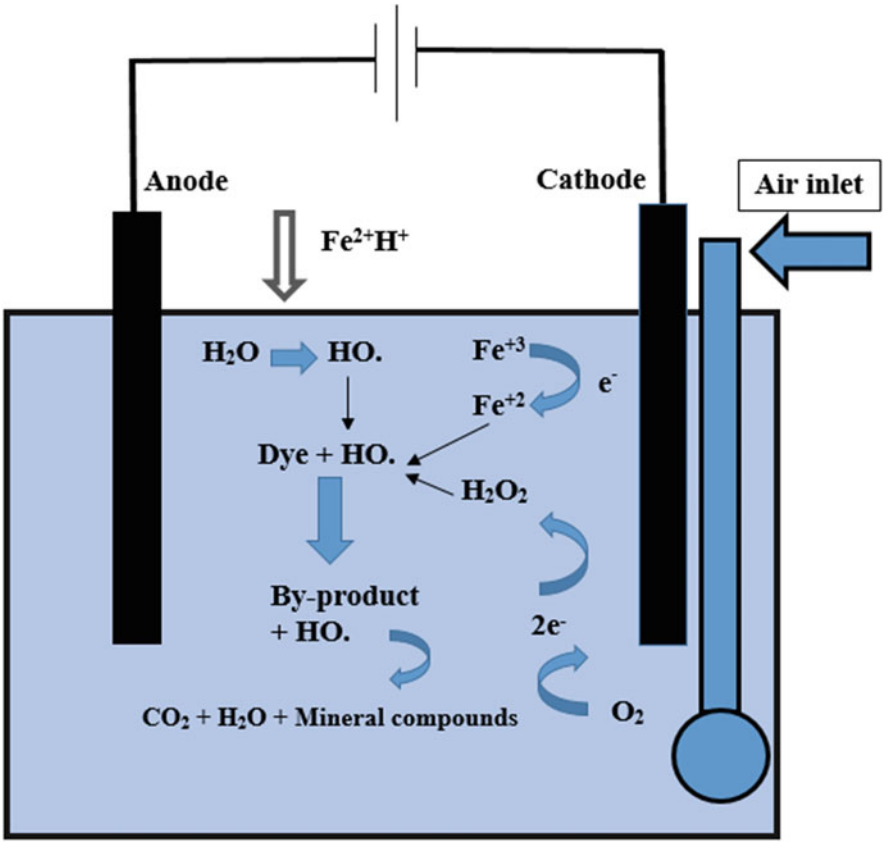


Fig. 18.7 A general representation of electro-oxidation

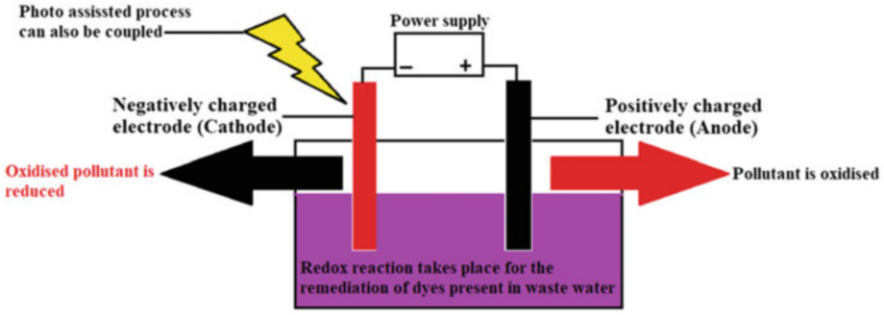


Fig. 18.8 General setup of electrolysis

such type of material should be selected for anode that can withstand corrosion. Among such materials carbon is one of the best, easily available and cost effective option. The corrosion tendency of carbon is almost negligible (Arif and Malik 2017).

Along with conventional electrolysis methods one of the most recent and promising techniques is the contact glow discharge electrolysis (CGDE) method for the removal of color from the water contaminated with dyes. CGDE is a type of electrochemical process, here development of plasma occurs by the glow discharge of direct-current between an electrode and electrolyte (Gao et al. 2003) CGDE is comparable to conventional electrolysis, the only difference is the requirement of high-voltage conditions that are necessary to originate plasma emission (Saksono et al. 2014). The enormous potential gradient accelerates the gaseous H_2O^+ ions of the plasma towards the plasma–liquid interface. As of the massive energy carried by these ions they ionize various water molecules releasing an immense amount of hydroxyl radicals (**.**OH). As prescribed earlier the hydroxyl radicals are very reactive and possess great oxidizing capability which makes them very short lived that can affect the rate of decolorization. In order to overcome this issue various types of catalyst can be added such as the addition of Fe^{2+} ions. These ions are capable to catalyze the decomposition of H_2O_2 and increase the productivity of **.**OH, overall enhancing the capability of decolorization of dyes. Using 40 mg/L of Fe^{2+} ion for 30 min can lead to the removal of Remazol Brilliant Blue up to 99.63% (Saksono et al. 2018).

According to the literature the air injection in CGDE is very important for the overall process efficiency. The air injection can simplify the generation of high energy electrons thus increasing the OH radical's production. In the presence of air the hydroxyl radicals react with the oxygen and generate other reactive fractions. The available oxygen has the tendency to synthesize O_3 and H_2O_2 after reacting with H_2O molecules. This phenomenon can be explained with the help of the following reactions (Zainah and Saksono 2017):

$$e + O_2 \rightarrow O\cdot + O\cdot + e \tag{18.4}$$

$$O\cdot + O_2 \rightarrow O_3 \tag{18.5}$$

$$\cdot O + H_2O \rightarrow \cdot OH + \cdot OH \tag{18.6}$$

$$e + H_2O \rightarrow H\cdot + \cdot OH + e \tag{18.7}$$

$$\cdot OH + O_2 \rightarrow HO_2\cdot + O\cdot \tag{18.8}$$

Eqs. (18.4), (18.5), (18.6), (18.7) depict in what way air injection harvests a large amount of reactive species (HO_2**.** and **.**O radicals) along with **.**OH. The reduction potential of HO_2**.** and **.**O active species (Augusto and Miyamoto 2011) is associated with these supplementary reactive species involved in the dye degradation (Budikania et al. 2019).

Above described methods are few of the recently discovered methods some are being employed by different textile industries whereas other require more in-depth

study. The poisonous organic dye remediation from the textile effluents is of vital importance for creating the harmony within the aquatic ecosystem. It is a very tedious task to opt any single treatment option for the complete removal of dyes. Each technique is accompanied with certain positive sides and down sides. The basic disadvantage of the chemical remediation methods is the requirement of special equipment and expertise. The chemical techniques are proved to be quite effective in terms of dye removal but in some cases toxic sludge can also be produced. This issue is being answered by the development of emerging techniques among which the most notable one is advanced oxidation processes. This process is highly effective for the complete mineralization of the organic dyes but there cost is very high which makes them suitable only for the developed nations. China is the world's largest trader of textile products. In 2017 China started first radiation waste water plant in Jinhua city. In that plant electron beam is employed for the treatment of textile waste water (He 2018). The establishment of effective, fiscal, and eco-friendly techniques to reduce the percentage of dye in wastewater up to an acceptable limit in a cost effective way is of paramount importance (Couto 2009). According to International Atomic Energy Agency (IAEA) this is the only technique that can remediate any kind of organic dye completely and safely without the release of any toxic by-product. This technique has the same problem like use of AOP that is it is quite expensive. Today, textile dyeing is responsible for a fifth of all global industrial wastewater pollution. Although some industrial nations use radiation to treat contaminated water from textile dyeing plants, some developing countries in Asia do not have the resources to minimize wastewater pollution. The IAEA plans to incorporate more radiation wastewater plants in China and other Asian countries in coming years. Other textile manufacturing countries, like Bangladesh, Sri Lanka and India, have also expressed interest in working with the IAEA to improve wastewater treatment sustainability at their factories.

18.5 Biological Remediation of Textile Effluents

The huge demand for environmentally friendly methods for industrial processes and wastewater treatment shifted focus on the biological treatments and techniques. Biological treatments are much cheaper and easily operable at various stages of textile effluent treatment and remediation. Among biological materials bacterial and fungal cultures and their enzymes are most commonly used methods to treat textile effluent (Rather et al. 2018). There are many advantages to use biological methods for textile industry effluent treatment;

- eco-friendly,
- cost effective,
- less sludge production,
- non-toxic metabolites,
- full mineralization (Hayat et al. 2015).

Bioremediation is the green technology which employs use of biological material and sources for the degradation and discoloration of textile dyes in wastewater. Microorganisms such as bacteria, fungi, yeast, and algae are used to disintegrate and absorb synthetic dyes. Many plant species are also quite efficient for the treatment of textile wastewater (Ekambaram et al. 2016). Bioremediation involves the process of degradation of toxic synthetic dyes by breaking bonds into less toxic inorganic compounds (Babu et al. 2015). Biological methods are broadly classified into aerobic and anaerobic, a combination of both and on the basis of oxygen requirements (Xu et al. 2018). The azo dyes degradation occurs in two steps, firstly under anaerobic conditions azo bonds breaks and forms aromatic amines that are toxic for bacterial culture and secondly the aromatic amines are further catabolized into less toxic metabolites under aerobic environment (Ajaz et al. 2019). The dye degradation and discoloration depends on many factors and it is influenced by the type and concentration of dyes in effluent, the culture load, pH, temperature and oxygen concentration (Holkar et al. 2016).

18.5.1 Bacterial Degradation

Bacteria are generally preferable for the remediation of textile wastewater because they grow quickly, easy to culture and amenable to genetic manipulations. In literature many bacterial species, i.e.; *Acinetobacter*, *Bacillus subtilis*, *Bacillus cereus*, *Corynebacterium* specie, *Clostridium* specie, *Dermacoccus*, *Enterococcus* species, *Streptococcus, faecalis*, *Pseudomonas, Staphylococcus* species, *Lactobacillus* sp., *Micrococcus* sp., *Rhizobium* sp., *Morganella* sp., *Klebsiellla* sp., and *Shewanella* specie have been reportedly degraded the textile dyes (Imran et al. 2016; Haghshenas et al. 2016). Azo dye degradation using the pure bacterial culture is effective but dye specific. Because of this using a single bacterial specie culture for large industrial unit with complex mixture of dyes in effluent is unfeasible (Kumar et al. 2018). Moreover, some bacterial species end up producing carcinogenic secondary products that require further detoxification. To avoid this, remediation processes involves using mixed or multispecies culture for complete mineralization of complex mixture of dyes (Ghosh et al. 2016).

The dye degradation may cause change in the composition of mixed bacterial culture which may change the efficacy of the process. The biodegradation process strongly dependent on pH, temperature, concentration of dye, capacity of microbial consortium to degrade a particular dye. Bacteria require optimum pH for the degradation of textile dyes and adaptability to varying pH enhances the treatment process. Bacterial cultures prefer the pH that is between the ranges of neutral to somewhat alkaline (7–9.5). Strongly acidic or basic pH conditions reduce the degradation efficacy of bacteria. Bacterial cell require optimum temperature condition (35–45 °C) for degradation of dyes in textile effluent and high temperatures usually cause cells to denature effecting removal efficiency. While high temperature causes the denaturation of enzymes in bacterial cells (Garg and Tripathi 2017).

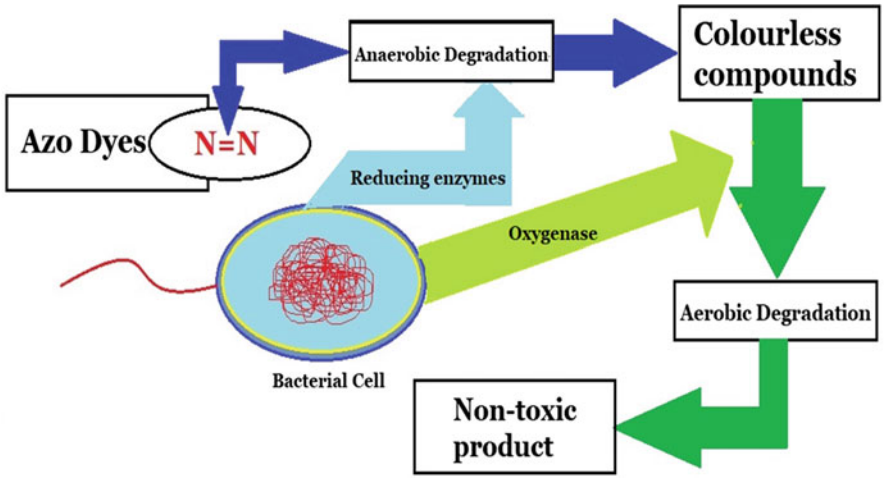


Fig. 18.9 Bacterial decolorization of azo dyes in the textile effluent

18.5.2 Degradation Mechanism

A combination of both anaerobic and aerobic conditions are a reasonable biological treatment strategy for degradation of dyes in textile effluent. The azo dyes are degraded with the help of azoreductase enzyme in anaerobic conditions with four electron transference **(**Fig. 18.9**).** The primary pathway is the reductive cleavage of azo bonds. Azoreductase enzyme reduces the dye into colorless amines that are very resistant and mineralized only in aerobic conditions (Misal and Gawai 2018; Singh et al. 2017). There are two types of azoreductase enzyme one is Flavin dependent azoreductases which requires NADH (nicotinamide adenine dinucleotide hydrogen), NADPH (nicotinamide adenine dinucleotide phosphate hydrogen), or FADH (flavin adenine dinucleotide) cofactor as an electron donor for reducing azo bond (Pande 2019). These were isolated from *Enterococcus faecalis* (AzoA) (Punj and John 2009) and *S. aureus* (Azo1) (Chen et al. 2005).

Other type is flavin-independent azoreductases does not contain flavin molecule in the structure nor they require any exogenous flavin for catalysis (Suzuki 2019). It was isolated and characterized from alkaliphilic and neutrophilic bacterial strains (Misal et al. 2015). The functional group present near the azo bond also influences the substrate specificity of azoreductases enzyme. Azoreductases enzyme can use some unstable electron donors such as 1-benzyl-1,4-dihydronicotinamide (Qi et al. 2017). To speed up the biodegradation process of azoreductase enzymes various redox mediator are used, such as riboflavin, Anthraquinone 2–6 disulphonate, sodium 1,2-naphthoquinone-4-sulfonate, and 2-hydroxy-1,4-naphthoquinone are notable examples (Santos et al. 2016; Dai et al. 2018).

Another enzyme NADH-DCIP reductase belongs to the bacterial mixed function oxidase system and takes part in the detoxification of xenobiotic compounds and especially decolorization of textile dyes (Song et al. 2018; Salokhe and Govindwar

1999). It reduces the DCIP (Dichlorophenolindophenol) using NADH as an electron donor. DCIP is blue in its oxidized form and becomes colorless after reduction (Parshetti et al. 2014). The intermediate products synthesized during dye decolorization can also be reduced by other enzymes such as hydroxylase and oxygenase produced by bacteria (Elisangela et al. 2009).

18.5.3 Degradation by Fungi

Fungi secrete many extracellular and intracellular enzymes to mineralize toxic chemical compounds (Sweety et al. 2017; Baltazar et al. 2018). The fungal mycelia due to increased cell to surface ratio is well equipped to solubilize substrates by secreting extracellular enzymes (Shahid et al. 2014b). Among fungal specie the white rot fungi is considered to be crucial for global carbon cycle because of their ability to mineralize the lignin in woody plants (Bruner et al. 2016). The enzymes from white rot fungi have high oxidative potential which is capable of decolorizing wide variety of textile dyes (Yesilada et al. 2018). Many fungal species such as *Pleurotus ostreatus, Pichia sp., Penicillium sp.,* and *Candida tropicalis* are capable of degrading azo dyes (Gou et al. 2009; Tan et al. 2013). The mechanism of dye decolorization by white rot fungi is depicted in (Fig. 18.10).

There two main enzymes which play central role in the biodegradation of textile dyes. The first is extracellular enzyme lignin peroxidases which is required to depolymerize lignin and attack the non-phenolic methoxy subunits. Second enzyme is manganese peroxidase belong to the class of oxidoreductases enzymes. It attacks the phenolic compounds through redox reactions facilitated by Mn^{2+}/Mn^{3+} ions (Abadulla et al. 2000). Another strong enzyme, Laccases, abundantly found in fungi is multicopper extracellular enzyme which use molecular oxygen to oxidize phenolic compounds (Karnwal et al. 2019). Laccases enzyme from white rot fungi can be produced by different methods of fermentation such as submerged, semisolid state or solid state with carbon and nitrogen sources as inducers (Vantamuri and Kaliwal 2016). Biosorption is reported to be the primary dye removal process in wood rotting basidiomycetes which involves moving the dye from the water phase to the solid phase (the bioadsorbent) while in biodegradation enzymes break bonds of dye and transformed into other chemical compounds (Holkar et al. 2016).

Biodegradation of metal complex dyes occurs in three steps. The first is dye is adsorbed to the fungus; second step leads to the splitting of metal complex bond and finally degradation of dyes takes place with release of transformed products in culture medium (Blanquez et al. 2004). Bioreactors are used for culturing fungi. There are many examples which include bioreactors that can degrade and decolorize the textile effluent at the same time which include processes based on immobilized fungi in fixed-bed reactors, rotating drum, packed bed, fluidized bed, and membrane bioreactors (Sen et al. 2016). In rotating reactor the microbial biofilm is formed on the surface of vertical disks suspended in liquid and in trickling reactors, biofilm is humidified by liquid (Kapdan and Kargi 2002). In membrane biofilm reactors stable gas supply is ensured for microbial biofilm by attaching it to porous gas permeable

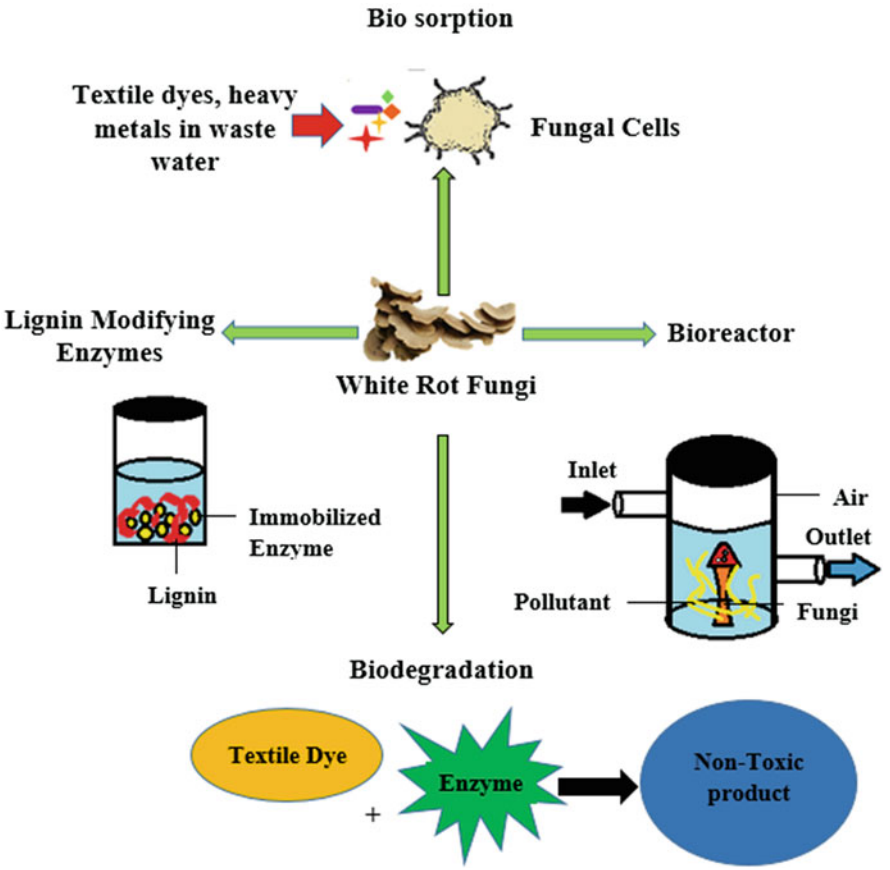


Fig. 18.10 Different methods of dye decolorization and degradation by white rot fungi

membrane (Lema and Omil 2001). These bioreactors are often disadvantageous due to mycelia aggregation, clogging, and electrode fouling (Hossain et al. 2016). Table 18.1 shows the dyes degraded by white rot fungi.

18.6 Phytoremediation of Textile Dyes Effluent

Phytoremediation of textile effluent treatment is based on using plant species that have ability and adaptability to remove toxic dyes from wastewater. Phytoremediation approach is holistic and eco-friendly technology with aesthetic value as well as cost effective method that can treat large volume of effluent (Malik et al. 2017). Plants large surface area due to root hairs accumulates nutrients necessary for growth (Ng et al. 2018). Phytoremediation is subdivided into rhizofiltration, phytoextraction, phytodegradation, phytostabilisation, and

Table 18.1 White Rot fungi potential for degrading different textile dyes

White rot fungal species	Type of dye	Reference
Bjerkandera adusta	Amaranth Reactive violet 5 Reactive blue 72	Gomi et al. 2011; Baratto et al. 2015
Dichomitus squalens	Remazol brilliant blue R Heterocyclic methylene blue	Novotný et al. 2012
Irpex lacteus	Malachite green	Yang et al. 2016
Phanerochaete chrysosporium	Reactive black 5 Reactive yellow MERL Reactive red ME4BL Congo red	Enayatizamir et al. 2011; Koyani et al. 2013; Bosco et al. 2017
Phlebia brevispora	Remazol brilliant blue R	Lee et al. 2017
Pleurotus ostreatus	Synazol red HF6BN	Ilyas et al. 2012
Trametes versicolor	Grey Lanaset G Acid orange 7 Acid blue 74 Reactive red 2	Gabarrell et al. 2012; Ramírez-Montoya et al. 2015

phytovolatilization according to the method and nature of contaminant as illustrated in (Fig. 18.11).

According to Pilon-Smits (2005) various physio chemical factors determine the efficiency of particular plant species to remove the textile dye from industrial wastewater such as pH of contaminant, temperature, humidity, nutrients, organic matter present in water, sediment or soil, availability of oxygen, microbial diversity, and biomass of plants used for phytoremediation.

Many plants in nature have remediation potential because of enzymes secreted by plant cells and some are genetically manipulated to do so. Plant enzymes (dehalogenase, nitroreductase, nitrilases, peroxidase, and laccase) found mostly on the external root surfaces of plants. Degradation activities of these enzymes depend on production, release rate, nature and concentration of the contaminant present in soil, sludge or water matrix (Dwivedi and Tomar 2018). Usually plant species with quick growth rate and fibrous deep roots such as grasses, herbs and creepers are favorable for phytoremediation of textile effluent (Ekambaram et al. 2018). Many species of wild plants such as *Typhonium flagelliforme, Phragmites australis, Rheum rabarbarum, Rumex hydrolapathum, and Blumea malcolmii* are also used in treating the textile effluent (Chandanshive et al. 2018). Plant species and aquatic macrophytes with degradation potential for textile dyes is given in (Table 18.2).

It has been speculated that dye decolorization induce an enzymatic stress response of a plant. The X-ray diffraction showed that *T. angustifolia* precipitate metal ion in root and leaf area (Nilratnisakorn et al. 2008). Due to protein molecules induction and enzymatic activity protons are released by plant cell membrane and cell wall so the dye-metal complex is translocated to semipermeable membrane without comprising photosynthesis process.

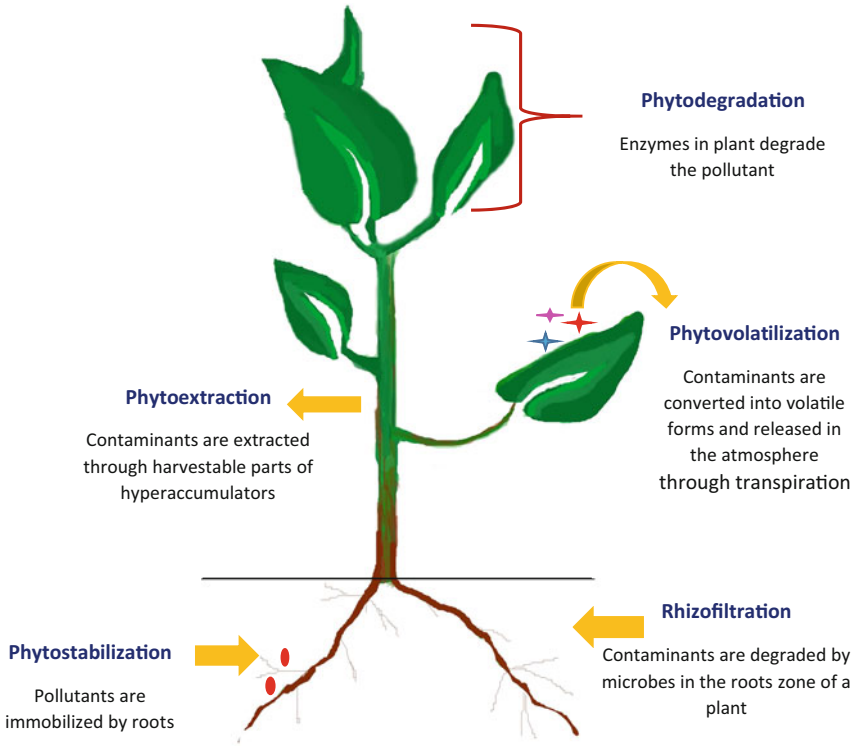


Fig. 18.11 Various methods of Phytoremediation

These molecules are then released into surrounding rhizosphere to maintain soil pH, gas composition through phytochemical reactions and relieving plants from toxic effects (Bassindale et al. 2003). Plant enzymes are pivotal for the degradation and decolorization of textile effluent. In a study *B. malcomii* enzymes decolorized the dye *Red 5B* with lignin peroxidase, tyrosinase, DCIP, reductase, azoreductase, and riboflavin reductase (Kagalkar et al. 2009). Peroxidases enzyme from *P. australis* was effective in degrading *acidic Orange 7* (Movafeghi et al. 2013) while peroxidases from *Cucurbita pepo* was more efficient for *Direct Yellow* degradation (Boucherit et al. 2013).

There are different methods of phytoremediation of textile effluent such as artificially created wetlands, vertical flow beds, hybrid systems, Fenton's oxidation and hydroponic (Muthusamy et al. 2018). The artificial or constructed wetlands were first used by Max Planck Institute in Germany by Dr. Seidel in 1950's. The novel experiment involved the use of plants for the compensation for the over fertilization, sewage pollution treatment, and siltation of inland water bodies. Experiments revealed that some giant reed species were able to remove reactive dyes form the textile effluent behaved differently than those grown in unpolluted environments (Alwared et al. 2020). Aquatic macrophytic treatment system (AMATS) using

Table 18.2 Phytoremediation potential of various plants

Serial #	Plant specie	Type of dye	Decolorization conc. %	Reference
1	*Tagetes patula*	Reactive blue 160	90%	Patil and Jadhav 2013
2	*Hydrocotyle vulgaris*	Basic red 46 (BR46)	95%	Vafaei et al. 2013
3	*Typha angustifolia*	Reactive blue 19	70%	Mahmood et al. 2014
4	*Alternanthera philoxeroides*	Remazol red (RR)	100%	Rane et al. 2015
5	*Azolla pinnata*	Malachite green	75%	Kooh et al. 2016
6	*Typha angustifolia* *Paspalum scrobiculatum*	Congo red	80% 73%	Chandanshive et al. 2017
7	*Azolla pinnata*	Methylene blue	85%	Al-Baldawi et al. 2018
8	*Asparagus densiflorus*	Rubin GFL	90.50%	Watharkar et al. 2018
9	*Pistia stratiotes*	Azul Marino Negro	90% 23%	Ferdes et al. 2019
10	*Lemna minor*	Methylene blue	80%	Imron et al. 2019

aquatic macrophytic plant species is well established method for removing textile dyes in effluent (Rane et al. 2015). The roots of floating plants are main route of heavy metal uptake while in case of submerging plants both roots and leaves remove heavy metals and uptake the nutrients. The submerged plant species provide remediation potential for both water and sediments and rootless plants are more efficient in extracting heavy metals from water (Schück and Greger 2020).

Despite being most eco-friendly technique, phytoremediation has some drawbacks. Phytoremediation is a time intensive technique which requires a several growth season for plant to clean up the effluent, but also the metabolites can be cytotoxic to plants. Moreover, phytoextraction and disposal of incarnated biomass can take several months. Bioremediation techniques for dye removal are convenient, cheap and have universal application due to ubiquitous nature of microbes involved for textile effluent treatment. But conventional methods are sometimes not very effective for treating effluent containing mixture of complex synthetic dyes. That leads to use of combination of physical, biological, and chemical methods for dyes degradation in effluent. Recently, research has been focused on making the biological methods more precise and target oriented. It is necessary to understand the dye degradation pathways by enzymes and factors that influences efficacy of certain enzymes produced by microbes to be more potent for complex mixture of textiles wastewater.

Bioinformatics plays a pivotal role in the advancement of biological treatment options for wastewater. The "in silico" molecular modelling and docking studies are useful tool for the screening of potential microbial consortium for textile dye

degradation and decolorization. Molecular docking predicts the binding of macromolecules (receptor) and a small molecule (ligand) efficiently. Another technique, Response surface methodology, a mathematical modelling tool for the analysis of degradation process is quite useful for predicting the most viable output of remediation process. The RSM approach is used to determine the optimal levels variable like temperature, pH, and dose to establish relationship between variables in degradation process. This modelling technique is helpful in optimizing the resource use and evaluates the relationship between various variables in the system (Khamparia and Jaspal 2017).

18.7 Conclusion

Untreated wastewater discharge from textile industries affects the aquatic ecosystem and aesthetics quality. It inhibits the plant growth, impairs photosynthetic functions, increases the biological and chemical oxygen demand and is detrimental for aquatic life. Moreover, recalcitrant chemicals enter the food chain to bio accumulate which lead to mutagenicity and carcinogenicity. Textile industry effluent is treated with various techniques based on biological, physical, and chemical methods. Every technique has its own set of advantages and disadvantages. In case of physical methods complete removal of pollutants is not possible. In terms of chemical methods, some provide 100% dye removal but they are not cost effective thus can only be employed by the developed nations. The bioremediation or mineralization of harmful textile dyes in effluent by the action of plants, bacteria, and fungal biomass is eco-friendly, inexpensive, readily available technology with significant potential for textile effluent treatment but like other methods it also has some drawbacks. The phytoremediation technology is rather slow and complex effluent might limit the efficiency if a particular plant species is not able to process the toxicity of effluent. Similarly, bacteria, fungi yeast could be utilized with much higher potential with modern outlook towards bioremediation equipped with molecular biology, genetic engineering, and nanotechnology. Biotechnology can be a great tool to promote sustainable practices in waste water treatment and textile dye degradation in near future. In order to promote complete removal of textile effluents developed nations are required to cooperate with developing nations. Development of such dyes are required that can degrade on their own after some specific time. Textile industry has progressed so fast throughout this era but it is the need of the hour to develop sustainable, cost effective, and robust remediation techniques accordingly.

References

Abadulla E, Tzanov T, Costa S, Robra K-H, Cavaco-Paulo A, Gübitz GM (2000) Decolorization and detoxification of textile dyes with a laccase from *Trametes hirsuta*. Appl Environ Microbiol 66:3357–3362

Abrahart EN (1977) Dyes as their intermediates. Chemical Publisher, New York, pp 1–12

Afrin D, Sumi MSE, Ali MR, Akter A, Khalekuzzaman M, Sikdar B, Islam MA (2018) Isolation, characterization of *Candidatus asiaticus* causal agent of greening disease in Citrus spp. and evaluation of its sensitivity pattern. Int J Pure App Biosci 6:33–43

Ahmad MM, Salim-ur-Rehman Z, Iqbal-Anjum FM, Sultan JI (2006) Genetic variability to essential oil composition in four citrus fruit species. Pak J Bot 38:319–324

Ahmed LM, Jassim MA, Mohammed MQ, Hamza DT (2018) Advanced oxidation processes for carmoisine (E122) dye in UVA/ZnO system: influencing pH, temperature and oxidant agents on dye solution. J Glob Pharma Technol 10(7):248–254

Ajayi IA, Oderinde RA, Kajogbola DO, Uponi JI (2006) Oil content and fatty acid composition of some underutilized legumes from Nigeria. Food Chem 99:115–120

Ajaz M, Shakeel S, Rehman A (2019) Microbial use for azo dye degradation-a strategy for dye bioremediation. Int Microbiol 23:149–158

Alane SK, Swami CS (2016) Antibacterial activity of plant extracts against *Xanthomonas axonopodis pv. Punicae* causing bacterial blight of pomegranate (*Punica granatum L.*). Biosci Discov 7:70–73

Al-Baldawi IA, Abdullah SRS, Anuar N, Hasan HA (2018) Phytotransformation of methylene blue from water using aquatic plant *(Azolla pinnata)*. Environ Technol Innov 11:15–22

Albrecht U, Fiehn O, Bowman KD (2016) Metabolic variations in different citrus rootstock cultivars associated with different responses to Huanglongbing. Plant Physiol Biochem 107:33–44

Aljeboree AM, Alshirifi AN, Alkaim AF (2017) Kinetics and equilibrium study for the adsorption of textile dyes on coconut shell activated carbon. Arab J Chem 10:3381–3393. https://doi.org/10.1016/j.arabjc.2014.01.020

AL-Juhaimi F, Ghafoor K (2013) Bioactive compounds, antioxidant and physico-chemical properties of juice from Lemon, Mandarin and Orange Fruits cultivated in Saudi Arabia. Pak J Bot 45(4):1193–1196

Al-Sum BA, Al-Arfaj AA (2013) Antimicrobial activity of the aqueous extract of mint plant. Sci J Clin Med 29:110–113

Alwared AI, Jaeel AJ, Ismail ZZ (2020) New application of eco-friendly biosorbent giant reed for removal of reactive dyes from water followed by sustainable path for recycling the dyes-loaded sludge in concrete mixes. J Mater Cycles Waste Manag 22:1036–1046

Ameta A, Ameta R, Ahuja M (2013) Photocatalytic degradation of methylene blue over ferric tungstate. Sci Rev Chem Commun 3(3):172–180

Arif MS, Malik SR (2017) Removal of dye from textile wastewater by electrolytic treatment. NFC IEFR J Eng Sci Res 5:1–5

Asghar Z, Ali W, Nasir A, Arshad A (2018) Atmospheric monitoring for ambient air quality parameters and source apportionment of city Faisalabad, Pakistan. Earth Sci Pak 2(1):1–4

Aslin SA (2014) Role of citrus fruits in health. J Pharm Sci Res 6:121–123

Augusto O, Miyamoto S (2011) Oxygen radicals and related species. Princ Free Radic Biomed 1:19–42

Axelsson J, Nilsson U, Terrazas E, Aliaga TA, Welander U (2006) Decolorization of the textile dyes Reactive Red 2 and Reactive Blue 4 using Bjerkandera sp. Strain BOL 13 in a continuous rotating biological contactor reactor. Enzyme Microb Technol 39(1):32–37

Babu SS, Mohandass C, Vijayaraj AS, Dhale MA (2015) Detoxification and color removal of Congo red by a novel Dietzia sp. (DTS26)–a microcosm approach. Ecotoxicol Environ Saf 114:52–60

Baeissa ES (2016) Photocatalytic degradation of malachite green dye using au/NaNbO3 nanoparticles. J Alloys Compd 672:564–570

Baltazar LM, Zamith-Miranda D, Burnet MC, Choi H, Nimrichter L, Nakayasu ES, Nosanchuk JD (2018) Concentration-dependent protein loading of extracellular vesicles released by Histoplasma capsulatum after antibody treatment and its modulatory action upon macrophages. Sci Rep 8(1):1–10

Baratto MC, Juarez-Moreno K, Pogni R, Basosi R, Vazquez-Duhalt R (2015) EPR and LC-MS studies on the mechanism of industrial dye decolorization by versatile peroxidase from Bjerkandera adusta. Environ Sci Pollut Res *22*(11):8683–8692

Bassindale AR, Brandstadt KF, Lane TH, Taylor PG (2003) Enzyme-catalysed siloxane bond formation. J Inorg Biochem 96(2–3):401–406

Bauer AW, Kirby WMM, Sherries JC, Tuck M (1966) Antibiotic susceptibility testing by a standardized disc diffusion method. Am J Clin Pathol 45:493–496

Bertani G (1951) 1951. Studies on Lysogenesis the mode of phage liberation by lysogenic *Escherichia coli*. J Bacteriol 62:293

Blanquez P, Casas N, Font X, Gabarrell X, Sarra M, Caminal G, Vicent T (2004) Mechanism of textile metal dye biotransformation by *Trametes versicolor*. Water Res 38:2166–2172

Bosco F, Mollea C, Ruggeri B (2017) Decolorization of Congo red by *Phanerochaete chrysosporium*: the role of biosorption and biodegradation. Environ Technol 38(20):2581–2588

Boucherit N, Abouseoud M, Adour L (2013) Degradation of direct azo dye by Cucurbita pepo free and immobilized peroxidase. J Environ Sci 25(6):1235–1244

Bové JM (2006) Huanglongbing: a destructive, newly-emerging, century-old disease of citrus. J Plant Pathol:7–37

Brillas E, Martínez-Huitle CA (2015) Decontamination of wastewaters containing synthetic organic dyes by electrochemical methods. An updated review. Appl Catal B Environ 166:603–643

Britto AJD, Gracelin DHS, Sebastian SR (2011) Antibacterial activity of a few medicinal plants against *Xanthomonas campestris* and *Aeromonas hydrophila*. J Biopesticides 4:57–60

Bruner VJ, Schreiner KM, Blair NE, Egerton L (2016) Chemical characterization of the degradation of necromass from four ascomycota fungi: implications for soil organic carbon turnover and storage. AGUFM 2016:B41D-0462

Budikania TS, Afriani K, Widiana I, Saksono N (2019) Decolorization of azo dyes using contact glow discharge electrolysis. J Environ Chem Eng 7(6):103466

Burt SA (2004) Essential oils: their antibacterial properties and potential applications in foods: review. Int J Food Microbiol 94:223–253

Carbonell-Caballero J, Alonso R, Ibañez V, Terol J, Talon M, Dopazo J (2015) A phylogenetic analysis of 34 chloroplast genomes elucidates the relationships between wild and domestic species within the genus citrus. Mol Biol Evol 32(8)

Chandanshive VV, Rane NR, Tamboli AS, Gholave AR, Khandare RV, Govindwar SP (2017) Co-plantation of aquatic macrophytes Typha angustifolia and Paspalum scrobiculatum for effective treatment of textile industry effluent. J Hazard Mater 338:47–56

Chandanshive VV, Kadam SK, Khandare RV, Kurade MB, Jeon BH, Jadhav JP, Govindwar SP (2018) In situ phytoremediation of dyes from textile wastewater using garden ornamental plants, effect on soil quality and plant growth. Chemosphere 210:968–976

Chen H, Hopper SL, Cerniglia CE (2005) Biochemical and molecular characterization of an azoreductase from *Staphylococcus aureus*, a tetrameric NADPH-dependent flavoprotein. Microbiology 151:1433–1441

Chequer FD, de Oliveira GAR, Ferraz ERA, Cardoso JC, Zanoni MB, de Oliveira DP (2013) Textile dyes: dyeing process and environmental impact. In: Eco-friendly textile dyeing and finishing. IntechOpen, London, pp 151–176

Chin EL, Mishchuk DO, Breska AP, Slupsky CM (2014) Metabolite signature of Candidatus Liberibacter asiaticus infection in two citrus varieties. J Agric Food Chem 62:6585–6591

Choi JW, Song HK, Lee W, Koo KK, Han C, Na BK (2004) Reduction of COD and colour of acid and reactive dyestuff wastewater using ozone. Korean J Chem Eng 21:398

Choudhury AKR (2018) Eco-friendly dyes and dyeing. Adv Mater Technol Environ 2:145–176

Correia VM, Stephenson T, Judd SJ (1994) Characterisation of textile wastewaters-a review. Environ Technol 15(10):917–929

Couto SR (2009) Dye removal by immobilised fungi. Biotechnol Adv 27(3):227–235

da Rocha Santana RM, Charamba LCV, do Nascimento GE, de Oliveira JGC, Sales DCS, Duarte MMMB, Napoleão DC (2019) Degradation of textile dyes employing advanced oxidative

processes: kinetic, equilibrium modeling, and toxicity study of seeds and bacteria. Water Air Soil Pollut 230(6):136

Dai R, Chen X, Xiang X, Wang Y, Wang F (2018) Understanding azo dye anaerobic bio-decolorization with artificial redox mediator supplement: considering the methane production. Bioresour Technol 249:799–808

De Castro MLFA, Abad MLB, Sumalinog DAG, Abarca RRM, Paoprasert P, de Luna MDG (2018) Adsorption of methylene blue dye and Cu (II) ions on EDTA-modified bentonite: isotherm, kinetic and thermodynamic studies. Sustain Environ Res 28(5):197–205

Desai PA, Kore VS (2011) Performance evaluation of effluent treatment plant for textile industry in Kolhapur of Maharashtra. Univers J Environ Res Technol 1(4):560–565

Devi LG, Kumar SG, Reddy KM, Munikrishnappa C (2009) Photo degradation of methyl Orange an azo dye by advanced fenton process using zero valent metallic iron: influence of various reaction parameters and its degradation mechanism. J Hazard Mater 164(2–3):459–467

Duthie G, Crozier A (2000) Plant-derived phenolic antioxidants. Curr Opin Lipidol 11:43–47

Dwivedi P, Tomar RS (2018) Bioremediation of textile effluent for degradation and decolourization of synthetic dyes: a review. Int J Curr Res Life Sci 7(04):1948–1951

Ekambaram SP, Perumal SS, Annamalai U (2016) Decolorization and biodegradation of remazol reactive dyes by *Clostridium* species. 3 Biotech 6:20

Ekambaram SP, Perumal SS, Rajendran D, Samivel D, Khan MN (2018) New approach of dye removal in textile effluent: a cost-effective management for cleanup of toxic dyes in textile effluent by water hyacinth. In: Toxicity and biodegradation testing. Humana Press, New York, pp 241–267

El Hassani K, Kalnina D, Turks M, Beakou BH, Anouar A (2019) Enhanced degradation of an azo dye by catalytic ozonation over Ni-containing layered double hydroxide nanocatalyst. Sep Purif Technol 210:764–774

Elisangela F, Andrea Z, Fabio DG, de Menezes Cristiano R, Regina DL, Artur CP (2009) Biodegradation of textile azo dyes by a facultative Staphylococcus arlettae strain VN-11 using a sequential microaerophilic/aerobic process. Int Biodeterior Biodegradation 63 (3):280–288

Ellmore GS, Feldberg RS (1994) *Alliin lyase* localization in bundle sheaths of Garlic cloves (*Allium sativum Linn*). Am J Bot 81:89–94

Enayatizamir N, Tabandeh F, Rodríguez-Couto S, Yakhchali B, Alikhani HA, Mohammadi L (2011) Biodegradation pathway and detoxification of the diazo dye reactive black 5 by *Phanerochaete chrysosporium*. Bioresour Technol 102(22):10359–10362

Ezejiofor TN, Eke NV, Okechukwu RI, Nwoguikpe RN, Duru CM (2011) Waste to wealth: industrial raw materials potential of peels of Nigerian sweet orange (*Citrus sinensis*). Afr J Biotechnol 10:6257–6264

Fancy SA, Rumpel K (2008) GC-MS-based metabolomics. In: Biomarker methods in drug discovery and development. Humana Press, pp 317–340

Faria PCC, Órfão JJM, Pereira MFR (2008) Activated carbon catalytic ozonation of oxamic and oxalic acids. Appl Catal B Environ 79(3):237–243

Ferdes M, Voicu G, Dinca M (2019) Chlorella vulgaris. Biotechnol Lett 24(6):953–960

Gabarrell X, Font M, Vicent T, Caminal G, Sarrà M, Blánquez P (2012) A comparative life cycle assessment of two treatment technologies for the Grey Lanaset G textile dye: biodegradation by Trametes versicolor and granular activated carbon adsorption. Int J Life Cycle Assess 17 (5):613–624

Gao J, Wang X, Hu Z, Deng H, Hou J, Lu X, Kang J (2003) Plasma degradation of dyes in water with contact glow discharge electrolysis. Water Res 37(2):267–272

Garg SK, Tripathi M (2017) Microbial strategies for discoloration and detoxification of azo dyes from textile effluents. Res J Microbiol 12:1–9

Ghanbari F, Moradi M (2016) Electrooxidation processes for dye degradation and colored wastewater treatment. CRC Press LLC, London

Ghosh S, Chowdhury R, Bhattacharya P (2016) Mixed consortia in bioprocesses: role of microbial interactions. Appl Microbiol Biotechnol 100(10):4283–4295

Gomi N, Yoshida S, Matsumoto K, Okudomi M, Konno H, Hisabori T, Sugano Y (2011) Degradation of the synthetic dye amaranth by the fungus *Bjerkandera adusta* Dec 1: inference of the degradation pathway from an analysis of decolorized products. Biodegradation 22 (6):1239–1245

Gou M, Qu Y, Zhou J, Ma F, Tan L (2009) Azo dye decolorization by a new fungal isolate, *Penicillium sp.* QQ and fungal-bacterial cocultures. J Hazard Mater 170:314–319

Goulas V, Manganaris GA (2012) Exploring the phytochemical content and the antioxidant potential of Citrus fruits grown in Cyprus. Food Chem 131:39–47

Guo Y, Chang X, Zhu C, Zhang S, Li X, Fu H, Lai Z (2019) De novo transcriptome combined with spectrophotometry and gas chromatography-mass spectrometer (GC-MS) reveals differentially expressed genes during accumulation of secondary metabolites in purple-leaf tea (*Camellia sinensis*). J Hortic Sci Biotechnol *94*:349–367

Gupta VK, Suhas S (2009) Application of low cost adsorbents for dye removal- a review. J Environ Manag 90:2313–2342

Gutowska A, Czaplińska JK, Jóźwiak WK (2006) Degradation mechanism of reactive orange 113 dye by H_2O_2/Fe^{2+} and ozone in aqueous solution. Dyes Pigments 74(1):41–46

Haghshenas H, Kay M, Dehghanian F (2016) Molecular dynamics study of biodegradation of azo dyes via their interactions with AzrC azoreductase. J Biomol Struct Dyn 34(3):453–462

Harborne JB (1973) Phytochemical methods. Chapman and Hall, Ltd., London, pp 49–188

Hasanbeigi A, Price L (2012) A review of energy use and energy efficiency technologies for the textile industry. Renew Sust Energ Rev 16(6):3648–3665

Hayat H, Mahmood Q, Pervez A (2015) Comparative decolorization of dyes in textile wastewater using biological and chemical treatment. Sep Purif Technol 154:149–153

He S (2018) Innovative solutions for wastewater treatment: case of China. In: IAEA technical cooperation programme: sixty years and beyond-contributing to development. Proceedings of an international conference. Companion CD-ROM

Holkar CR, Jadhav AJ, Pinjari DV, Mahamuni NM, Pandit AB (2016) A critical review on textile wastewater treatments: possible approaches. J Environ Manag 182:351–366

Hossain K, Quaik S, Ismail N, Rafatullah M, Avasan M, Shaik R (2016) Bioremediation and detoxification of the textile wastewater with membrane bioreactor using the white-rot fungus and reuse of wastewater. Iran J Biotechnol 14(3):154–162

Hughes BG, Lawson LD (1991) Antimicrobial effects of *Allium sativum* (garlic), *Allium ampeloprasum* (elephant garlic), and *Allium cepa* (onion), garlic compounds and commercial garlic supplement products. Phytother Res 5(4):154–158

IARC Working Group on the Evaluation of Carcinogenic Risk to Humans (2010) General introduction to the chemistry of dyes. In: Some aromatic amines, organic dyes, and related exposures, IARC monographs on the evaluation of carcinogenic risks to humans, no. 99. International Agency for Research on Cancer, Lyon. https://www.ncbi.nlm.nih.gov/books/NBK385442/

Iftikhar I, Khan A, Rashid A, Mughal SM, Iqbal Z, Batool A, Abbas M, Khan MM, Muhammad S, Jaksani MJ (2009) Occurrence and distribution of *Citrus Tristeza Clostero virus* in the Punjab and NWFP, Pakistan. Pak J Bot 41(1):373–380

Ilyas S, Sultan SS, Rehman A (2012) Decolourization and degradation of azo dye, Synozol red HF6BN, by Pleurotus ostreatus. Afr J Biotechnol 11(88):15422–15429

Imran M, Negm F, Hussain S (2016) Characterization and purification of membrane-bound azoreductase from azo dye degrading *Shewanella* sp. strain IFN4. CLEAN Soil Air Water 44 (11):1523–1530

Imron MF, Kurniawan SB, Soegianto A, Wahyudianto FE (2019) Phytoremediation of methylene blue using duckweed (Lemna minor). Heliyon 5(8):2206

Ismail M, Akhtar K, Khan MI, Kamal T, Khan MA, M Asiri A, Khan SB (2019) Pollution, toxicity and carcinogenicity of organic dyes and their catalytic bio-remediation. Curr Pharm Des 25 (34):3645–3663

Jain S (2010) Indian textile industry: a growth perspective. A presentation in Singapore

Javed N, Ahmad R, Anwar SA, Javed M. Zia, A. 2007. Citrus diseases and their management. International Symposium on Prospects of Horticultural Industry in Pakistan, 28–30th March, 2007. Institute of Horticultural Science, University of Agriculture, Faisalabad

Jayalakshmi R, Jeyanthi J (2019) Simultaneous removal of binary dye from textile effluent using cobalt ferrite-alginate nanocomposite: performance and mechanism. Microchem J 145:791–800

Jichao Y (2010) Textile industry development and science & technology innovation in China. Cotton Text Technol 1(002):7–11

Kagalkar AN, Jagtap UB, Jadhav JP, Bapat VA, Govindwar SP (2009) Biotechnological strategies for phytoremediation of the sulfonated azo dye direct red 5B using Blumea malcolmii hook. Bioresour Technol 100(18):4104–4110

Kapdan IK, Kargi F (2002) Simultaneous biodegradation and adsorption of textile dyestuff in an activated sludge unit. Process Biochem 37(9):973–981

Karnwal A, Singh S, Kumar V, Sidhu GK, Dhanjal DS, Datta S, Singh J (2019) Fungal enzymes for the textile industry. In: Recent advancement in white biotechnology through fungi. Springer, Cham, pp 459–482

Kausar A, Iqbal M, Javed A, Aftab K, Bhatti HN, Nouren S (2018) Dyes adsorption using clay and modified clay: a review. J Mol Liq 256:395–407

Kell D, Brown M, Davey H, Dunn W, Spasic I, Oliver S (2005) Metabolic foot printing and systems biology: the medium is the message. Nature Rev Microbiol AOP, 9

Khamparia S, Jaspal D (2017) Study of decolorisation of binary dye mixture by response surface methodology. J Environ Manag 201:316–326

Khan AA, Khan M (2010) Pakistan textile industry facing new challenges. Res J Int Stud 14 (14):21–29

Khataee AR, Vafaei F, Jannatkhah M (2013) Biosorption of three textile dyes from contaminated water by filamentous green algal Spirogyra sp.: kinetic, isotherm and thermodynamic studies. Int Biodeter Biodegr 83:33–40

Kiefl J, Kohlenberg B, Hartmann A, Obst K, Paetz S, Krammer GE et al (2018) Investigation on key molecules of Huanglongbing (HLB)-induced orange juice off-flavor. J Agric Food Chem 66:2370–2377

Killiny N (2017) Metabolite signature of the phloem sap of fourteen citrus varieties with different degrees of tolerance to *Candidatus Liberibacter asiaticus*. Physiol Mol Plant Pathol *97*:20–29

Kiran S, Nosheen S, Abrar S, Javed S, Aslam N, Afzal G, Ijaz F (2019) Remediation of textile effluents via physical and chemical methods for a safe environment. In: Textiles and clothing. Scrivener Publishing, Beverly, MA, pp 191–234

Kooh MR, Lim LB, Lim LH, Dhari MK (2016) Phytoremediation capability of Azolla pinnata for the removal of malachite green from aqueous solution. J Environ Biotechnol Res 5(1):10–17

Koyani RD, Sanghvi GV, Sharma RK, Rajput KS (2013) Contribution of lignin degrading enzymes in decolourisation and degradation of reactive textile dyes. Int Biodeter Biodegr 77:1–9

Kumar MA, Baskaralingam P, Aathika ARS, Sivanesan S (2018) Role of bacterial consortia in bioremediation of textile recalcitrant compounds. In: Waste bioremediation. Springer, Singapore, pp 165–183

Laszlo JA (1995) Electrolyte effects on hydrolyzed reactive dye binding to quaternized cellulose. Textile Chem Color 27(4):25

Lee AH, Jang Y, Kim GH, Kim JJ, Lee SS, Ahn BJ (2017) Decolorizing an anthraquinone dye by Phlebia brevispora: intra-species characterization. Eng Life Sci 17(2):125–131

Leksomboon C, Thaveechai N, Kositratana W (2001) Potential of plant extracts for controlling citrus canker of lime. Kasetsart J (Nat Sci) 35(4):392–396

Lema JM, Omil F (2001) Anaerobic treatment: a key technology for a sustainable management of wastes in Europe. Water Sci Technol 44(8):133–140

Liu Y, Heying E, Tanumihardjo SA (2012) Histroy, global distribution, and nutritional importance of citrus fruits. Compr Rev Food Sci Food Saf 11:530–545

Mahmood S, Mahmood S, Mahmood S (2014) Adsorption/desorption of Direct Yellow 28 on apatitic phosphate: mechanism, kinetic and thermodynamic studies. J Assoc Arab Univ Basic Appl Sci 16(1):64–73

Malik N, Maan AA, Pasha TS, Akhtar S, Ali T (2010) Role of hazard control measures in occupational health and safety in the textile industry of Pakistan. Pak J Agric Sci 47(1):72–76

Malik ZH, Ravindran KC, Sathiyaraj GANESAN (2017) Phytoremediation: a novel strategy and eco-friendly green technology for removal of toxic metals. Int J Agric Environ Res 3(1):1–18

Meziane M, Goumri H (2014) The antimicrobial effect of extracts of *Melia Azedarach* on some pathogenic micro-organisms. Int J Appl Nat Sci 3(4):173–180

Misal SA, Gawai KR (2018) Azoreductase: a key player of xenobiotic metabolism. Bioresour Bioprocess 5(1):1–9

Misal SA, Humne VT, Lokhande PD, Gawai KR (2015) Biotransformation of nitro aromatic compounds by flavin-free NADH-azoreductase. J Bioremed Biodegr 6:2–6

Mostafa M (2015) Waste water treatment in textile industries-the concept and current removal technologies. J Biodivers Environ Sci 7(1):501–525

Mousset E, Oturan N, Oturan MA (2018) An unprecedented route of OH radical reactivity evidenced by an electrocatalytical process: ipso-substitution with perhalogenocarbon compounds. Appl Catal B Environ 226:135–146

Movafeghi A, Khataee AR, Torbati S, Zarei M, Lisar SSY (2013) Bioremoval of C.I. basic red 46 as an azo dye from contaminated water by Lemna minor L.: modeling of key factor by neural network. Environ Prog Sustain Energy 32(4):1082–1089

Mukherjee A, Khandker S, Islam MR, Shahid SB (2011) Efficacy of some plant extracts on the Mycelial growth of *Colleto trichumgloeosporioides*. J Bangladesh Agric Univ 9:43–47

Muneer T, Maubleu S, Asif M (2006) Prospects of solar water heating for textile industry in Pakistan. Renew Sust Energ Rev 10(1):1–23

Muthusamy S, Govindaraj D, Rajendran K (2018) Phytoremediation of textile dye effluents. In: Bioremediation: applications for environmental protection and management. Springer, Singapore, pp 359–373

Nassar MM, Magdy YH (1997) Removal of different basic dyes from aqueous solutions by adsorption on palm-fruit bunch particles. Chem Eng J 66(3):223–226

Nassar MY, Mohamed TY, Ahmed IS, Samir I (2017) MgO nanostructure via a sol-gel combustion synthesis method using different fuels: an efficient nano-adsorbent for the removal of some anionic textile dyes. J Mol Liq 225:730–740

Neycee MA, Nematzadeh GHA, Dehestani A, Alavi M (2012) Evaluation of antibacterial effects of Chinaberry (Melia azedarach) against gram-positive and gram-negative bacteria. 4(11):709–712

Ng CWW, Tasnim R, Capobianco V, Coo JL (2018) Influence of soil nutrients on plant characteristics and soil hydrological responses. Geotech Lett 8(1):19–24

Nilratnisakorn S, Thiravetyan P, Nakbanpote W (2008) Synthetic reactive dye wastewater treatment by narrow-leaved cattail: studied by XRD and FTIR. Asian J Energy Environ 9:231–252

Novotný Č, Trošt N, Šušla M, Svobodová K, Mikesková H, Válková H, Pavko A (2012) The use of the fungus Dichomitus squalens for degradation in rotating biological contactor conditions. Bioresour Technol 114:241–246

Okwu DE (2008) Citrus fruits: a rich source of phytochemicals and their role in human health. Int J Chem Sci 6(2):451–471

O'Neill C, Hawkes FR, Hawkes DL, Lourenço ND, Pinheiro HM, Delée W (1999) Colour in textile effluents–sources, measurement, discharge consents and simulation: a review. J Chem Technol Biotechnol Int Res Process Environ Clean Technol 74(11):1009–1018

Ortuno AA, Baidez P, Gomez MC, Arcas I, Porras AG, Del Rio JA (2006) *Citrus paradisi* and *Citrus sinensis* flavonoids: their influence in the defence mechanism against *Penicillium digitatum*. Food Chem J 98(2):351–358

Pande LM (2019) Enhanced adsorption capacity of designed bentonite and alginate beads for the effective removal of methylene blue. Appl Clay Sci 169:102–111
Parshetti GK, Chowdhury S, Balasubramanian R (2014) Hydrothermal conversion of urban food waste to chars for removal of textile dyes from contaminated waters. Bioresour Technol 161:310–319
Patil AV, Jadhav JP (2013) Evaluation of phytoremediation potential of Tagetes patula L. for the degradation of textile dye reactive blue 160 and assessment of the toxicity of degraded metabolites by cytogenotoxicity. Chemosphere 92(2):225–232
Paula BMD, Raithore S, Manthey JA, Baldwin EA, Bai J, Zhao W, Plotto A (2018) Active taste compounds in juice from oranges symptomatic for Huanglongbing (HLB) citrus greening disease. LWT 91:518–525
Peng L, Zhang Y, Wang Y, Zeng X, Peng N, Yu A (2015) Energy efficiency and influencing factor analysis in the overall Chinese textile industry. Energy 93:1222–1229
Perez-Cacho PR, Rouseff RL (2008) Fresh squeezed orange juice odor: a review. Crit Rev Food Sci Nutr *48*(7):681–695
Pilon-Smits E (2005) Phytoremediation. Annu Rev Plant Biol 56:15–39
Plotto A, Baldwin E, McCollum G, Manthey J, Narciso J, Irey M (2010) Effect of Liberibacter infection (Huanglongbing or "Greening" disease) of citrus on orange juice flavor quality by sensory evaluation. J Food Sci *75*(4):220–230
Punj S, John GH (2009) Purification and identification of an FMN-dependent NAD(P)H azoreductase from *Enterococcus faecalis*. Curr Issues Mol Biol 11:59–66
Qi J, Paul CE, Hollmann F, Tischler D (2017) Changing the electron donor improves azoreductase dye degrading activity at neutral pH. Enzym Microb Technol 100:17–19. https://doi.org/10.1016/j.enzmictec.2017.02.003
Raichurkar P, Ramachandran M (2015) Recent trends and developments in textile industry in India. Int J Text Eng Process 1(4):47–50
Ramachandran P, Sundharam R, Palaniyappan J, Munusamy AP (2013) Potential process implicated in bioremediation of textile effluents: a review. Adv Appl Sci Res 4(1):131–145
Ramírez-Montoya LA, Hernández-Montoya V, Montes-Morán MA, Jáuregui-Rincón J, Cervantes FJ (2015) Decolorization of dyes with different molecular properties using free and immobilized laccases from Trametes versicolor. J Mol Liq 212:30–37
Rane NR, Chandanshive VV, Watharkar AD, Khandare RV, Patil TS, Pawar PK, Govindwar SP (2015) Phytoremediation of sulfonated Remazol red dye and textile effluents by Alternanthera philoxeroides: an anatomical, enzymatic and pilot scale study. Water Res 83:271–281
Rani B, Kumar V, Singh J, Bisht S, Teotia P, Sharma S, Kela R (2014) Bioremediation of dyes by fungi isolated from contaminated dye effluent sites for bio-usability. Braz J Microbiol 45 (3):1055–1063. https://doi.org/10.1590/s1517-83822014000300039
Rao MJ, Ding F, Wang N, Deng X, Xu Q (2018) Metabolic mechanisms of host species against citrus Huanglongbing (greening disease). Crit Rev Plant Sci 37(6):496–511
Rather LJ, Akhter S, Hassan QP (2018) Bioremediation: green and sustainable technology for textile effluent treatment. In: Sustainable innovations in textile chemistry and dyes. Springer, Singapore, pp 75–91
Rishi K, Singh R (2003) Chemical components and insecticidal properties of Bakain (*Melia azedarach L.*) – a review. Agric Rev 24(2):101–115
Royer B, Cardoso NF (2009) Applications of Brazilian pine-fruit shell in natural and carbonized forms as adsorbents to removal of methylene blue from aqueous solutions-kinetic and equilibrium study. J Hazard Mater 164(2–3):1213–1222
Saeed M, Ahmad A, Boddula R, ul Haq A, Azhar A (2018) Ag and MnO: an effective catalyst for photo-degradation of rhodamine B dye. Environ Chem Lett 16(1):287–294
Saksono N, Nugraha I, Gozan M, Bismo S (2014) Plasma formation energy and hydroxyl production on contact glow discharge electrolysis. Int J Arts Sci 7(3):71
Saksono N, Sukreni T, Naibaho AL, Bismo S (2018) Effect of direct air injection through anode in plasma electrolysis process for batik dye wastewater treatment. E3S Web Conf 67:01008

Salokhe MD, Govindwar SP (1999) Effect of carbon source on the biotransformation enzymes in Serratia marcescens. World J Microbiol Biotechnol 15(2):229–232
Santos GC, Forss J, Welander U, Corso CR (2016) Redox mediator evaluation in the azo dye biodegradation. In: Microbes in the spotlight: recent progress in the understanding of beneficial and harmful microorganisms. BrownWalker, Boca Raton, p 126
Schück M, Greger M (2020) Screening the capacity of 34 wetland plant species to remove heavy metals from water. Int J Environ Res Public Health 17(13):4623
Sen SK, Raut S, Bandyopadhyay P, Raut S (2016) Fungal decolouration and degradation of azo dyes: a review. Fungal Biol Rev 30(3):112–133
Shahid M, Islam S, Mohammad F (2013) Recent advancements in natural dye applications: a review. J Clean Prod 53:310–331
Shahid A, Singh J, Bisht S, Teotia P, Kumar V (2014a) Biodegradation of textile dyes by fungi isolated from North Indian field soil. Environ Asia 6(2):51–57
Shahid M, Farrukh MA, Umar AA, Khaleeq-ur-Rahman M (2014b) Solvent controlled synthesis of CaO-MgO nanocomposites and their application in the photodegradation of organic pollutants of industrial waste. Russ J Phys Chem A 88(5):836–844
Shahnah SM, Ali S, Ansari H, Bagri P (2007) New Sequiterpene derivative from fruit peel of *Citrus Limo (Linn) Burn*. Aust J Pharm Sci 75:165–170
Sharma M, Dhiman R (2016) Determinants affecting Indian textile exports: a review. Biz Bytes J Manag Technol 6:193–199
Siddiqui S (2014) Evaluation of anti-bacterial activity of local flora of Bundelkhand region of Jhansi-India against plant pathogenic bacteria *Xanthomonas campestris pv. Campestris*. J Exp Biol Agric Sci 2(2)
Singh RP, Singh PK, Singh RL (2017) Role of azoreductases in bacterial decolorization of azo dyes. Toxicol Int 21(2):160–166
Song Z, Song L, Shao Y, Tan L (2018) Degradation and detoxification of azo dyes by a salt-tolerant yeast *Cyberlindnera samutprakarnensis* S4 under high-salt conditions. World J Microbiol Biotechnol 34(9):131
Stoyanova M, Konova P, Nikolov P, Naydenov A, Mehandjiev D (2006) Alumina-supported nickel oxide for ozone decomposition and catalytic ozonation of CO and VOCs. Chem Eng J 122 (1–2):41–46
Sukanya SL, Sudisha J, Haripasand P, Niranjana SR, Prakash HS, Fathima SK (2009) Antimicrobial activity of leaf extracts of Indian medicinal plants against clinical and phyto-pathogenic bacteria. Afr J Biotechnol 8(23):6677–6682
Sun YL, Kang HM, Han SO, Park YC, Hong SW (2015) Taxonomy and phylogeny of the genus citrus based on the nuclear ribosomal DNA its region sequence. Pak J Bot 47(1):95–101
Suresh K, Deepa P, Harisaranraj R, Vaira AV (2008) Antimicrobial and phytochemical investigation of the leaves of *Carica papaya L.*, *Cynodon dactylon L. Pers.*, *Euphorbia Hirta L.*, *Melia azedarach L.* and *Psidium guajava L. Ethnobotanical Leaflets* 12:1184–1191
Suzuki H (2019) Remarkable diversification of bacterial azoreductases: primary sequences, structures, substrates, physiological roles, and biotechnological applications. Appl Microbiol Biotechnol 103:3965–3978. https://doi.org/10.1007/s00253-019-09775-2
Swallah MS, Sun H, Affoh R, Fu H, Yu H (2020) Antioxidant potential overviews of secondary metabolites (polyphenols) in fruits. Int J Food Sci 2020
Sweety VS, Kumar M, Sharma S, Kumar V, Garg SK (2017) Mycoremediation of textile dyes: application of novel autochthonous fungal isolates. Environ Asia 10(2):147–161
Tan IAW, Ahmad AL, Hameed BH (2008) Adsorption of basic dye using activated carbon prepared from oil palm shell: batch and fixed bed studies. Desalination 225(1–3):13–28
Tan L, Ning S, Zhang X, Shi S (2013) Aerobic decolorization and degradation of azo dyes by growing cells of a newly isolated yeast *Candida tropicalis* TL-F1. Bioresour Technol 138:307–313
Tara N, Siddiqui SI, Rathi G, Chaudhry SA, Asiri AM (2020) Nano-engineered adsorbent for the removal of dyes from water: a review. Curr Anal Chem 16(1):14–40

Tarkwa JB, Oturan N, Acayanka E, Laminsi S, Oturan MA (2019) Photo-Fenton oxidation of Orange G azo dye: process optimization and mineralization mechanism. Environ Chem Lett 17(1):473–479

Tipu MMH, Rahman MM, Islam MM, Elahi FE, Jahan R, Islam MR (2020) Citrus greening disease (HLB) on Citrus reticulata (Mandarin) caused by Candidatus Liberibacter asiaticus in Bangladesh. Physiol Mol Plant Pathol 112:101558

Uday USP, Bandyopadhyay TK, Bhunia B (2016) Bioremediation and detoxification technology for treatment of dye (s) from textile effluent. Text Wastewater Treat 4:75–92

Vafaei F, Movafeghi A, Khataee AR, Zarei M, Lisar SS (2013) Potential of Hydrocotyle vulgaris for phytoremediation of a textile dye: inducing antioxidant response in roots and leaves. Ecotoxicol Environ Saf 93:128–134

Vantamuri AB, Kaliwal BB (2016) Purification and characterization of laccase from Marasmius species BBKAV79 and effective decolorization of selected textile dyes. 3 Biotech 6:189–198

Vilaseca M, Gutie MC, Grimau VL, Mesas ML, Crespi M (2010) Biological treatment of a textile effluent after electrochemical oxidation of reactive dyes. Water Environ Res 82:176–181

Wang X, Su D, Li HB (2011) Treatment of textile dye wastewater by electrocoagulation method. Adv Mater Res 281:276–279

Warnert J (2012) Asian citrus psyllid and huanglongbing disease threaten California citrus. Calif Agric *66*(4):127–130

Watharkar AD, Kadam SK, Khandare RV, Kolekar PD, Jeon BH, Jadhav JP, Govindwar SP (2018) Asparagus densiflorus in a vertical subsurface flow phytoreactor for treatment of real textile effluent: a lab to land approach for in situ soil remediation. Ecotoxicol Environ Saf 161:70–77

Xiao J, Lv W, Xie Z, Tan Y, Song Y, Zheng Q (2016) Environmentally friendly reduced graphene oxide as a broad-spectrum adsorbent for anionic and cationic dyes via π–π interactions. J Mater Chem A 4(31):12126–12135

Xu BM, Baker GL, Sarnoski PJ, Goodrich-Schneider RM (2017) A comparison of the volatile components of cold pressed Hamlin and Valencia (*Citrus sinensis* (L.) Osbeck) orange oils affected by Huanglongbing. J Food Qual 2017

Xu H, Yang B, Liu Y, Li F, Shen C, Ma C, Sand W (2018) Recent advances in anaerobic biological processes for textile printing and dyeing wastewater treatment: a mini-review. World J Microbiol Biotechnol 34(11):165

Yang X, Zheng J, Lu Y, Jia R (2016) Degradation and detoxification of the triphenylmethane dye malachite green catalyzed by crude manganese peroxidase from *Irpex lacteus* F17. Environ Sci Pollut Res 23(10):9585–9597

Yang L, Qian Y, Zhou X (2019) Current status of textile industry wastewater treatment in China: a mini review. In: Minimisation of wastewater emissions from textile finishing industries. Vulkan Verlag GmbH, Essen, p 23

Yao L, Yu Q, Huang M, Hung W, Grosser J, Chen S, Gmitter FG (2019) Proteomic and metabolomic analyses provide insight into the off-flavour of fruits from citrus trees infected with '*Candidatus Liberibacter asiaticus*'. Horticulture Res 6(1):1–13

Yesilada O, Birhanli E, Geckil H (2018) Bioremediation and decolorization of textile dyes by white rot fungi and laccase enzymes. In: Prasad R (ed) Mycoremediation and environmental sustainability. Fungal biology. Springer, Cham

Zahid M, Bhatti IA, Adeel S, Saba S (2017) Modification of cotton fabric for textile dyeing: industrial mercerization versus gamma irradiation. J Text Inst 108(2):287–292

Zainah, Saksono N (2017) Degradation of textile dyes Remazol brilliant blue using plasma electrolysis method with the addition of microbubble and Fe^{2+} ion. In: AIP conference proceedings, vol 1904. AIP Publishing, Melville, NY, p 020028

Ziarani GM, Moradi R, Lashgari N, Kruger HG (2018) Metal-free synthetic organic dyes. Elsevier

Remediation of Toxic Environmental Pollutants Using Nanoparticles and Integrated Nano-Bio Systems

19

Amrita Kharangate-Lad and Nezlyn Cressida D'Souza

Abstract

Rapid industrialization and urbanization have led to the release of many toxic contaminants in the environment. Environmental pollution is a major concern as it affects health and well-being of all organisms. The toxicity and health hazards associated with the environmental pollutants requires clean-up from the soil and water. Remediation using nanotechnology is an effective alternative to conventional physicochemical methods as it is eco-friendly and economical. In this chapter we emphasize the use of nanoparticles in the remediation of toxic environmental pollutants such as heavy metals, hydrocarbons, antibiotics, hormones, dyes, and recalcitrant agro-based and organohalide compounds. Nanoparticles are synthesized biogenically which involves its synthesis using plants and microorganisms. Nanobioremediation is a technology that integrates microbial bioremediation and nanoremediation. This chapter provides a brief outlook on applications of nanobioremediation through integrated nano-bio systems in removal of organic or inorganic toxic pollutants and discusses the implications of using these integrated systems on a larger scale. The benefit of this collaboration is the development of more efficient, cost-effective, environmentally friendly solutions in remediation of toxic environmental pollutants.

Keywords

Nanoparticles · Microbes · Synthesis · Toxic pollutants · Remediation

A. Kharangate-Lad (✉)
Department of Biochemistry, School of Chemical Sciences, Goa University, Goa, India

N. C. D'Souza
Department of Post Graduate Studies in Food Technology, Carmel College of Arts, Science and Commerce, Goa, India

© The Author(s), under exclusive licence to Springer Nature Singapore Pte Ltd. 2021

V. Kumar et al. (eds.), *Rhizobiont in Bioremediation of Hazardous Waste*,
https://doi.org/10.1007/978-981-16-0602-1_19

19.1 Introduction

Environmental pollution is undeniably a major issue that the society faces. The environment gets polluted with toxic compounds released due to industrialization and unplanned urbanization. Toxic pollutants like heavy metals, particulate matter, industrial effluents, sewage, pesticides, fertilizers, oil spills, and other organic compounds are a few examples of environmental pollutants. The use of conventional physical and chemical technologies in the treatment of contaminated soils and water is expensive as they have high energy requirements and usually leave behind hazardous waste residues. Therefore, cost-effective bioremediation technologies that use microorganisms to detoxify and transform pollutants have been developed for the treatment of polluted soils and water (Abatenh et al. 2017; Kumar et al. 2018; Tomei and Daugulis 2013). Another technology that is being explored currently is the use of nanoparticles in cleaning up toxic pollutants from contaminated sites. Nanoparticles have highly desirable properties that favour their application in remediation of recalcitrant pollutants from soil and water.

19.2 Properties of Nanoparticles

Nanoparticles possess unique physicochemical properties and therefore, nanotechnology has gained a lot of attention in the last decade. Nanoparticles are nanoscopic particles having dimensions within the range of 1–100 nm. Due to their nanoscale size these particles exhibit exceptional physicochemical properties such as high energy, large specific surface area, and unique visible properties (Fig. 19.1). Nanoparticles by virtue of their small size have properties that differ from the bulk metal. They exhibit physical and chemical properties that are a virtue of their nano-size. The nano-size of the particles imparts them with unique chemical properties such as large surface per unit area and high reactivity. Nanoparticles exhibit plasmon resonance as owing to their small size they have the ability to confine their electrons and produce quantum effects. The media used in the synthesis of nanoparticles and the number of bioactive compounds present in the media directly influence the chemical and morphological properties of nanoparticles (Yadav et al. 2017).

Based on the chemistry, the nanoparticles are broadly classified into organic and inorganic. Organic nanoparticles include carbon nanoparticles (like carbon nanotubes (CNT)), while inorganic nanoparticles include metals (such as nanoscale zerovalent iron (nZVI), palladium, cadmium), noble metals (gold and silver), semiconductors (copper, zinc oxide, and titanium oxide), and magnetic nanoparticles (maghemite, magnetite) (Guerra et al. 2018).

Nanoparticles have different ways of interacting with each other, some tend to remain as individual moieties, while others tend to group together, depending upon the attractive or repulsive forces acting between them. Agglomeration of nanoparticles is often linked with oxidation-induced-instability, which leads to decrease in the surface area and reactivity of the particles. Coating of nanoparticle with suitable stabilizers increases their adsorbing capacity while decreasing their

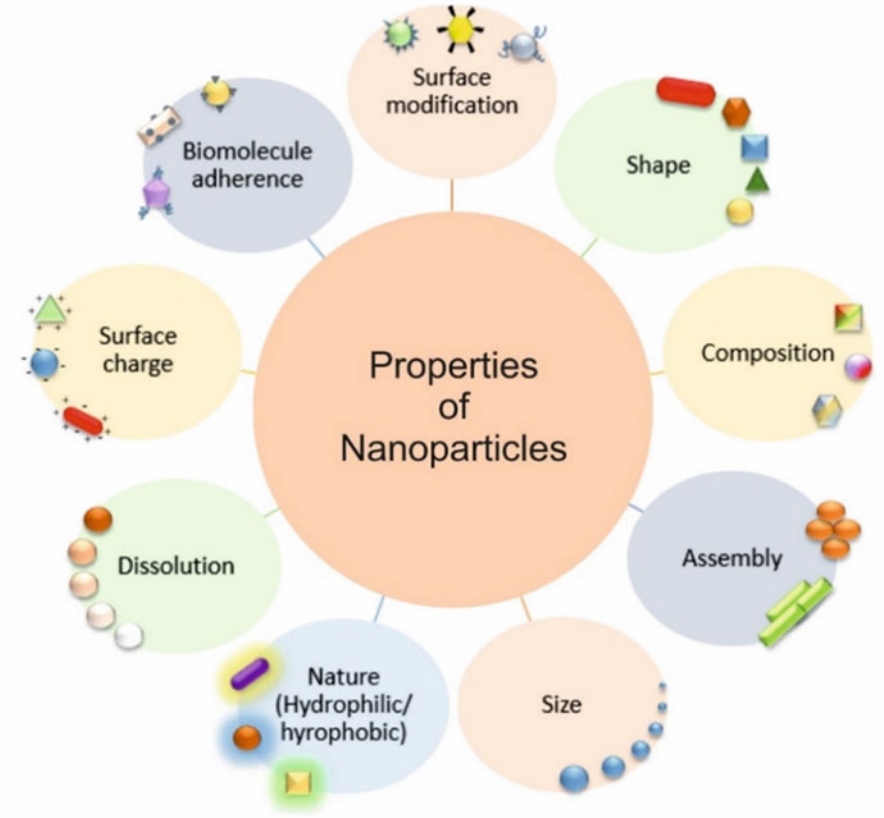


Fig. 19.1 Properties of nanoparticles

tendency to agglomerate. Immobilization with organic polymers such as lactate, gaur gum, gellan gum, etc. enhances their interaction with the toxic compounds by improving nanoparticle mobility, stability, and reactivity. Nanoparticles can be designed to exhibit specific physical properties and chemical composition in order to target specific pollutants (Sakulchaicharoen et al. 2010).

19.3 Nanoparticles and Nanomaterials

Morphologically, nanoparticles can be spheres, sheets, cylinders, and tubes (Pal et al. 2019). However, they differ from nanomaterials owing to their dimensions. Nanomaterials have been defined as "a manufactured or natural material that possesses unbound, aggregated, or agglomerated particles where external dimensions are between 1 and 100 nm size range", according to the EU Commission (Jeevanandam et al. 2018). Nanomaterials therefore have a length of 1–1000 nm in at

least one dimension. Based on the shape, size, structure, and composition, nanomaterials can be classified into nanoclusters, nanofibres, nanotubes, nanoshells, and nanocomposites.

Nanomaterials have successfully demonstrated their ability to degrade environmental pollutants from soil and ground/surface water. Metal-based nanomaterials composed of silver (Ag) nanoparticles have been used for disinfection of water and soil from *Escherichia coli* and *Pseudomonas aeruginosa*. Titanium dioxide (TiO_2) nanoparticles have been proven efficient against *Escherichia coli,* MS-2 phage and hepatitis B virus. Other titanium-based nanoparticles have been reportedly used for remediation of aromatic hydrocarbons (phenanthrene), chlorinated compounds (2-chlorophenol), organic pollutants (endotoxins), microorganisms (*Escherichia coli* and *Staphylococcus aureus*), dyes (Rhodamine B), and biological nitrogen (nitric oxide) (Guerra et al. 2018). Binary mixed oxides, iron nanoparticles, and bimetallic nanoparticles have been used for the treatment of water containing methylene blue, heavy metals, and chlorinated and brominated compounds, respectively (Jeevanandam et al. 2018). Due to their minute size and surface properties, they can enter very small spaces in the soil and attain access to contaminants well below the subsurface level. Since movement of these nanoparticles is governed by Brownian motion, they can remain suspended in groundwater facilitating wider transport of the particles and more efficient interaction with the contaminant (Tratnyek and Johnson 2006).

19.4 Synthesis of Nanoparticles

The modification of surface properties of the nanoparticle improves its interaction and compatibility with the pollutant of interest. Nanoparticles, in general, are synthesized using two approaches: top-down and bottom-up. The top-down approach centres on gradual degradation of bulk materials to nanosized particles, while the bottom-up approach involves assembly of atoms and molecules into a nanoparticle (Narayanan and Sakthivel 2010). The former approach involves usage of expensive and energy-intensive physical methods, while the latter can be further sub-classified into chemical and biological methods. The employment of high-priced toxic solvents and extreme physical conditions (such as high pressure and temperature) in chemical synthesis of nanoparticles renders the chemical process as environmentally unfriendly (Narayanan and Sakthivel 2010). Biological methods, which utilizes plants and microbes (algae, bacteria, yeasts, actinomycetes, and fungi) serve as an eco-friendly and less expensive alternative to top-down synthesis of nanoparticles (Fig. 19.2) (Sastry et al. 2003).

19.4.1 Biogenic Production of Nanoparticles Using Plants

The biosynthesis of nanoparticles generally entails oxidation–reduction reactions. Plants and microorganisms have enzymes and produce antioxidizing and reducing

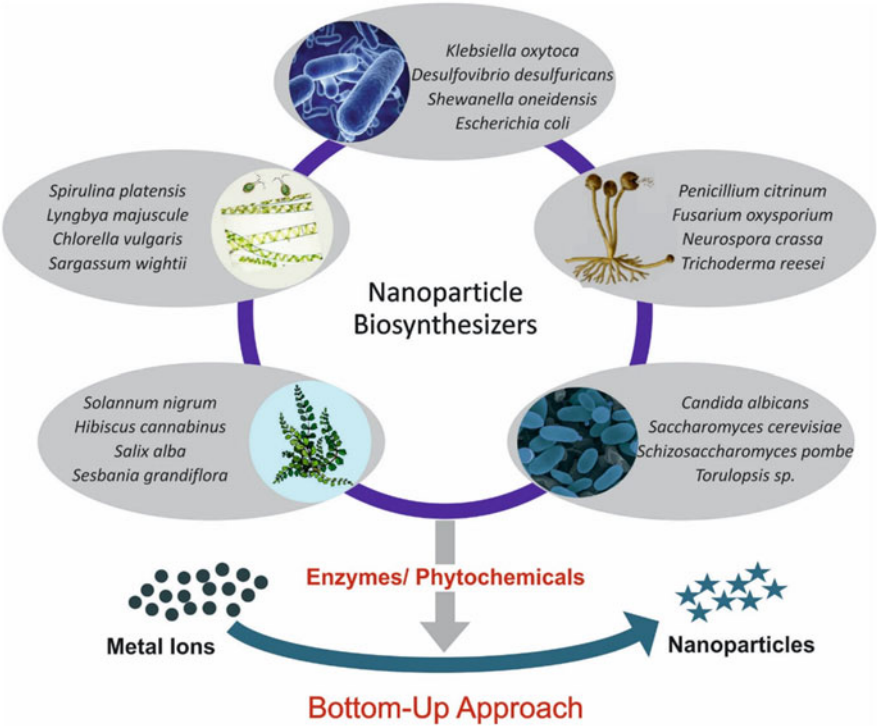


Fig. 19.2 Biogenic synthesis of nanoparticles using bottom-up approach

phytochemicals, which facilitate reduction and detoxification of accumulated metal ions. In the synthesis of metal/metal oxide nanoparticles, plant extracts (from roots, leaves, flowers, stems) are reported to be effective as they contain phytochemicals such as amides, aldehydes, ascorbic acids, carboxylic acids, flavones, ketones, phenols, and terpenoids. These compounds have been reported to have ability to reduce metal salts into metal nanoparticles. Plants such as Alfalfa, oats, Tulsi, lemon, Aloe vera have been reported to be used in production of silver and gold nanoparticles (Singh et al. 2016). Through optimization of process parameters, nanoparticles of desired sizes and morphologies can be biosynthesized (Iravani 2014). The application of whole plants or their phytochemical extracts in synthesis of nanoparticles has been demonstrated through numerous studies (Hussain et al. 2016). Biogenic production using plants is a preferred method as it is easier to scale-up (Megharaj et al. 2011).

19.4.2 Biogenic Production of Nanoparticles Using Microorganisms

Microbes possess highly versatile and effective catalytic mechanisms that enable degradation of various toxic compounds (Watanabe 2001). Additionally, microbes

are ubiquitous, much easier to culture and manipulate, have high growth rates, and require low cost investment. Silver nanoparticles have been biogenically produced by using bacteria such as *Arthrobacter gangotriensis, Aeromonas* sp. SH10, *Bacillus amyloliquefaciens, Bacillus cecembensis, Bacillus indicus, Bacillus cereus, Corynebacterium* sp. SH09, *Escherichia coli, Enterobacter cloacae, Geobacter* sp., *Lactobacillus casei, Phaeocystis antarctica, Pseudomonas proteolytica,* and *Shewanella oneidensis.* Gold nanoparticles have been reported to be extensively produced using *Bacillus subtilis* 168, *Bacillus megaterium* D01, *Desulfovibrio desulfuricans*, *Escherichia coli* DH5a, *Plectonema boryanum* UTEX 485, *Rhodopseudomonas capsulate,* and *Shewanella alga*. Fungi have been used to synthesize zinc, gold, silver, and titanium metal/metal oxide nanoparticles. Biosynthesis of silver and gold nanoparticles by *Saccharomyces cerevisiae* has been reported (Singh et al. 2016).

Microorganisms synthesize inorganic nanoparticles by assimilating metal ions from the surrounding environment and converting them to their elemental form using enzymes. Heterotrophic sulphate reducing bacteria have been reported to reduce gold-(I)-thiosulphate complex ($Au\ (S_2O_3)_2^{3-}$) to elemental gold (Au^0) (Lengke and Southam 2006). Similarly, *Stenotrophomonas maltophilia* SELTE02 mediated transformation of selenite (SeO_3^{2-}) to elemental selenium (Se^0) (Gregorio et al. 2005). Microbial biosynthesis can be achieved through intracellular and extracellular routes. The intracellular method consists of transporting metal ions into the cell, followed by enzymatic reactions, whereas the extracellular method involves adsorption of the metal ions on the cell surface, followed by enzyme-moderated reduction (Zhang et al. 2011). Microorganisms are known to synthesize various types of nanoparticles including metallic nanoparticles (gold, silver, cobalt, chromium, and other metals), magnetic, non-magnetic nanoparticles, and alloy nanoparticles (Li et al. 2011).

The biogenic method of nanoparticle production is an enzyme-mediated "green" synthesis of nanoparticles (Fig. 19.2). It allows elimination of costly, inefficient methods that involve use of expensive, hazardous solvents (such as sodium borohydride, ammoniacal silver nitrate) and produce toxic by-products. Furthermore, the particles generated by biogenic processes have greater surface area and higher catalytic reactivity (Mohanpuria et al. 2008). Table 19.1 lists microorganisms involved in the biogenic synthesis of various nanoparticles.

19.5 Nanoparticles: Mechanism of Action

Nanoparticles exhibit surface and chemical properties that are distinct from the bulk metal due to their nano-size. The nano-size increases the mechanical, magnetic, electrical, and optical properties of the nanoparticles. Nanoparticles catalyse processes such as adsorption and chemical reactions such as photocatalysis, precipitation, reduction, oxidation, and hydrogen peroxide dependent oxidation (Fenton reactions). The adsorption capacity of nanoparticles is being used to develop sorbents like carbon nanotubes and zeolites that have demonstrated efficient removal

Table 19.1 Biogenic production of nanoparticles by microorganisms

Biogenic production of nanoparticles by microorganisms		
Nanoparticle	Microorganism	References
Iron (Fe)	*Pleurotus* sp.	Mazumdar and Haloi 2011
	Bacillus subtilis	Sundaram et al. 2012
	Escherichia coli	Arcon et al. 2012
	Klebsiella oxytoca	Anghel et al. 2012
	Chaetomium globosum	Elcey et al. 2014
Zinc (Zn)	*Desulfobacteriaceae*	Labrenz et al. 2000
	Lactobacillus sp.	Selvarajan and Mohanasrinivasan 2013
	Streptomyces sp.	
	Aspergillus terreus	Raliya and Tarafdar 2013
	Sphingobacterium thalpophilum	Raliya and Tarafdar 2014; Rajabairavi et al. 2017
Palladium (Pd)	*Bacillus sphaericus*	Creamer et al. 2007
	Desulfovibrio desulfuricans	Gurunathan et al. 2015
	Bacillus benzeovorans	Omajali et al. 2015
	Shewanella sp.	Zhang and Hu 2017
	Geobacter sulfurreducens	Yates et al. 2013
Copper (Cu)	*Penicillium aurantiogriseum*	Honary et al. 2012
	Penicillium citrinum	Cuevas et al. 2015
	Penicillium waksmanii	Tiwari et al. 2016
	Stereum hirsutum	Parveen et al. 2016
	Bacillus cereus	Parveen et al. 2016
	Pseudomonas sp., *Serratia* sp.	Parveen et al. 2016
Silver (Ag)	*Bacillus licheniformis*	Kalimuthu et al. 2008
	Trichoderma reesei	Nanda and Saravanan 2009
	Cladosporium cladosporioides	Balaji et al. 2009
	Candida sp.	Kumar et al. 2011
	Streptomyces naganishii	Alani et al. 2012
Gold (Au)	*Rhodococcus* sp., *Streptomyces* sp.	Ahmad et al. 2003
	Aspergillus fumigatus, A. flavus	Gupta and Bector 2013
	Rhodopseudomonas capsulata	He et al. 2007
	Stenotrophomonas maltophilia	Nangia et al. 2009
	Penicillium brevicompactum	Mishra et al. 2011
Titanium (Ti)	*Lactobacillus* sp.	Prasad et al. 2007
	Bacillus subtilis	Vishnu Kirthi et al. 2011
	Aspergillus flavus	Rajakumar et al. 2012
	Aspergillus terreus	Raliya and Tarafdar 2014
	Bacillus amyloliquefaciens	Khan and Fulekar 2016
Cadmium (Cd)	*Escherichia coli*	Sweeney et al. 2004
	Rhodopseudomonas palustris	Bai et al. 2009
	Fusarium sp.	Reyes et al. 2009
	Bacillus amyloliquefaciens	Singh et al. 2011
	Bacillus licheniformis	Shivashankarappa and Sanjay 2015

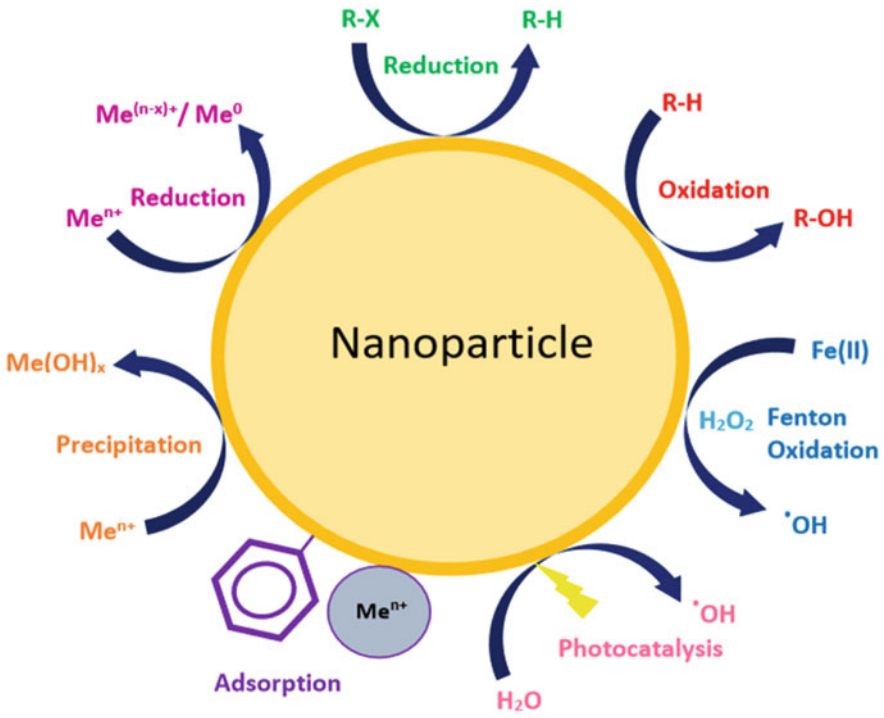


Fig. 19.3 Mechanisms catalysed by nanoparticles in degrading toxic pollutants

of anions and metals from drinking water (Yaqoob et al. 2020). Nanoparticles mediate the transformation of toxic metals into their respective hydroxides by precipitation. Nanoparticles play a crucial role in nanobioremediation by catalysing reactions and generating hydrogen ions that aid the microorganisms to further detoxify and transform the compound. The high reactivity and larger surface area for interaction offer the nanoparticles the characteristic property of having high oxidation potential. Metal oxide nanoparticles have been shown to catalyse oxidation reactions that can transform toxic pollutants such as hydrocarbons. Nanoparticles can absorb photons and act as nanophotocatalysts. The larger surface area of nanoparticles increases the oxidation of organic pollutants at the surface of the nanoparticles resulting in their degradation. TiO_2 is the most commonly used nano-photocatalyst in treatment of wastewater, due to its low cost, chemical stability, easy availability, and zero toxicity. Composite nanomaterials like copper oxide doped (CuO-doped) zinc oxides (ZnO) have been used to catalyse the Fenton oxidation. Fenton oxidation is a H_2O_2-assisted photo-decomposition of toxic pollutant in the presence of solar radiation (Banik and Basumallick 2017). Figure 19.3 summarizes the mechanisms catalysed by nanoparticles in degradation of toxic pollutants.

19.6 Remediation of Toxic Metals Using Nanoparticles

Heavy metals constitute a group of metals and metalloids that have atomic density higher than 4000 kg/m^3 (Edelstein and Ben-Hur 2018). Although plants need various heavy metals such as molybdenum, zinc, iron, etc. for basic metabolic activities, at higher concentrations, these metals are harmful to the plant (Vardhan et al. 2019). Heavy metals are toxic to humans even at low concentrations. Due to urbanization, population explosion, and rapid industrialization, soil and water resources end up as heavy metal sinks. Bioremediation measures thus play an important role in restoring balance within these contaminated environments, failure of which would lead to bioaccumulation and biomagnification of these toxic metals at the cellular level.

Nanomaterials such as bimetallic nanoparticles, metal oxides, nanoscale zeolites, and carbon nanotubes have been considered for metal remediation. Iron oxide nanoparticles have been extensively studied in metal detoxification owing to their ability to be separated easily from the reaction media and due to their low toxicity. Immobilization of accumulated heavy metals in soil plays a crucial role in their transformation and detoxification. Nanoparticles such as nano-alginate, bentonite-nZVI, zerovalent iron nanoparticles, nanocarbon, and dendrimers have been used to immobilize the heavy metals in soil (Helal et al. 2016).

Nano-hydroxyapatite, a phosphate-based nanomaterial has demonstrated significant results in clean-up of Pb contaminated soils. It has also been reported to immobilize other heavy metals such as Cr, Zn, Cd, and Cu. Studies on both graphene oxide nanoparticles and nZVI nanoparticles have been reported in relation to increasing the bioavailability of arsenic and other metals in polluted soils (Baragaño et al. 2020). Similar studies using graphene as the adsorbent showed removal of arsenic by 80% from wastewater. The advantages of this nanomaterial are its ability to be recycled and reused. A nanocomposite with reduced graphene oxide and Fe_3O_4 has been studied for the removal of Pb^{2+} ions from water by co-precipitation and has been found to be efficient. Other graphene-based nanomaterials have been successfully used for the removal of heavy metals such as Cu (II), Fe (II), Mn (II), and Pb (II). Activated carbon nanomaterial has been successfully applied in the removal of heavy metals such as Zn^{+2} and Al^{+3} ions and has demonstrated an efficiency up to 92%. In wastewater treatment, it showed an absorption capacity of up to 50% for Cu^{+2} ions. Other activated carbon nanomaterials have been successfully employed in remediation of heavy metals such as Pb^{+2}, Cd^{+2}, Cu^{+2}, Ni^{+2}, and Zn^{+2} (Baby et al. 2019). The role of various environmental factors affecting the remediation of heavy metals by iron-based nanoparticles has been studied. This study also focused on the toxicity of these nanoparticles on the living organisms (Latif et al. 2020). Hydrous iron oxide-based nanomaterials have been found to remove heavy metals like Pb (II), Cu (II), Cd (II), and Ni (II). However, they have been found to be most effective in removal of arsenic (V) from drinking water. Nanomaterials based on manganese oxides have been used for the treatment of metals such as Tl (I), U, Pb (II), Zn (II),

Hg (II), Cd (II), and Cu (II) and have now been considered promising in removal of heavy metals from polluted water. Polyvinylpyrrolidone-coated magnetic nanoparticles (PVP-Fe_3O_4 nanoparticles) have shown significant efficiency (100%) in the removal of Cd, Cr, Ni, and Pb. Hexavalent chromium (VI) is a prevalent inorganic pollutant that is known to be toxic, mutagenic, and carcinogenic (Valko et al. 2005). Remediation of Cr (VI) involves its reduction to trivalent Cr (III), a less toxic, non-carcinogenic form that can be precipitated into hydroxides. This reaction serves as a key step for the removal of Cr (VI) from aqueous solutions (Mabbett et al. 2004). Iron nanoparticles such as ferromagnetic carbon-coated nanoparticles have been used to remove 95% of Cr (VI) from aqueous solutions. Table 19.2 shows the use of nanoparticles in heavy metals remediation.

19.7 Remediation of Hydrocarbons Using Nanoparticles

Hydrocarbon pollution refers to the contamination of the environment by organic polycyclic aromatic hydrocarbons (PAH) or crude oil (petroleum hydrocarbons) compounds. Oil pollution has severe environmental and ecological consequences. Crude oil and its derivatives are considered as some of the most pervasive environmental pollutants. The leakage of crude oils into aquatic systems results in wide-ranging contamination. Oil sludge is a thick complex emulsion made up of various petroleum hydrocarbons, heavy metals, sediments, and water. It is composed of alkanes, aromatics, resin, and asphaltenes and contains volatile and semi-volatile organic compounds, which are reported to be genotoxic (Srivastava et al. 2019). Unintentional and deliberate spillage of oil into the environment leads to transfer of toxic organic materials into the food chain.

Due to their unique physicochemical properties, nanoparticles have gained tremendous interest in oil biodegradation. Nanoparticles can decrease the hydrophobicity of these hydrocarbon compounds and thus increase their bioavailability for bioremediation. Graphene-doped TiO_2 nanoparticles have demonstrated adsorption and photodegradation of phenanthrene, fluoranthene, and benzopyrene to phthalic and benzoic acid; oxygenated and hydroxylated PAHs; acyclic hydrocarbons and alcohols (Bai et al. 2017). Similarly, iron hexacyanoferrate (FeHCF) nanoparticles have been employed in degradation of anthracene, chrysene, and fluorine. It was also established that aromatic hydrocarbon adsorption by the FeHCF followed a molecular weight dependent trend: anthracene > phenanthrene > fluorene > chrysene > benzopyrene (Shanker et al. 2017). Bimetallic magnetic Pt/Pd nanoparticles supported on magnetic silica reduced anthracene to non-toxic partially hydrogenated species. Furthermore, compared to monometallic nanoparticles, the bimetallic particles displayed enhanced activity post recycling (Zanato et al. 2017). Nanoparticles are efficient in degrading organic compounds such as benzophenone and phenol. Benzophenone-3 is an ultraviolet absorber, and thus they can be degraded using catalytic ozonation. Manganese oxide and cobalt oxide nanoparticles immobilized on ceramic membrane displayed remarkable

Table 19.2 Nanoparticles used in remediation of heavy metals

Nanoparticles used in remediation of heavy metals		
Pollutant	Nanoparticle	References
Copper (Cu)	Amino-functionalized magnetic nanoparticles	Hao et al. 2010
	Polydopamine nanoparticles	Farnad et al. 2012
	Maghemite nanoparticles	Rajput et al. 2017
	nZVI	Boente et al. 2018
	Graphene oxide–manganese oxide nanoparticles composite	Wan et al. 2018
Chromium (VI) (Cr)	Chitosan-nZVI (nanoscale zerovalent iron) nanoparticles	Geng et al. 2009
	Magnetite–maghemite nanoparticles	Chowdhury and Yanful 2010
	Cerium oxide nanoparticles	Contreras et al. 2015
	CTAB modified magnetic nanoparticles	Elfeky et al. 2017
	Magnetic alkaline– Lignin−dopamine nanoparticles	Dai et al. 2019
Arsenic (As)	Magnetite–maghemite nanoparticles	Chowdhury and Yanful 2010
	Iron oxide nanoparticles	Shipley et al. 2011
	Cupric oxide nanoparticles	Reddy et al. 2013
	γ-Aluminium oxide nanoparticles	Ghosh et al. 2019
	Magnetic iron-titanium binary oxide composite	Deng et al. 2019
Cadmium (Cd)	Cerium oxide nanoparticles	Contreras et al. 2015
	Iron phosphate (vivianite) nanoparticles	Qiao et al. 2017
	EDTA functionalized iron oxide nanoparticles	Huang and Keller 2015
	Silica-coated iron oxide nanoparticles	Ghafoor and Ata 2017
	Graphene oxide–manganese oxide nanoparticles composite	Wan et al. 2018
Lead (Pb)	Iron phosphate (vivianite) nanoparticles	Liu and Zhao 2007
	Cerium oxide nanoparticles	Contreras et al. 2015
	EDTA functionalized iron oxide nanoparticles	Huang and Keller 2015
	L-cysteine stabilized nZVI nanoparticles	Bagbi et al. 2017
	Maghemite nanoparticles	Rajput et al. 2017
Mercury (Hg)	Carboxymethyl cellulose stabilized iron sulphide nanoparticles	Gong et al. 2012
	Citrate-coated gold nanoparticles	Ojea-Jiménez et al. 2012
	Silica-coated magnetite nanoparticles	Mohmood et al. 2016
	Inorganic magnetic sulphide nanoparticles	Patel et al. 2018

catalytic ozonation of benzophenone-3 (Guo et al. 2016). Reduced graphene oxide silver nanoparticles (rGO-Ag) were demonstrated to successfully breakdown phenol (Bhunia and Jana 2014). ZnO and magnetite-zinc oxide (Fe_3O_4-ZnO) hybrid

nanoparticles have been studied in the degradation of phenols and the hybrid nanoparticles were found to be more efficient (Feng et al. 2014). UV-irradiated semiconductor catalysts such as titanium dioxide have been used in photodegradation of organic contaminants (Banik and Basumallick 2017). Calcium peroxide nanoparticles have been reported to exhibit remarkable degradation of benzene and toluene (Mosmeri et al. 2017; Qian et al. 2013). Removal of benzene from aqueous solutions has also been carried out using magnetite nanoparticles. The nano-magnetic particles have been reported to decompose 98.7% and 94.5% of the benzene in batch and continuous conditions, respectively. Furthermore, these particles can easily desorb benzene and be reused for its removal (Amin et al. 2013). Magnetite nanoparticles catalysed decomposition of p-nitrophenol to aromatic intermediates such as benzoquinone and hydroquinone, which were further oxidized by hydrogen peroxide. The nanoparticles exhibited the ability to be magnetically separated from the sludge and reused (Sun and Lemley 2011). Magnesium doped magnetite nanoparticles have been reported to effectively decompose hexachlorobenzene, a precursor of carcinogenic and mutagenic compounds (Su et al. 2014).

The remediation of petroleum-based hydrocarbons using nanoparticle-stabilized surfactants has been explored (Ali et al. 2020). Iron nanoparticles produced biogenically from *Vaccinium floribundum* showed a significant removal of up to 86% and 88% in the total petroleum hydrocarbons from polluted soil and water, respectively (Murgueitio et al. 2018). Raw and distillate forms of petroleum oil were treated with nanocarbon scavengers which efficiently sequestered these hydrocarbons by 80% and 91%, respectively (Daza et al. 2017). Polyvinylpyrrolidone (PVP) coated magnetite nanoparticles (NP) have demonstrated remediation of lower chain alkanes by 70% and higher chain alkanes by 65% after incubation of 1 h. However, the efficiency of degradation of these alkanes increased significantly on incubation of the nanoparticles with oil degrading bacteria (Alabresm et al. 2018). Table 19.3 enlists integrated systems studied for hydrocarbon degradation. Other studies have shown significant results in degradation of hydrocarbons using nanobioremediation, which has been discussed further in this chapter.

19.8 Remediation of Hormones, Antibiotics, and Medicinal Drugs Using Nanoparticles

Antibiotics and hormones are emerging pollutants. Modern healthcare and their extensive use in farming results in their release in effluent and wash waters leading to contamination of groundwater and soil. Their recalcitrant nature makes them persist in the soil and water and lead to serious effects on the environment and human health.

Table 19.3 Nanoparticles used in remediation of hydrocarbon pollutants

Nanoparticles used in remediation of hydrocarbons		
Pollutant	Nanoparticle	References
Polycyclic aromatic hydrocarbons (PAHs)		
Pyrene	Haematite nanoparticles	Jorfi et al. 2016
Phenanthrene, fluoranthene, benzopyrene	Titanium dioxide nanoparticles	Bai et al. 2017
Anthracene, phenanthrene, chrysene, fluorene, and benzopyrene	Iron hexacyanoferrate nanoparticles	Shanker et al. 2017
Anthracene	Bimetallic magnetic Pt/Pd nanoparticles	Zanato et al. 2017
Benzophenone-3	Manganese oxide and cobalt oxide nanoparticles coated on ceramic membrane	Guo et al. 2016
Phenol	Magnetite and zinc oxide hybrid nanoparticles Reduced graphene oxide silver nanoparticles (rGO-Ag)	Feng et al. 2014; Bhunia and Jana 2014
Petroleum-based hydrocarbons		
Total petroleum hydrocarbons	Iron nanoparticles	Murgueitio et al. 2018
Raw and distillate forms of petroleum oil	Nanocarbon nanoparticles	Daza et al. 2017
Alkanes	Polyvinylpyrrolidone (PVP) coated magnetite nanoparticles	Alabresm et al. 2018

19.8.1 Remediation of Antibiotics

Nanoparticles have been reported to clean up even low concentrations of these compounds. Many nanoparticles like zerovalent iron nanoparticles have exhibited the ability to remove antibiotics such as sulfacetamide from the aqueous solution by 61% (Table 19.4). Bimetallic $CuFe20_4$ nanoparticles have been efficiently used for the removal of amoxicillin from aqueous solutions. Photocatalytic degradation of ciprofloxacin has also been reported using graphene oxide/nanocellulose composite. Similar degradation studies have also been reported on ciprofloxacin using zerovalent iron nanoparticles. Tetracycline degradation was successfully carried out by nanoscale zero-valent iron (nZVI) and Fe/Ni bimetallic nanoparticles in aqueous solution. Although Fe/Ni nanoparticles performed better that nZVI, the removal efficiency of both the particles was reported to decrease with increase in pH, thus asserting that the degradation process is pH-dependent (Dong et al. 2018b). UiO-66, a zirconium based nanoparticle doped with cobalt was reported to adsorb and degrade tetracycline via photocatalysis. Factors affecting the adsorption process included dosage of the nanoparticles, coexisting ions, pH, and initial concentration of the antibiotic (Cao et al. 2018). The Oxone process has been utilized to degrade organic compounds. In this process, Oxone [peroxymonosulfate (PMS)] is

Table 19.4 Nanoparticles used in remediation of antibiotics, medicinal drugs, and hormones

Nanoparticles used in remediation of antibiotics, medicinal drugs, and hormones		
Pollutant	Nanoparticle	References
Antibiotics		
Amoxicillin	Copper-iron bimetallic nanoparticles	Malakootian et al. 2019
Ceftriaxone	Fe_3O_4 nanoparticles	Malakootian et al. 2019
Sulfacetamide	Zerovalent iron nanoparticles	Malakootian et al. 2019
Tetracycline	Fe/Ni bimetallic nanoparticles Cobalt-doped UiO-66 nanoparticles Martite nanoparticles Cu/Fe bimetallic particle ZnS nanoparticles Titanium oxide nanocomposite	Dong et al. 2018b; Cao et al. 2018; Soltani et al. 2018; Malakootian et al. 2019
Ciprofloxacin	Zinc oxide nanoparticles Fe-doped zinc oxide nanoparticles Titanium oxide nanoparticles Cupric oxide nanoparticles Graphene oxide/ nanocellulose composite Zerovalent iron nanoparticles	Gharaghani and Malakootian 2017; Das et al. 2018; Malakootian et al. 2020
Levofloxacin	Zn oxide nanoparticles, Graphene oxide sheets	El-Maraghy et al. 2020
Hormones		
Estrone	Polystyrene nanoparticles Titanium dioxide nanoparticles	Akanyeti et al. 2017; Czech and Rubinowska 2013
17-ß-Estradiol	Manganese oxide nanoparticles Magnetic biochar nanoparticles	Han et al. 2014; Dong et al. 2018a
Medicinal drugs		
Paracetamol	Activated carbon nanoparticles	Baby et al. 2019
Carbamazepine	Haematite nanoparticles Magnetite nanoparticles	Rajendran and Sen 2018; Liu et al. 2018
Ibuprofen	Nanoscale zerovalent iron (nZVI)	Machado et al. 2013

combined with a source of transition metals to generation sulphate ions, which catalyse the redox process. Martite (α-Fe_2O_3) nanoparticles have been found to activate the Oxone process to degrade the recalcitrant antibiotic (Soltani et al. 2018).

The degradation of ciprofloxacin, another commonly used antibiotic, was proved both spectrophotometrically and microbiologically by the loss of antibiotic activity, using Fe-doped-ZnO nanoparticles (Das et al. 2018). Immobilized nanoparticles allow easy placement and removal of aqueous contaminants. Moreover, it resolves complications related to separation of catalysts from the solution, as well as allows reusability of nanoparticles. ZnO immobilized on a glass plate exhibited nano-photocatalysis of ciprofloxacin with high removal efficiency (Gharaghani and Malakootian 2017). Similarly, TiO_2 nanoparticles immobilized on a glass plate were shown to adsorb and photodegrade ciprofloxacin and also resulted in decreased sludge production (Malakootian et al. 2019). Other antibiotics such as ampicillin, amoxicillin, and penicillin were reduced by bentonite-supported Fe/Ni nanoparticles (Weng et al. 2018).

19.8.2 Remediation of Medicinal Drugs

Medicinal drugs such as paracetamol, carbamazepine, and ibuprofen not just pollute water bodies, but pose a significant threat to aquatic communities. As in case of other organic compounds, a variety of nanoparticles have been researched for their applicability in degrading these recalcitrant compounds. Ibuprofen reduction can be carried out by nZVI nanoparticles. While effective on lab scale, simulation of the nanoremediation with ibuprofen contaminated soil concluded that the degradation process is slower in aqueous systems, but without any significant impact on contaminant degradation efficiency (Machado et al. 2013). Haematite nanoparticles were demonstrated to be effective adsorbents of carbamazepine and thus offer a potential remediation method for the adsorptive elimination of drugs from contaminated aquatic systems (Table 19.4) (Rajendran and Sen 2018). Magnetite nanoparticles were also confirmed to effectively remove carbamazepine (Liu et al. 2018). Nanoparticles have also been proved effective in reducing chlorhexidine, a commonly used antiseptic component. Photocatalytic degradation of chlorhexidine was successfully concluded using titanium dioxide nanoparticles as photocatalyst (Das et al. 2014). Activated carbon nanoparticles have been reportedly used for the bioremediation of methylene and paracetamol from hospital wastewaters (Baby et al. 2019).

19.8.3 Remediation of Hormones

Naturally synthesized and synthetic hormones are one of the most potent trace contaminants released into soil and water bodies. Apart from excretion and disposal of hormones, application of animal faeces as manure to fields allows transmission of endogenous hormones into soil and ultimately in water bodies. These hormones and

endocrine disruptors are known to affect the reproductive health of various animals by disrupting sexual function and promoting abnormal sexual development. As with other organic compounds, nZVI, under oxidative conditions, was found to adsorb and degrade 17β-estradiol (Table 19.4) (a popular endocrine disrupting chemical) and 17α-ethinylestradiol (a synthetic birth control drug) into less bioactive estrone (Jarosova et al. 2015). Biochar, a pyrogenic black carbon product of biomass pyrolysis can be used to derive nanosized biochar particles due to their nanoporous structure, good stability, multiple functional groups, and easy availability. Magnetic biochar nanoparticles (Mag-BCNPs) are a composite of nanosized biochar nanoparticles and magnetic iron nanoparticles (Fe_3O_4). This composite was demonstrated to effectively reduce 17β-estradiol. Post remediation, the Mag-BCNPs can be recovered using a magnet, and the biochar can be desorbed by purging with ozone, thus allowing easy regeneration of the nanoparticles (Dong et al. 2018a). Carboxymethyl cellulose (CMC) stabilized manganese oxide nanoparticles have also been studied for their 17β-estradiol degrading activity (Han et al. 2014). Estrones can be removed from wastewater using TiO_2-assisted photocatalysis (Czech and Rubinowska 2013). A hybrid polystyrene nanoparticle-ultrafiltration system with renewable nanoparticles acts as a lucrative solution to filtering estrone from contaminated water. However, due to the higher permeability of the filtration system compared to that of nanofiltration/reverse osmosis systems, estrone removal capacity of 40% was achieved. However, replacing the filtration system with a finer one can increase success of the designed system (Akanyeti et al. 2017). Table 19.4 shows the use of nanoparticles in remediation of antibiotics, medicinal drugs, and hormones.

19.9 Remediation of Dyes and Organic Solvents Using Nanoparticles

With the onset of industrialization, the synthesis and utilization of various organic compounds have increased exponentially. These organic compounds include dyes which are released into the environment through anthropogenic activities. These pollutants are known to have neurotoxic, mutagenic, and carcinogenic effects on biological systems (Das and Chandran 2011). Various studies using nanoparticles have been carried out on degradation of the dyes. Nanomaterials such as reduced graphene oxide, (rGO)-TiO_2 has been successfully applied for the bioremediation of Alizarin Red S. Other studies have also reported the use of graphene oxide nanomaterials in association with TiO_2 or ZnO in photodegradation of methylene blue. Bimetallic nanoparticles of iron (Fe) and nickel (Ni) showed significant results in cleaning up of the azo dye Orange G from wastewater (Foster et al. 2019). Similarly, remarkable efficiency was exhibited when absorbent made of ZnO nanoparticle was used to remove azo dyes, amaranth, and methyl orange from aqueous solution (Zafar et al. 2019). Tara and others (Tara et al. 2020) have summarized the nanoparticles used in the removal of Azo dyes and the efficiency of removal of these

Table 19.5 Nanoparticles used in remediation of dyes and organic solvents

Nanoparticles used in remediation of dyes, and organic solvents		
Pollutant	Nanoparticle	References
Dyes		
Dye containing effluents	Nickel nanoparticles	Kale and Kane 2017
Azo dyes	ZVI nanoparticles Cerium loaded copper oxide Iron nanoparticle	Tara et al. 2020
Methylene blue, Congo red	Copper oxide nanoparticles Copper oxide nanoneedles Graphene oxide sheets	Tara et al. 2020
Cationic and anionic dyes	Nickel doped zinc oxide nanoparticle	Tara et al. 2020
Coomassie brilliant blue, Amido black 10B	Copper oxide nanoneedles Graphene oxide sheets	Tara et al. 2020
Malachite green, methyl violet	Magnetic NPs coated with poly (dimethylaminoethyl acrylamide) and methyl acrylate on modified with Fe_3O_4 nanoparticles	Tara et al. 2020
Methylene blue	Copper oxide nanoparticles activated with montmorillonite clay	Tara et al. 2020
Methylene blue, methyl orange, rhodamine B, organic dyes	Silver nanocomposite, Silver nanoparticles	Tara et al. 2020; Bhakya et al. 2015
Amaranth and methyl orange	ZnO nanoparticles	Zafar et al. 2019
Orange G	Fe and nickel nanoparticles	Foster et al. 2019
Organic solvents		
TCE	Zerovalent iron nanoparticles	Ibrahem et al. 2012
p-Nitrophenol	Magnetite nanoparticles	Sun and Lemley 2011
Hexachlorobenzene	Magnetic micro/nano Fe_xO_y-CeO_2 composite Mg-doped iron oxide nanoparticles	Jia et al. 2010; Su et al. 2014
Benzene	Magnetite nanoparticles Calcium peroxide nanoparticles	Amin et al. 2013; Mosmeri et al. 2017
Toluene	Calcium peroxide nanoparticles Tungsten doped titanium dioxide nanoparticles	Qian et al. 2013; Poorkarimi et al. 2017

dyes by the respective nanoparticles. Table 19.5 summarizes different nanoparticles that are involved in remediation of dyes and organic solvents.

Nanoscale iron nanoparticles have shown significant efficiency in removal of chlorinated organic solvents contaminating groundwater (Zhang and Elliott 2006). Zerovalent iron nanoparticles have been used for the remediation of

trichloroethylene (TCE). It was considered an efficient reducing catalyst and resulted in fast degradation of TCE from contaminated soils (Ibrahem et al. 2012).

19.10 Remediation of Agro-Based Compounds Using Nanoparticles

Agro-based compounds such as herbicides, fungicides, pesticides, weedicides are extensively used in agriculture. These compounds leach and contaminate the surrounding soil and water bodies. Due to the complex chemical structure of these compounds they are recalcitrant in nature and tend to persist in the environment for a long time. Nanoparticles have been found to be efficient in removal of pesticides from contaminated sites by adsorption and photodegradation of these compounds (Table 19.6). Nanomaterials such as zinc oxide, titanium dioxide, and silver have been reported to photocatalyse the degradation of pesticides. Metal nanocomposites and polymer matrix nanocomposites have been successfully used in the removal of organic and inorganic pollutants. Iron nanoparticles have been successfully used in remediation of carbamate pesticides such as methomyl. Fe_3O_4 nanoparticles have

Table 19.6 Nanoparticles used in remediation of agro-based compounds

Nanoparticles used in remediation of agro-based compounds		
Pollutant	Nanoparticle	References
Aldrin	Fe_3O_4 nanoparticles	Sahithya and Das 2015
Alachlor	Nanoscale zerovalent iron (nZVI)	Bezbaruah et al. 2009
Eldrin	Fe_3O_4 nanoparticles	Sahithya and Das 2015
Lindane	Fe_3O_4 nanoparticles, silver nanoparticles	Sahithya and Das 2015
	Nanoscale zerovalent iron (nZVI)	Elliott et al. 2009
Organophosphate pesticides	TiO_2, ZnO, Au-TiO_2, CuO nanoparticles	Sahithya and Das 2015
Atrazine	Nanoscale zerovalent iron (nZVI)	Bezbaruah et al. 2009
Chlorpyrifos	Silver and gold nanoparticles	Bootharaju and Pradeep 2012
DDT	Mixed metal oxides nanoparticles	Manav et al. 2018
Profenofos (organophosphorous pesticide)	Fe/Ni bimetallic nanoparticles	Mansouriieh and Khosravi 2015
Malathion	Iron oxide nanoparticles and iron oxide/gold nanoparticles Magnetite nanoparticles and gold coated magnetic nanoparticles	Fouad et al. 2015
Acetamiprid	Fe/Ni bimetallic nanoparticles	Marcelo et al. 2016

been applied for their efficiency in clean-up of organochlorine pesticides such as aldrin, endrin, and lindane. Silver nanoparticles have also been efficient in remediation of pesticide lindane. Organophosphate pesticides such as monocrotophos, malathion, chlorpyrifos, dichlorvos have been photo-catalytically degraded using nanoparticles such as titanium dioxide, zinc oxide, gold-titanium dioxide, and copper oxide, respectively.

Gold-titanium dioxide (Au-TiO_2) nanoparticles have been reported to photocatalyse the degradation of chloridazon (Sahithya and Das 2015). Rapid anoxic degradation of pesticide alachlor (2-Chloro-2′,6′-diethyl-*N*-(methoxymethyl)-acetanilide) has been reported using nZVI. The reaction resulted in dechlorinated alachlor, which was significantly more biodegradable in comparison to its parent compound (Bezbaruah et al. 2009) (Table 19.6). The nZVI nanoparticles have been documented to degrade lindane (γ-hexachlorocyclohexane), a commonly used organochlorine pesticide, into benzene, diphenyl, and di/tetra/penta forms of the compound (Elliott et al. 2009). Silver and gold nanoparticles have exhibited remarkable ability to decompose chlorpyrifos, an organophosphorothioate pesticide, to 3,5,6-trichloro-2-pyridinol and diethyl thiophosphate at room temperature. These nanoparticles have also demonstrated an ability to be regenerated and reused (Bootharaju and Pradeep 2012). Catalytic degradation of Profenofos (an organophosphorous pesticide) and acetamiprid (a neonicotinoid insecticide) using Fe/Ni bimetallic nanoparticles has been reported (Marcelo et al. 2016; Mansouriieh and Khosravi 2015). $MgCeO_3$ and $MgFe_2O_4$ are mixed metal oxides that have been studied for degradation of DDT (dichlorodiphenyltrichloroethane), a well-known harmful organochlorine insecticide. Both mixed oxides degraded DDT to less toxic compounds DDD (dichlorodiphenyldichloroethane), DDE (dichlorodiphenyldichloroethylene), and simpler compounds within the first reaction hour (Manav et al. 2018). Zerovalent metal nanoparticles, semiconductor nanoparticles, and some bimetallic nanoparticles have been documented to treat environmental pollutants such as azo dyes, pesticides (chlorpyrifos and organochlorines), nitroaromatics, hormones, and antibiotics (Foster et al. 2019).

19.11 Remediation of Organohalide Compounds Using Nanoparticles

Organohalide compounds such as polybrominated diphenyl ethers (PBDEs), dioxins, polychlorinated biphenyls (PCBs), and chlorinated aliphatic hydrocarbons (CAH) are omnipresent, highly toxic fat-soluble compounds. Being insoluble in water, their low bioavailability hinders biodegradation by aquatic microbes. PCBs are toxic organohalide compounds classified as persistent organic pollutants. Various nanoparticles have been studied for their remediation. Pd/Fe bimetallic nanoparticles and nZVI have been reported to catalyse hydro-dechlorination of hexachlorobiphenyl (Chen et al. 2014). Carbon-modified titanium dioxide (CM-*n*-TiO_2) nanoparticles were reportedly used in photocatalytic degradation of PCB mixtures Aroclor 1254 and Aroclor 1260 (Shaban et al. 2016). Surfactants enhance

Table 19.7 Nanoparticles used in remediation of organohalide compounds

Polychlorinated biphenyls (PCBs)		
Pollutant	Nanoparticle	References
2-chlorobiphenyl	Palladium–aluminium (Pd/Al) bimetallic nanoparticles	Yang et al. 2013
Penta, hexa, hepta, and octobiphenyls	Nanoscale zerovalent iron (nZVI)	Gomes et al. 2014
2,2′,4,4′,5,5′-hexachlorobiphenyl	Nanoscale zerovalent iron (nZVI)	Chen et al. 2014
Aroclor 1254 and Aroclor 1260	Carbon-modified titanium dioxide (CM-*n*-TiO_2) nanoparticles	Shaban et al. 2016

solubilization of hydrophobic organic compounds, hence their integration with nanoparticles may lead to increase in bioremediation efficiency. In a combined electro-remediation set-up consisting of electrodialysis, non-ionic detergents (Saponin and Tween-80), and nZVI nanoparticles, degradation of up to 76% PCBs was reportedly achieved within 5 days. However, in a set-up with just surfactant and nanoparticles, the remediation efficiency was low, thus supporting the assumption that the surfactant will not always enhance nanoparticle activity (Gomes et al. 2014). Similar observations were made pertaining to remediation of 4-chlorophenol and 2-chlorobiphenyl using palladium-aluminium (Pd/Al) bimetallic nanoparticles (Table 19.7). While the nanoparticles by themselves were capable of degrading the PCBs, addition of ionic and non-ionic surfactants led to decrease in hydrodechlorination of the organic compounds (Yang et al. 2013). Polychlorinated aliphatic compounds such as trichloroethylene can be remediated using nanoparticles. Polymethyl methacrylate coated nZVI have also been reported capable in reducing trichloroethylene (Wang and Chiu 2009). Bimetallic Ni/Fe nanoparticles immobilized in hydrophilic nylon-66 membrane have been reported to completely dechlorinate trichloroethylene within 25 min. The immobilization of nanoparticles improved the reactivity and longevity of the nanoparticles (Parshetti and Doong 2009).

19.12 Nanobioremediation Using Integrated Nano-Bio Systems

Microbial bioremediation or nanoremediation, by itself offers multiple advantages over conventional treatment methods, but also has multiple noteworthy limitations. Microbial degradation of toxic compounds is a time-consuming process that can take over a year. Its effectiveness varies with conditions such as pH, nutrients, temperature, and other environmental conditions (Abatenh et al. 2017; Kumar et al. 2018). Integration of nanotechnology with microbial bioremediation can overcome these limitations and provide a better alternative to pollutant remediation. The reaction of the toxic pollutant with nanoparticles transforms the pollutant into compounds more easily metabolized by microorganisms. Therefore, nanobioremediation is a

promising alternative in remediation technologies involving detoxification of toxic pollutants.

Nanobioremediation can be described as a combination of nanotechnology and bioremediation systems, wherein the former enhances the effectiveness of the latter. Therefore, nanobioremediation offers the benefits of both nanotechnology and bioremediation. The application of nanobioremediation can be done using two approaches. The sequential approach involves subjecting the contaminant to nanoparticles followed by exposure to the bioagent. The nanoparticles break down the contaminants to simpler compounds, allowing the bioagent to metabolize it further. In the concurrent or combined approach, the nanoparticle and biological agent is injected into the system simultaneously (Tratnyek and Johnson 2006; Karn et al. 2009). While both these methods seem to be practical alternatives to conventional technologies, more research and development is needed for their execution on a larger scale.

The most significant advantage of using nanoparticles in remediation is their application in both in situ and ex situ conditions. In ex situ remediation, the contaminated soil is excavated, while the contaminated groundwater is extracted and treated with nanoparticles on-site or off-site. In in situ treatment methods, nanoparticles are directly injected at the site of contamination where it degrades the contaminant. Compared to conventional methods, nanobioremediation is best suited for in situ treatment of contaminated soil and groundwater as the exceptional properties and colloidal nature of nanoparticles allow deep penetration up to the water table, a feat that is not possible to achieve with ex situ methods. Furthermore, nanoparticles enhance the reaction rates of microorganisms, thus allowing better degradation of pollutants (Karn et al. 2009). The ability of nanoparticles to degrade pollutants in association with biological systems presents opportunity for development of more efficient nano-bio integrated technologies. Apart from treatment and remediation of contaminated sites, nanoparticles can be applied to pollution sensing and pollution prevention.

19.13 Nanobioremediation of Toxic Heavy Metals

Integrated systems have great scope in metal bioremediation. Nanoparticles in combination with microorganisms have been used successfully to remediate heavy metals. Nanoscale zerovalent iron (nZVI) is smaller and more reactive than microscale zerovalent iron (ZVI) and therefore offers elevated reactive surface area, higher reactivity, and better injectability into aquifers, thus making them valuable in bioremediation of polluted sites (Li et al. 2006). However, due to their tendency to agglomerate and form larger particles, the reactivity of the nanoparticles decreases. Thus, direct application of free nZVI in remediation of contaminated soil and water could lead to overall decrease in efficiency of nanoparticles and leaching of iron into aquatic bodies. The immobilization of nZVI onto biodegradable, porous materials (beads) helps to overcome agglomeration. The toxic pollutant diffuses into beads and comes in contact with the entrapped nanoparticles. Similar studies on

Table 19.8 Nano-Bio integrated systems for remediation of Chromium (VI)

Integrated systems for remediation of toxic Chromium (VI)			
Metal pollutant	Nanoparticle	Bioagent	References
Bacteria			
Chromium (VI)	CNTs	*Shewanella oneidensis* MR-1	Yan et al. 2013
	CNTs	*Pseudomonas aeruginosa*	Pang et al. 2011
	Bio-Pd	*Clostridium pasteurianum* BC1	Chidambaram et al. 2010
Consortium			
Chromium (VI)	nZVI	Whey microbiota	Nemecek et al. 2016
Chromium (VI)	nZVI	Consortia of *Bacillus subtilis*, *Escherichia coli,* and *Acinetobacter junii*	Ravikumar et al. 2016

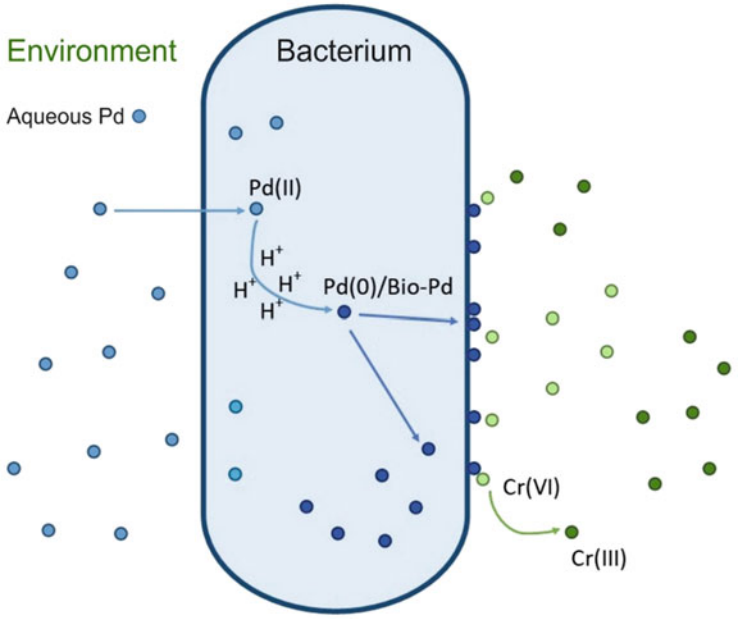


Fig. 19.4 Integrated Bio-Pd system in chromium remediation. The anaerobic hydrogen-producing bacterium accumulates aqueous palladium and reduces it to Bio-Pd, which further reduces toxic chromium (VI) to its less toxic form, Cr (III)

immobilization of nZVI on calcium alginate (nZVI−C − A beads), in presence of microbial biofilm has been shown to be effective in reducing Cr (VI) to Cr (III) (Ravikumar et al. 2016). Table 19.8 depicts various studies carried out using integrated nano-bio systems for remediation of chromium (VI).

The Bio-Pd (bio-reduced-Pd) integrated system is an innovative method for in situ remediation of toxic metals (Fig. 19.4). Bio-Pd generation is a novel system

wherein bacterium, in the presence of hydrogen, reduces and precipitates accumulated palladium, Pd (II) into Pd nanoparticles (Pd (0)). The two-step remediation system involves synthesis of Pd nanoparticles (bio-Pd) followed by reaction with the contaminant. Although this two-step process is suitable for ex-situ remediation, hydrogen supply acts as a technical and commercial challenge. *Clostridium pasteurianum* BC1, an anaerobic hydrogen producer, allows coupling of in situ production of H_2 with in situ synthesis of nanoparticles, which further catalyses the degradation of contaminants. The bio-Pd synthesized by *Clostridium pasteurianum* BC1 successfully demonstrated the reduction of Cr (VI) to Cr (III) (Chidambaram et al. 2010).

Nanomaterials have been used to augment the metal-reduction efficiency of microorganisms. Compared to suspended cells, immobilized microorganisms allow continuous and stable bioreduction of Cr (VI). However, the alginate used for immobilization can lower the reduction efficiency due to its effect on electron and mass transport. Impregnation of organic nanomaterial such as carbon nanotubes (CNTs) has proved to enhance the mechanical strength and bioreduction capacity. The immobilization of *Shewanella oneidensis* MR-1 in alginate/CNT beads was shown to yield a higher reduction efficiency compared to the controls, possibly due to accelerated electron transfer (Yan et al. 2013). CNT-modified polyvinyl alcohol and sodium alginate matrix using immobilized *Pseudomonas aeruginosa* also enhanced bioreduction efficiency of the microorganism (Pang et al. 2011). Additionally, these modified beads can be reused effectively multiple times. This technique of CNTs impregnated immobilization can be applied to various other biological reduction processes and can be tested on various other pollutants.

19.14 Nanobioremediation of Polycyclic Aromatic Hydrocarbons (PAHs)

Hydrocarbons and organic pollutants are persistent in nature. The chances of degrading these compounds increase on application of nano-bio integrated systems. Hydrophobic polycyclic aromatic compounds (PAH) such as carbazole and indenopyrene are toxic and carcinogenic environmental pollutants. *Sphingomonas* sp. XLDN2–5 cells magnetically immobilized in Fe_3O_4 nanoparticle containing gellan gum matrix were proved to be effective in degrading carbazole. The addition of Fe_3O_4 nanoparticles to immobilized bacterial cells significantly enhanced its biodegradation activity (Wang et al. 2007). Yeast strains of *Candida tropicalis* NN4 have been reported to enhance indenopyrene biodegradation activity of zerovalent iron nanoparticles by producing glycolipid biosurfactant (Ojha et al. 2019). *Rhodococcus erythropolis* IGTS8 combined with magnetite (Fe_3O_4) nanoparticles have been found to effectively desulphurize dibenzothiophene (DBT), a recalcitrant organo-sulphur compound released on combustion of fossil fuels, to 2-hydroxybiphenyl (2-HBP). The nanoparticles have been reported to enhance cell growth rate, in comparison with the controls containing either the bacteria or the nanoparticles (Karimi et al. 2017). Immobilized *Pseudomonas*

Table 19.9 Integrated nano-bio systems for remediation of polycyclic aromatic hydrocarbons

Integrated nano-bio systems for remediation of polycyclic aromatic hydrocarbons			
Nanoparticle	Bioagent	Pollutant	References
Polycyclic aromatic hydrocarbons			
Fe^0 nanoparticles (ZVI)	*Candida tropicalis* NN4	Indenopyrene (InP)	Ojha et al. 2019
Pd/nFe bimetallic nanoparticles	Laccase enzyme from *Trametes versicolor*	Triclosan	Bokare et al. 2010
Magnetite (Fe_3O_4) nanoparticles	*Pseudomonas delafieldii*	Dibenzothiophene	Shan et al. 2005
Fe_3O_4 nanoparticles + gellan gum gel beads	*Sphingomonas* sp.	Carbazole	Wang et al. 2007
Magnetite nanoparticles	*Rhodococcus erythropolis* IGTS8	Dibenzothiophene (DBT)	Karimi et al. 2017
Nitro-aromatic compound			
Fe^0 nanoparticles (ZVI)	Methanogenic anaerobes	RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine)	Oh et al. 2001

delafieldii coated with magnetite nanoparticles are also effective in degrading DBT (Shan et al. 2005). Successful degradation of a pollutant depends on its chemical structure. Some pollutants can be degraded completely, while others are broken down to less toxic moieties.

Triclosan, a halogenated aromatic hydrocarbon compound, is a commonly used antibacterial and antifungal component of soaps, toothpaste, and deodorants. Although triclosan is not considered as chemical pollutant of high concern currently, its degraded by-products have been detected in soil, wastewater, drinking water, and even human breast milk. Triclosan has been reported to bioaccumulate in various aquatic species, raising concern of it being an emerging toxic contaminant (Dhillon et al. 2015). Complete biotransformation of triclosan to non-toxic oligomers has been reported via sequential nanobioremediation. Pd/nFe bimetallic nanoparticles, under anaerobic conditions, dechlorinated triclosan to 2-phenoxyphenol, which, in the absence of nanoparticles, was oxidized into non-toxic products by laccase enzyme isolated from *Trametes versicolor* (Bokare et al. 2010). Table 19.9 lists some of the integrated nano-bio systems used for bioremediation of polycyclic aromatic hydrocarbons.

19.15 Nanobioremediation of Petroleum-Based Hydrocarbons

Although the studies conducted on nanobioremediation of oil sludge are few, researchers have demonstrated successful degradation of aliphatic and aromatic hydrocarbons of oil sludge using an integrated system of nanoparticles and microorganisms. The nanoparticles decrease the hydrophobicity of the hydrocarbons allowing them to be accessible to the microorganisms for degradation. The bacteria,

Table 19.10 Integrated systems for remediation of petroleum-based hydrocarbon pollutants

Integrated systems for remediation of petroleum-based hydrocarbon pollutants			
Nanoparticle	Bioagent	Pollutant	References
Fe_2O_3 and Fe_3O_4 nanoparticles	*Thalassospira* sp.	Oil sludge	Rizi et al. 2017a
Fe_2O_3 and Fe_3O_4 nanoparticles	*Chromohalobacter* sp.	Oil sludge	Rizi et al. 2017b
Consortium			
ZnO nanoparticles	*Bacillus, Pseudomonas, Achromobacter,* and *Microbacterium*	Crude oil	Ismail et al. 2013
NiO nanoparticles	*Halomonas xianhensis* A, *Halomonas zincidurans* B6, *Pseudomonas stutzeri* ATCC 17588, and *Halomonas salifodinae* BC7	Crude oil	El-Sheshtawy et al. 2017

Thalassospira sp. and *Chromohalobacter* sp. isolated from an oil site in the Persian Gulf has been studied to successfully degrade oil sludge into various non-toxic compounds. The addition of Fe_2O_3 and Fe_3O_4 nanoparticles, at low concentrations, further enhanced degradation of the compounds, without negatively impacting bacterial growth rate (Rizi et al. 2017a, b).

The interaction between nanoparticles and bacteria may not always be synergistic; nanoparticles can have toxic effects on the microbe and thus reduce its bioremediation potential. Crude oil degradation by the isolated bacteria: *Bacillus, Pseudomonas, Achromobacter,* and *Microbacterium sp.* was deemed successful; but addition of ZnO nanoparticles to *Pseudomonas* decreased its growth rate and lowered bioremediation potential (Ismail et al. 2013). This reduction can be attributed to inhibitory effect of the nanoparticles on the bacterium.

Low bioavailability of crude oil and their poor aqueous solubility obstructs microbial degradation. Nevertheless, evolved mechanisms allow many aquatic microbes to utilize these hydrophobic compounds as a source of carbon. Crude oil degrading bacteria produce biosurfactants and bioemulsifiers that permit bacterial adhesion to hydrocarbons and increase aqueous solubility of crude oil components, thus enhancing its biodegradation. Microcosms containing consortia of *Halomonas xianhensis, Halomonas zincidurans, Pseudomonas stutzeri,* and *Halomonas salifodinae*, along with nickel oxide (NiO) nanoparticles and biosurfactants were found to degrade different membered ring polyaromatics, and 90% of the crude oil sample, compared to microcosms with either biosurfactants or nanoparticles (El-Sheshtawy et al. 2017). Table 19.10 lists some of the integrated nano-bio systems used for remediation of petroleum-based hydrocarbons.

Nanoparticle assisted microbial degradation of hydrocarbon plays a significant role in hydrocarbon decontamination. However, many aspects of nanobioremediation need to be studied such as the innate properties of the nanoparticles, their impact on the microorganisms, the reaction conditions and whether sequential or combined treatment systems need to be applied. Also, the

effect of biosurfactants and bioemulsifiers on the biodegradation of hydrocarbon contaminated sites needs to be evaluated prior to large-scale application of the integrated system.

19.16 Bioremediation of Organic Solvents and Antibiotics

The organic solvent, trichloroethylene (TCE), is an industrial solvent and is a common soil contaminant which is toxic at low levels. Due to its mobility in groundwater and high density, remediation of TCE can be challenging. Combination of nanoscale zerovalent iron (nZVI) along with bacteria *Dehalococcoides* sp. (Table 19.11) has demonstrated successful dechlorination and degradation of TCE to non-toxic compounds in comparison to controls that either contained the microorganism or the nanometal. It was also reported that the combination enhanced the rate of degradation as the nZVI stimulated bacterial growth by providing the bacteria with hydrogen which was utilized to dehalogenate the chlorinated compound (Xiu et al. 2010).

Antibiotics find their way into soil and aquatic systems due to their incessant use in farming and poultry. Due to their continual input into the environment, antibiotics have been classified as pseudo-persistent organic pollutants (Ma and Zhai 2014). These compounds resist biodegradation due to their antimicrobial properties. While nanoparticles and a few microorganisms are known to individually degrade these compounds to certain extent, integrated remediation can offer a cost-effective and more efficient alternative. A combined nano-bio system using MgO nanoparticles has been reported to accelerate the rate of degradation of the antibiotic Cefdinir, by enhancing the cell membrane permeability of yeast *Candida* sp. (Table 19.11) (Adikesavan and Nilanjana 2016). Table 19.11 also enlists some of the other contaminants that have been studied for their remediation using an integrated system of nanoparticles and microbes. Thus, nanoparticles are known to assist microbial activities, but their effect on microbial reaction rates is yet to be studied.

19.17 Bioremediation of Organohalide Compounds

Organohalide compounds are the most persistent toxic compounds that contaminate the soil and water ecosystems. Under aerobic conditions, nZVI has been reported to enhance the degradation of polybrominated diphenyl ethers (PDBE) such as tetrabromo-diphenyl-ether (BDE-47) by *Pseudomonas stutzeri* with increase in incubation time (Huang et al. 2016). PDBEs such as di-, tri-, and deca-BDEs can be degraded into bromophenols by subjecting it to nZVI followed by biological treatment using *Sphingomonas* sp. PH-07. The combination of *Sphingomonas* sp. PH-07 and nZVI is also effective in degrading tetrachlorodibenzo-p dioxin (TCDD), the most toxic dioxin compound (Kim et al. 2012). Nanoparticles integrated with biosurfactant producing bacteria can potentially remediate PCBs. The sequential treatment of PCBs with Pd/Fe nanoparticles followed by bioremediation with

Table 19.11 Nano-bio integrated systems for remediation of recalcitrant organic pollutants

Nano-bio integrated systems for remediation of recalcitrant organic pollutants			
Nanoparticle	Bioagent	Pollutant	References
Organic solvents			
Fe^0 nanoparticles (ZVI)	*Methanosarcina thermophila*	Carbon tetrachloride and chloroform	Novak et al. 1998
nZVI	*Dehalococcoides* sp.	Trichloroethylene (TCE)	Xiu et al. 2010
Antibiotics			
MgO nanoparticles	*Candida* sp. SMN04	Cefdinir (antibiotic)	Adikesavan and Nilanjana 2016
Organohalide compounds			
nZVI	*Sphingomonas* sp. PH-07	Polybrominated diphenyl ethers (PBDEs)	Kim et al. 2012
Pd/nFe bimetallic nanoparticles	*Sphingomonas wittichii* RW1	2,3,7,8-Tetrachlorodibenzo-p dioxin	Bokare et al. 2012
Carboxymethyl cellulose (CMC)-Pd/nFe bimetallic nanoparticles	*Sphingomonas* sp. NM05	γ-Hexachlorohexane (insecticide)	Singh et al. 2013
Magnetite nanoparticles	*Enterobacter aerogenes*	Organophosphate (pesticide)	Daumann et al. 2014
Pd/nFe bimetallic nanoparticles	*Burkholderia xenovorans*	Polychlorinated biphenyls (PCBs)	Le et al. 2015
Pd^0 nanoparticles	*Shewanella oneidensis* MR-1	Polychlorinated biphenyls (PCBs)	Windt et al. 2005
nZVI	*Dehalobacter* sp., *Sedimentibacter* sp., *Dehalogenimonas* sp.	Chlorinated aliphatic hydrocarbons (CAH)	Koenig et al. 2016
nZVI	*Pseudomonas stutzeri*	Polybrominated diphenyl ethers (PBDEs)	Huang et al. 2016
nZVI	*Bacillus* sp.	Polychlorinated biphenyls (PCBs)	Zhang et al. 2016

biosurfactant producing *Burkholderia xenovorans* resulted in formation of less toxic and harmless compounds (Le et al. 2015). The Bio-Pd-*Shewanella oneidensis* MR-1 system serves as a self-sustaining model for remediation, wherein the bacteria adsorb palladium nanoparticles, reduce it to zerovalent state, and precipitate it. These bio-reduced Pd (bio-Pd) nanoparticles were able to dechlorinate a wide range of chlorinated PCB congeners, without any selectivity (Windt et al. 2005). Culture medium dominated by organochlorine respiring bacteria *Dehalobacter* sp., *Sedimentibacter* sp., and *Dehalogenimonas* sp. when combined with nZVI

completely reduce CAH such as dichloroethane and trichloroethane to ethane (Koenig et al. 2016). Carboxymethyl cellulose (CMC) stabilized bimetallic nanoparticles (CMC-Pd/nFe0) integrated with *Sphingomonas* sp. have been demonstrated to degrade γ-hexachlorohexane (γ-HCH), a commonly used insecticide. The stabilized nanoparticles demonstrated to have a biostimulatory effect on the bacterial cells (Singh et al. 2013). Likewise, zerovalent iron (ZVI) has been reported to enhance *Methanosarcina thermophila* mediated dechlorination of compounds such as chloroform and carbon tetrachloride, by serving as an electron donor (Novak et al. 1998). Table 19.11 lists nano-bio systems that are used for remediation of recalcitrant organic compounds.

19.18 Fate of Nanoparticles

While it is implicit that nanoparticles have various applications in the field of bioremediation, the extensive use of these nanoparticles and their subsequent release into the environment is a major concern, especially in cases of in situ remediation. Therefore, the zerovalent iron nanoparticles are currently the only nanoparticles on field application (Kharangate 2015). These particles, once released into the environment, may find channels to enter the food chain, deposit in various organisms, and manifest toxic effects. Nanoparticles have been studied to have toxicity affects that can be attributed to its size. Even nanoparticles of inert metals such as gold have shown to have toxic effects on biological systems (Jeevanandam et al. 2018). Due to the shortage of investigations of the toxicological effects of these nanoparticles, a sub-speciality of nanotechnology, known as nanotoxicology has been developed (Colvin 2003; Niazi and Gu 2009).

Compared to plants, invertebrates, and vertebrates, microorganisms exhibit widespread and diverse reactions to nanoparticles (Oberdorster et al. 2009). The toxic effects depend on the nature of the nanoparticle and its interaction with the microbial species. In case of rhizosphere resident bacteria *Pseudomonas chlororaphis* O6, CuO nanoparticles were demonstrated to neutralize the charge on the EPS colloids and release ions that disrupt the homeostatic control within the cell. Similar mechanisms of disrupting homeostatic mechanisms of the cell have been observed with ZnO nanoparticles (Dimpka et al. 2011).

Application of nanoparticles in remediation processes results in the discharge of these nanoparticles in the soil and aquatic ecosystems wherein they encounter and interact with various microorganisms, which are sensitive to these particles. Due to their nano-size, large surface area, and high reactivity, nanoparticles can destroy the microbial membrane and generate reactive oxygen species (ROS) that are known to disrupt cellular processes (Cecchin et al. 2016). Studies conducted on nanoparticles released in natural aqueous environments confirm that the nanoparticles react and conjugate with biological molecules such as DNA, RNA, proteins as well and lysophospholipids which facilitate their solubilization in water (Ke and Qiao 2007; Niazi and Gu 2009). Since microbes can assimilate nanoparticles, it can lead to accumulation in the food chain and ultimately build-up to toxic levels in humans.

Recovery of released nanoparticles from natural systems seems impossible, extensive research is needed to understand their potential toxic effects on various biological systems, prior to their large-scale application in nanobioremediation of contaminated sites.

Furthermore, soil microorganisms play an important role in regulating biogeochemical cycles and also possess natural mechanisms to degrade contaminants. Drastic reduction in populations of these beneficial organisms can lead to ecological imbalance. Despite their adaptability, nanoparticles used for in situ remediation can have a bactericidal effect on the inherent microbiota. Thus, determining the interactions between native microorganisms, the contaminant and the nanoparticle to be used prior to application is imperative for sustainable remediation of polluted sites.

19.19 Conclusion

Integrated systems have a lot of potential in remediating various organic and inorganic contaminants from polluted environments. Nanobioremediation has the ability to reduce the overall cost for environmental clean-up on large-scale application. While ex situ nanobioremediation is still at an infant stage, in situ application of nanoremediation and nanobioremediation to soil and ground/surface water can reduce contaminant to near-zero levels. Microbe-assisted intracellular/extracellular synthesis of biogenic nanoparticles acts as a novel, environment friendly, cost-effective strategy to supply tailored nanoparticles for remediation projects. Additionally, the possibility of intentionally tuning nanoparticles opens up new avenues in nanoremediation. Although this approach is a favourable alternative to conventional methods, nano-toxicity associated environmental risks are still unclear and need further research. Moreover, the effect of parameters like pH, temperature, ionic strength, presence of competing or inhibitory substances, etc. on remediation efficiency of the nanobioremediation method needs to be evaluated. But once these gaps are filled, integrated nano-bio systems can be applied on a larger scale.

Acknowledgement The authors wish to thank Pankaj Lad for graphic designing of the diagrams and for his valuable inputs in the chapter.

References

Abatenh E, Gizaw B, Tsegaye Z, Wassie M (2017) The role of microorganisms in bioremediation- a review. Open J Environ Biol 2(1):38–46. https://doi.org/10.17352/ojeb.000007

Adikesavan S, Nilanjana D (2016) Degradation of Cefdinir by *Candida* Sp. SMN04 and MgO nanoparticles—an integrated (nano-bio) approach. Environ Prog Sustain Energy 35 (3):706–714. https://doi.org/10.1002/ep.12279

Ahmad A, Senapati S, Khan MI, Kumar R, Ramani R, Srinivas V, Sastry M (2003) Intracellular synthesis of gold nanoparticles by a novel alkalotolerant actinomycete *Rhodococcus* sp. Nanotechnology 14(7):824. https://doi.org/10.1088/0957-4484/14/7/323

Akanyeti I, Kraft A, Ferrari MC (2017) Hybrid polystyrene nanoparticle-ultrafiltration system for hormone removal from water. J Water Process Eng 17:102–109. https://doi.org/10.1016/j.jwpe.2017.02.014

Alabresm A, Chen YP, Decho AW, Lead J (2018) A novel method for the synergistic remediation of oil-water mixtures using nanoparticles and oil-degrading bacteria. Sci Total Environ 630:1292–1297. https://doi.org/10.1016/j.scitotenv.2018.02.277

Alani F, Moo-Young M, Anderson W (2012) Biosynthesis of silver nanoparticles by a new strain of *Streptomyces sp.* compared with *Aspergillus fumigatus*. World J Microbiol Biotechnol 28:1081–1086. https://doi.org/10.1007/s11274-011-0906-0

Ali N, Bilal M, Khan A, Ali F, Iqbal HMN (2020) Effective exploitation of anionic, non-ionic, and nanoparticle-stabilized surfactant foams for petroleum hydrocarbon contaminated soil remediation. Sci Total Environ 704:135391. https://doi.org/10.1016/j.envpol.2020.114728

Amin MA, Bina B, Majd AMS, Pourzamani H (2013) Benzene removal by nano magnetic particles under continuous condition from aqueous solutions. Front Environ Sci Eng 8(3):345–356. https://doi.org/10.1007/s11783-013-0574-4

Anghel L, Balasolu M, Ishchenko LA, Stolyar SV, Kurkin TS, Rogachev AV, Kuklin A, Kovalev YS, Raikher YL, Iskhakov RS, Duca G (2012) Characterization of biosynthesized nanoparticles produced by *Klebsiella oxytoca*. J Phys Conf Ser 351:012005. https://doi.org/10.1088/1742-6596/351/1/012005

Arcon I, Piccolo O, Paganelli S, Baldi F (2012) XAS analysis of a nanostructured iron polysaccharide produced anaerobically by a strain of *Klebsiella oxytoca*. Biometals 25(5):875. https://doi.org/10.1007/s10534-012-9554-6

Baby R, Saifullah B, Hussein MZ (2019) Carbon nanomaterials for the treatment of heavy metal-contaminated water and environmental remediation. Nanoscale Res Lett 14:341. https://doi.org/10.1186/s11671-019-3167-8

Bagbi Y, Sarswat A, Tiwari S, Mohan D, Pandey A, Solanki PR (2017) Synthesis of L-cysteine stabilized zero-valent iron (nZVI) nanoparticles for lead remediation from water. Environ Nanotechnol Monit Manag 7:34–45. https://doi.org/10.1016/j.enmm.2016.11.008

Bai HJ, Zhang ZM, Guo Y, Yang GE (2009) Biosynthesis of cadmium Sulphide nanoparticles by photosynthetic bacteria *Rhodopseudomonas palustris*. Colloids Surf B Biointerfaces 70 (1):142–146. https://doi.org/10.1016/colsurfb.2008.12.025

Bai H, Zhou J, Zhang H, Tang G (2017) Enhanced adsorbability and photocatalytic activity of TiO2-graphene composite for polycyclic aromatic hydrocarbons removal in aqueous phase. Colloids Surf B Biointerfaces 150:68–77. https://doi.org/10.1016/j.colsurfb.2016.11.017

Balaji DS, Basavaraja S, Deshpande R, Bedre DM, Prabhakar BK, Venkataraman A (2009) Extracellular biosynthesis of functionalized silver nanoparticles by strains of *Cladosporium cladosporioides* fungus. Colloids Surf B Biointerfaces 68:88. https://doi.org/10.1016/j.colsurfb.2008.09.022

Banik J, Basumallick S (2017) Nanoparticle-assisted photo-Fenton reaction for photo-decomposition of humic acid. Appl Water Sci 7(7):4159–4163. https://doi.org/10.1007/s13201-017-0566-9

Baragaño D, Forján R, Welte L, Gallego JLR (2020) Nanoremediation of As and metals polluted soils by means of graphene oxide nanoparticles. Sci Rep 10:1896. https://doi.org/10.1038/s41598-020-58852-4

Bezbaruah AN, Thompson JM, Chrisholm BJ (2009) Remediation of alachlor and atrazine contaminated water with zero-valent iron nanoparticles. J Environ Sci Health B 44 (6):518–524. https://doi.org/10.1080/03601230902997501

Bhakya S, Muthukrishnan S, Sukumaran M, Muthukumar M, Senthil Kumar T (2015) Catalytic degradation of organic dyes using synthesized silver nanoparticles: a green approach. J Bioremed Biodegr 6:312. https://doi.org/10.4172/2155-6199.1000312

Bhunia SK, Jana NR (2014) Reduced graphene oxide-silver nanoparticle composite as visible light photocatalyst for degradation of colorless endocrine disruptors. ACS Appl Mater Interfaces 6 (22):20085–20092. https://doi.org/10.1021/am505677x

Boente C, Sierra C, Martínez-Blanco D, Menendez-Aguado JM, Gallego JR (2018) Nanoscale zero-valent iron-assisted soil washing for the removal of potentially toxic elements. J Hazard Mater 350:55–65. https://doi.org/10.1016/j.jhazmat.2018.02.016

Bokare V, Murugesan K, Kim YM, Jeon JR, Kim EJ, Chang YS (2010) Degradation of triclosan by an integrated nano-bio redox process. Bioresour Technol 101(16):6354–6360. https://doi.org/10.1016/j.biortech.2010.03.062

Bokare V, Murugesan K, Kim JH, Kim EJ, Chang YS (2012) Integrated hybrid treatment for the remediation of 2,3,7,8-tetrachlorodibenzo-p-dioxin. Sci Total Environ 435-436:563–566. https://doi.org/10.1016/j.scitotenv.2012.07.079

Bootharaju MS, Pradeep T (2012) Understanding the degradation pathway of pesticide chlorpyrifos by noble metal nanoparticles. Langmuir 28(5):2671–2679. https://doi.org/10.1021/la2050515

Cao J, Yang Z, Xiong W, Zhou Y, Peng Y, Li X, Zhou C, Xu R, Zhan Y (2018) One-step synthesis of co-doped UiO-66 nanoparticle with enhanced removal efficiency of tetracycline: simultaneous adsorption and photocatalysis. Chem Eng J 353:126–137. https://doi.org/10.1016/j.cej.2018.07.060

Cecchin I, Reddy KR, Thomé A, Tessaro EF, Schnaid F (2016) Nanobioremediation: integration of nanoparticles and bioremediation for sustainable remediation of chlorinated organic contaminants in soils. Int Biodeterior Biodegrad 119:419–428. https://doi.org/10.1016/j.ibiod.2016.09.027

Chen X, Yao X, Yu C, Su X, Shen C, Chen C, Huang R, Xu X (2014) Hydrodechlorination of polychlorinated biphenyls in contaminated soil from an e-waste recycling area, using nanoscale zerovalent iron and Pd/Fe bimetallic nanoparticles. Environ Sci Pollut Res 21:5201–5210. https://doi.org/10.1007/s11356-013-2089-8

Chidambaram D, Hennebel T, Taghavi S, Mast J, Boon N, Verstraete W, Van der Lelie D, Fitts JP (2010) Concomitant microbial generation of palladium nanoparticles and hydrogen to immobilize chromate. Environ Sci Technol 44(19):7635–7640. https://doi.org/10.1021/es101559r

Chowdhury SR, Yanful EK (2010) Arsenic and chromium removal by mixed magnetite–maghemite nanoparticles and the effect of phosphate on removal. J Environ Manag 91 (11):2238–2247. https://doi.org/10.1016/j.jenvman.2010.06.003

Colvin VL (2003) The potential environmental impact of engineered nanomaterials. Nat Biotechnol 21:1166–1170. https://doi.org/10.1038/nbt875

Contreras AR, Casals E, Puntes V, Komilis D, Sanchez A, Font X (2015) Use of cerium oxide (CeO2) nanoparticles for the adsorption of dissolved cadmium (II), lead (II) and chromium (VI) at two different pHs in single and multi-component systems. Global NEST J 17(3):536–543

Creamer NJ, Mikheenko IP, Yong P, Deplanche K, Sanyahumbi D, Wood J, Pollmann K, Merroun M, Selenska-Pobell S, Macaskie LE (2007) Novel supported Pd hydrogenation bionanocatalyst for hybrid homogeneous/heterogeneous catalysis. Catal Today 128:80–87. https://doi.org/10.1016/j.cattod.2007.04.014

Cuevas R, Duran N, Diez MC, Tortella GR, Rubilar O (2015) Extracellular biosynthesis of copper and copper oxide nanoparticles by *Stereum hirsutum*, a native white-rot fungus from Chilean forests. J Nanomater 2015:789089. https://doi.org/10.1155/2015/789089

Czech B, Rubinowska K (2013) TiO_2-assisted photocatalytic degradation of diclofenac, metoprolol, estrone, chloramphenicol as endocrine disruptors in water. Adsorption 19:619–630. https://doi.org/10.1007/s10450-013-9485-8

Dai L, Li Y, Liu R, Si C, Ni Y (2019) Green mussel-inspired lignin magnetic nanoparticles with high adsorptive capacity and environmental friendliness for chromium(III) removal. Int J Biol Macromol 132:478–486. https://doi.org/10.1016/j.ijbiomac.2019.03.222

Das N, Chandran P (2011) Microbial degradation of petroleum hydrocarbon contaminants: an overview. Biotechnol Res Int 1:1–13. https://doi.org/10.4061/2011/941810

Das R, Sarkar S, Chakraborty S, Choi H, Bhattacharjee C (2014) Remediation of antiseptic components in wastewater by photocatalysis using TiO2 nanoparticles. Ind Eng Chem Res 53:3012–3020. https://doi.org/10.1021/ie403817z

Das S, Ghosh S, Misra AJ, Tamhankar AJ, Mishra A, Lundborg CS, Tripathy SK (2018) Sunlight assisted photocatalytic degradation of ciprofloxacin in water using Fe doped ZnO nanoparticles for potential public health applications. Int J Environ Res Public Health 15:2440. https://doi.org/10.3390/ijerph15112440

Daumann LJ, Larrabee JA, Ollis D, Schenk G, Gahan LR (2014) Immobilization of the enzyme GpdQ on magnetite nanoparticles for organophosphate pesticide bioremediation. J Inorg Biochem 131:1–7. https://doi.org/10.1016/j.jinorgbio.2013.10.007

Daza EA, Misra SK, Scott J, Tripathi I, Promisel C, Sharma BK, Topczewski J, Chaudhuri S, Pan D (2017) Multi-Shell nano-carbo scavengers for petroleum spill remediation. Sci Rep 7:41880. https://doi.org/10.1038/srep41880

Deng M, Wu X, Zhu A, Zhang Q, Liu Q (2019) Well-dispersed TiO_2 nanoparticles anchored on Fe_3O_4 magnetic nanosheets for efficient arsenic removal. J Environ Manag 237:63–74. https://doi.org/10.1016/j.jenvman.2019.02.037

Dhillon GS, Kaur S, Pulicharla R, Brar SK, Cledon M, Verma M, Surampalli RY (2015) Triclosan: current status, occurrence, environmental risks and bioaccumulation potential. Int J Environ Res Public Health 12:5657–5684. https://doi.org/10.3390/ijerph120505657

Dimpka CO, Calder A, Britt DW, McLean JE, Anderson AJ (2011) Responses of soil bacterium *Pseudomonas choraphis* O6 to commercial metal oxide nanoparticles compared with responses to metal ions. Environ Pollut 159:1749–1756. https://doi.org/10.1016/j.envpol.2011.04.020

Dong X, He L, Hu H, Liu N, Gao S, Piao Y (2018a) Removal of 17β-estradiol by using highly adsorptive magnetic biochar nanoparticles from aqueous solution. Chem Eng J 352:371–379. https://doi.org/10.1016/j.cej.2018.07.025

Dong H, Jiang Z, Zhang C, Deng J, Hou K, Cheng Y, Zhang L, Zeng G (2018b) Removal of tetracycline by Fe/Ni bimetallic nanoparticles in aqueous solution. J Colloid Interface Sci 513:117–125. https://doi.org/10.1016/j.jcis.2017.11.021

Edelstein M, Ben-Hur M (2018) Heavy metals and metalloids: sources, risks and strategies to reduce their accumulation in horticultural crops. Sci Hortic 234(14):431–444. https://doi.org/10.1016/j.scienta.2017.12.039

Elcey C, Kuruvilla AT, Thomas D (2014) Synthesis of magnetite nanoparticles from optimized iron reducing bacteria isolated from iron ore mining sites. Int J Curr Microbiol Appl Sci 3:408–417

Elfeky SA, Mahmoud SE, Youssef AF (2017) Applications of CTAB modified magnetic nanoparticles for removal of chromium (VI) from contaminated water. J Adv Res 8 (4):435–443. https://doi.org/10.1016/j.jare.2017.06.002

Elliott DW, Lien H-L, Zhand W-X (2009) Degradation of Lindane by zero-valent Iron nanoparticles. J Environ Eng 135(5):317–324. https://doi.org/10.1061/(ASCE)0733-9372(2009)135:5(317)

El-Maraghy CM, El-Borady OM, El-Naem OA (2020) Effective removal of levofloxacin from pharmaceutical wastewater using synthesized zinc oxide, graphene oxide nanoparticles compared with their combination. Sci Rep 10:5914. https://doi.org/10.1038/s41598-020-61742-4

El-Sheshtawy HS, Khalil NM, Ahmed W, Nabila AA (2017) Enhancement the bioremediation of crude oil by nanoparticle and biosurfactants. Egypt J Chem 60(5):835–848

Farnad N, Farhadi K, Voelcker NH (2012) Polydopamine nanoparticles as a new and highly selective biosorbent for the removal of copper (II) ions from aqueous solutions. Water Air Soil Pollut 223:3535–3544. https://doi.org/10.1007/s11270-012-1131-7

Feng X, Gua H, Patel K, Zhou H, Lou X (2014) High performance, recoverable Fe_3O_4-Zno nanoparticles for enhanced photocatalytic degradation of phenol. Chem Eng J 244:327–334. https://doi.org/10.1016/j.cej.2014.01.075

Foster SL, Estoque K, Voecks M, Rentz N, Greenlee LF (2019) Removal of synthetic azo dye using bimetallic nickel-iron nanoparticles. J Nanomater 2019:9807605. https://doi.org/10.1155/2019/9807605

Fouad DM, El-Said WA, Mohamed MB (2015) Spectroscopic characterization of magnetic Fe3O4-au core shell nanoparticles. Spectrochim Acta A Mol Biomol Spectrosc 140:392–397. https://doi.org/10.1016/j.saa.2014.12.097

Geng B, Jin Z, Li T, Qi X (2009) Kinetics of hexavalent chromium removal from water by chitosan - Fe^0 nanoparticles. Chemosphere 75(6):825–830. https://doi.org/10.1016/j.chemosphere.2009.01.009

Ghafoor S, Ata S (2017) Synthesis of carboxyl-modified Fe_3O_4-SiO_2 nanoparticles and their utilization for the remediation of cadmium and nickel from aqueous solution. J Chil Chem Soc 62(3):3588–3592. https://doi.org/10.4067/s0717-97072017000303588

Gharaghani MA, Malakootian M (2017) Photocatalytic degradation of the antibiotic ciprofloxacin by ZnO nanoparticles immobilized on a glass plate. Desalin Water Treat 89:304–314. https://doi.org/10.5004/dwt.2017.21378

Ghosh S, Prabhakar R, Samadder SR (2019) Performance of γ-aluminium oxide nanoparticles for arsenic removal from groundwater. Clean Techn Environ Policy 21:121–138. https://doi.org/10.1007/s10098-018-1622-3

Gomes HI, Dias-Ferreira C, Ottosen LM, Ribeiro AB (2014) Electrodialytic remediation of polychlorinated biphenyls contaminated soil with iron nanoparticles and two different surfactants. J Colloid Interface Sci 433:189–195. https://doi.org/10.1016/j.jcis.2014.07.022

Gong Y, Liu Y, Xiong Z, Kaback D, Zhao D (2012) Immobilization of mercury in field soil and sediment using carboxymethyl cellulose stabilized iron sulfide nanoparticles. Nanotechnology 23(29):4007. https://doi.org/10.1088/0957-4484/23/29/294007

Gregorio SD, Lampis S, Vallini G (2005) Selenite precipitation by rhizospheric strain of *Stenotrophomonas sp.* isolated from the root system of *Astragalus bisulcatus*: a biotechnological perspective. Environ Int 31(2):233–241. https://doi.org/10.1016/j.envint.2004.09.021

Guerra FD, Attia MF, Whitehead DC, Alexis F (2018) Nanotechnology for environmental remediation: materials and applications. Molecules 23(7):1760. https://doi.org/10.3390/molecules23071760

Guo Y, Xu B, Qi F (2016) A novel ceramic membrane coated with MnO_2-Co_3O_4 nanoparticles catalytic ozonation for benzophenone-3 degradation in aqueous solution: fabrication, characterization and performance. Chem Eng J 287:381–389. https://doi.org/10.1016/j.cej.2015.11.067

Gupta S, Bector S (2013) Biosynthesis of extracellular and intracellular gold nanoparticles by *Aspergillus fumigatus* and *Aspergillus flavus*. Antonie Van Leeuwenhoek 103:1113–1123. https://doi.org/10.1007/s10482-013-9892-6

Gurunathan S, Kim ES, Han JW, Park JH, Kim JH (2015) Green chemistry approach for synthesis of effective anticancer palladium nanoparticles. Molecules 20(12):22476. https://doi.org/10.3390/molecules201219860

Han B, Zhang M, Zhao D, Feng Y (2014) Degradation of aqueous and soil-absorbed estradiol using a new class of stabilized manganese oxide nanoparticles. Water Res 70:288–299. https://doi.org/10.1016/j.watres.2014.12.017

Hao Y-M, Man C, Hu Z-B (2010) Effective removal of cu (II) ions from aqueous solution by amino-functionalized magnetic nanoparticles. J Hazard Mater 184:392–399. https://doi.org/10.1016/j.jhazmat.2010.08.048

He S, Guo Z, Zhang Y, Zhang S, Wang J, Gu N (2007) Biosynthesis of gold nanoparticles using the bacteria *Rhodopseudomonas capsulate*. Mater Lett 61(18):3984–3987. https://doi.org/10.1016/j.matlett.2007.01.018

Helal MID, Khater HA, Marzoog A (2016) Application of nanotechnology in remediation of heavy metals polluted soils. J Arid Land Stud 26(3):129–137. https://doi.org/10.14976/jals.26.3_129

Honary S, Barabadi H, Gharael-Fathabad E, Naghibi F (2012) Green synthesis of copper oxide nanoparticles using *Penicillium aurantiogriseum, Penicillium citrinum* and *Penicillium waksmanii*. Dig J Nanomater Bios 7(3):999–1005

Huang Y, Keller AA (2015) EDTA functionalized magnetic nanoparticle sorbents for cadmium and lead contaminated water treatment. Water Res 80:159–168. https://doi.org/10.1016/j.watres.2015.05.011

Huang Z, Chen Y, Hu Y (2016) The role of nanoscale zerovalent iron particles in the biosorption and biodegradation of BDE-47 by *Pseudomonas stutzeri* under aerobic conditions. Int Biodeterior Biodegrad 112:51–58. https://doi.org/10.1016/j.ibiod.2016.04.039

Hussain I, Singh NB, Singh A, Singh H, Singh SC (2016) Green synthesis of nanoparticles and its potential application. Biotechnol Lett 38:545–560. https://doi.org/10.1007/s10529-015-2026-7

Ibrahem AK, Moghny TA, Mustafa YM, Maysour N, El-Dars F, Hassan R (2012) Degradation of trichloroethylene contaminated soil by zero-valent iron nanoparticles. ISRN Soil Sci 2012:270830. https://doi.org/10.5402/2012/270830

Iravani S (2014) Bacteria in nanoparticle synthesis: current status and future prospects. Int Sch Res 2014:359316. https://doi.org/10.1155/2014/359316

Ismail W, Alhamad NA, El-Sayed WS, El Naya AM, Chiang YR, Hamzah RY (2013) Bacterial degradation of the saturate fraction of Arabian light crude oil: biosurfactant production and the effect of ZnO nanoparticles. J Pet Environ Biotechnol 4(6):125–131. https://doi.org/10.4172/2157-7463.1000163

Jarosova B, Filip J, Hilsherova K, Tucek J, Simek Z, Giesy JP, Zboril R, Blaha L (2015) Can zero-valent iron nanoparticles remove waterborne estrogens? J Environ Manag 150:387–392. https://doi.org/10.1016/j.jenvman.2014.12.007

Jeevanandam J, Barhoum A, Chan YS, Dufresne A, Danquah MK (2018) Review on nanoparticles and nanostructured materials: history, sources, toxicity and regulations. Beilstein J Nanotechnol 9:050–1074. https://doi.org/10.3762/bjnano.9.98

Jia MK, Su GJ, Zheng MH, Zhang B, Lin SJ (2010) Synthesis of a magnetic micro/nano FexOy-CeO2 composite and its application for degradation of hexachlorobenzene. Sci China Chem 53 (6):1266–1272. https://doi.org/10.1007/s11426-010-3164-3

Jorfi S, Samaei MR, Soltani RDC, Khozani AT, Ahmadi M, Barzegar G, Reshadatian N, Mehrabi N (2016) Enhancement the bioremediation of pyrene-contaminated soils using a hematite nano-particle based modified Fenton oxidation in a sequenced approach. Soil Sediment Contam 26 (2):141–156. https://doi.org/10.1080/15320383.2017.1255875

Kale R, Kane P (2017) Colour removal using nanoparticles. Text Cloth Sustain 2:4. https://doi.org/10.1186/s40689-016-0015-4

Kalimuthu K, Babu RS, Venkataraman D, Bilai M, Gurunanthan S (2008) Biosynthesis of silver nanocrystals by *Bacillus licheniformis*. Colloids Surf B 65(1):150–153. https://doi.org/10.1016/j.colsurfb.2008.02.018

Karimi E, Jeffryes C, Yazdian F, Sepahi AA (2017) DBT desulfurization by decorating Rhodococcus erythropolis IGTS8 using magnetic Fe_3O_4 nanoparticles in a bioreactor. Eng Life Sci 17:528–535. https://doi.org/10.1002/elsc.201600080

Karn B, Kuiken T, Otto M (2009) Nanotechnology and in situ remediation: a review of the benefits and potential risks. Environ Health Perspect 17(12):1813–1831. https://doi.org/10.1289/ehp.0900793

Ke PC, Qiao R (2007) Carbon nanomaterials in biological systems. J Phys Condens Matter 19:373101. https://doi.org/10.1088/0953-8984/19/37/373101

Khan R, Fulekar MH (2016) Biosynthesis of titanium dioxide nanoparticles using *Bacillus amyloliquefaciens* culture and enhancement of its photocatalytic activity for the degradation of a sulfonated textile dye reactive red 31. J Colloid Interface Sci 475:184–191. https://doi.org/10.1016/j.jcis.2016.05.001

Kharangate AP (2015) Halophilic and halotolerant bacteria adhered to particulate matter in the mangrove ecosystem. PhD thesis, Goa University, Goa, India

Kim YM, Murugesan K, Chang Y-Y, Kim EJ, Changa YS (2012) Degradation of polybrominated diphenyl ethers by a sequential treatment with nanoscale zerovalent iron and aerobic biodegradation. J Chem Technol Biotechnol 87:216–224. https://doi.org/10.1002/jctb.2699

Koenig JC, Boparai HK, Lee MJ, O'Carroll DM, Barnes RJ, Manefield MJ (2016) Particles and enzymes: combining nanoscale zero valent iron and organochlorine respiring bacteria for the detoxification of chloroethane mixtures. J Hazard Mater 308:106–112. https://doi.org/10.1016/j.jhazmat.2015.12.0360304-3894

Kumar D, Karthik L, Kumar G, Roa KB (2011) Biosynthesis of silver nanoparticles from marine yeast and their antimicrobial activity against multidrug resistant pathogens. Pharmacol Online 3:1100

Kumar V, Shahi SK, Singh S (2018) Bioremediation: an eco-sustainable approach for restoration of contaminated sites. In: Singh J, Sharma D, Kumar G, Sharma N (eds) Microbial bioprospecting for sustainable development. Springer, Singapore, pp 115–136. https://doi.org/10.1007/978-981-13-0053-0_6

Labrenz M, Druschel GK, Thomsen-Ebert T, Gilbert B, Welch SA, Kemner KM, Logan GA, Summons RE, De Stasio G, Bond PL, Lai B, Kelly SD, Banfield JF (2000) Formation of sphalerite (ZnS) deposits in natural biofilms of sulphate-reducing bacteria. Science 290 (5497):1744. https://doi.org/10.1126/science.290.5497.1744

Latif A, Sheng D, Sun K, Si Y, Azeem M, Abbas A, Bilal M (2020) Remediation of heavy metals polluted environment using Fe-based nanoparticles: mechanisms, influencing factors, and environmental implications. Environ Pollut 264:114728. https://doi.org/10.1016/j.envpol.2020.114728

Le TT, Nguyen KH, Jeon JR, Francis AJ, Chang YS (2015) Nano/ bio treatment of polychlorinated biphenyls with evaluation of comparative toxicity. J Hazard Mater 287:335–341. https://doi.org/10.1016/j.jhazmat.2015.02.001

Lengke MF, Southam G (2006) Bioaccumulation of gold by sulphate-reducing bacteria cultured in the presence of gold(I)-thiosulphate complex. Geochim Cosmochim Acta 70(14):3646–3661. https://doi.org/10.1016/j.gca.2006.04.018

Li XQ, Elliott DW, Zhang WX (2006) Zero-valent iron nanoparticles for abatement of environmental pollutants: materials and engineering aspects. Crit Rev Solid State Mater Sci 31 (4):111–122. https://doi.org/10.1080/10408430601057611

Li X, Xu H, Chen Z, Chen G (2011) Biosynthesis of nanoparticles by microorganisms and their applications. Nanostruct Med Pharm 2011:270974. https://doi.org/10.1155/2011/270974

Liu R, Zhao D (2007) Reducing leachability and bioaccessibility of lead in soils using a new class of stabilized iron phosphate nanoparticles. Water Res 41:2491–2502. https://doi.org/10.1016/j.watres.2007.03.026

Liu K, Yu JC, Dong H, Wu JCS, Hoffmann MR (2018) Degradation and mineralization of carbamazepine using an electro-Fenton reaction catalyzed by magnetite nanoparticles fixed on an electrocatalytic carbon fiber textile cathode. Environ Sci Technol 52(21):12667–12674. https://doi.org/10.1021/acs.est.8b03916

Ma J, Zhai G (2014) Antibiotic contamination: a global environment issue. J Bioremed Biodegr 5:5. https://doi.org/10.4172/2155-6199.1000e157

Mabbett AN, Lloyd JR, Macaskie LE (2004) Reduction of Cr (VI) by "Palladized"-biomass of *Desulfovibrio desulfuricans* ATCC 29577. Biotechnol Bioeng 87:104–109. https://doi.org/10.1002/bit.20105

Machado S, Stawinski S, Slonina P, Pinto AR, Grosso JP, Nouws HPA, Albergaria JT, Delerue-Matos C (2013) Application of green zero-valent iron nanoparticles to the remediation of soils contaminated with ibuprofen. Sci Total Environ 461-462:323–329. https://doi.org/10.1016/j.scitotenv.2013.05.016

Malakootian M, Yaseri M, Faraji M (2019) Removal of antibiotics from aqueous solutions by nanoparticles: a systematic review and meta-analysis. Environ Sci Pollut Res 26:8444–8458. https://doi.org/10.1007/s11356-019-04227-w

Malakootian M, Nasiri A, Gharaghani MA (2020) Photocatalytic degradation of ciprofloxacin antibiotic by TiO2 nanoparticles immobilized on a glass plate. Chem Eng Commun 207 (1):56–72. https://doi.org/10.1080/00986445.2019.1573168

Manav N, Dwivedi V, Bhagi AK (2018) Degradation of DDT, a pesticide by mixed metal oxides nanoparticles. In: Parmar V, Malhotra P, Mathur D (eds) Green chemistry in environmental sustainability and chemical education. Springer, Singapore. https://doi.org/10.1007/978-981-10-8390-7_9

Mansouriieh N, Khosravi M (2015) Optimization of profenofos organophosphorus pesticide degradation by zero-valent bimetallic nanoparticles using response surface methodology. Arab J Chem 12(8):2524–2532. https://doi.org/10.1016/j.arabjc.2015.04.009

Marcelo CR, Lopes RP, Cruz JC, Nascimento MA, Silva AA, Lima CF (2016) Evaluation of different parameters on the acetamiprid degradation by bimetallic Fe/Ni nanoparticles. Sep Purif Technol 171:256–262. https://doi.org/10.1016/j.seppur.2016.07.032

Mazumdar H, Haloi N (2011) A study on biosynthesis of Iron nanoparticles by *Pleurotus sp*. J Microbiol Biotechnol Res 39(1):39–49

Megharaj M, Ramakrishnan B, Venkateshwarlu K, Sethunathan N, Naidu R (2011) Bioremediation approaches for organic pollutants: a critical perspective. Environ Int 37(8):1362–1275. https://doi.org/10.1016/j.envint.2011.06.003

Mishra A, Tripathy SK, Wahab R, Jeong SH, Hwang I, Yang YB, Kim YS, Shin HS, Yun SI (2011) Microbial synthesis of gold nanoparticles using the fungus *Penicillium brevicompactum* and their cytotoxic effects against mouse mayo blast cancer C_2C_{12} cells. Appl Microbiol Biotechnol 92:617–630. https://doi.org/10.1007/s00253-011-3556-0

Mohanpuria P, Rana NK, Yadav SK (2008) Biosynthesis of nanoparticles: technological concepts and future applications. J Nanopart Res 10(3):507–517. https://doi.org/10.1007/s11051-007-9275-x

Mohmood I, Lopes CB, Lopes I, Tavares DS, Soares AMVM, Duarte AC, Trindade T, Ahmad I, Pereira E (2016) Remediation of mercury contaminated saltwater with functionalized silica coated magnetite nanoparticles. Sci Total Environ 557–558:712–721. https://doi.org/10.1016/j.scitotenv.2016.03.075

Mosmeri H, Alaie E, Shavandi M, Dastgheib SMM, Tasharrofi S (2017) Benzene-contaminated groundwater remediation using calcium peroxide nanoparticles: synthesis and process optimization. Environ Monit Assess 189:452. https://doi.org/10.1007/s10661-017-6157-2

Murgueitio E, Cumbal L, Abril M, Izquierdo A, Debut A, Tinoco O (2018) Green synthesis of iron nanoparticles: application on the removal of petroleum oil from contaminated water and soils. J Nanotechnol 2018:4184769. https://doi.org/10.1155/2018/4184769

Nanda A, Saravanan M (2009) Biosynthesis of silver nanoparticles from *Staphylococcus aureus* and its antimicrobial activity against MRSA and MRSE. Nanomed Nanotechnol Biol Med 5 (4):452. https://doi.org/10.1016/j.nano.2009.01.012

Nangia Y, Wangoo N, Goyal N, Shekhawat G, Suri CR (2009) A novel bacterial isolate *Stenotrophomonas maltophilia* as living factory for synthesis of gold nanoparticles. Microb Cell Factories 8:39. https://doi.org/10.1186/1475-2859-9-39

Narayanan KB, Sakthivel N (2010) Biological synthesis of metal nanoparticles by microbes. Adv Colloid Interface Sci 156:1–13. https://doi.org/10.1016/j.cis.2010.02.001

Nemecek J, Pokorny P, Lhotsky O, Knytl V, Najmanova P, Steinova J, Cernik M, Filipova A, Filip J, Cajthaml T (2016) Combined nano-biotechnology for in-situ remediation of mixed contamination of groundwater by hexavalent chromium and chlorinated solvents. Sci Total Environ 563–564:822–834. https://doi.org/10.1016/j.scitotenv.2016.01.019

Niazi JH, Gu MB (2009) Toxicity of metallic nanoparticles in microorganisms – a review. In: Kim YJ, Platt U, Gu MB, Iwahashi H (eds) Atmospheric and environmental monitoring. Springer, Dordrecht. https://doi.org/10.1007/978-1-4020-9674-7_12

Novak P, Daniels L, Parkin G (1998) Enhanced dechlorination of carbon tetrachloride and chloroform in the presence of elemental iron *and Methanosarcina barkeri*, *Methanosarcina thermophila*, or *Methanosaeta concilii*. Environ Sci Technol 32:1438–1443

Oberdorster G, Stone V, Donaldson K (2009) Toxicology of nanoparticles: a historical perspective. J Nanotoxicol 1(1):2–25. https://doi.org/10.1080/17435390701314761

Oh BT, Just CL, Alvarez PJ (2001) Hexahydro-1, 3, 5-trinitro-1, 3, 5-triazine mineralization by zerovalent iron and mixed anaerobic cultures. Environ Sci Technol 35(21):4341–4346. https://doi.org/10.1021/es010852e

Ojea-Jiménez I, López X, Arbiol J, Puntes V (2012) Citrate-coated gold nanoparticles as smart scavengers for mercury (II) removal from polluted waters. ACS Nano 6(3):2253–2260. https://doi.org/10.1021/nn204313a

Ojha N, Mandal SK, Das N (2019) Enhanced degradation of indeno(1,2,3-cd) pyrene using *Candida tropicalis* NN4 in presence of iron nanoparticles and produced biosurfactant: a statistical approach. Biotech 9:86. https://doi.org/10.1007/s13205-019-1623-x

Omajali JB, Mikheenko IP, Merroun ML, Wood J, Macaskie LE (2015) Characterization of intracellular palladium nanoparticles synthesized by *Desulfovibrio desulfuricans* and *Bacillus benzeovorans*. J Nanopart Res 17:264. https://doi.org/10.1007/s11051-015-3067-5

Pal G, Rai P, Pandey A (2019) Green synthesis of nanoparticles: a greener approach for a cleaner future. In: Shukla AK, Iravani S (eds) Green synthesis, characterization and applications of nanoparticles. Elsevier, Amsterdam, pp 1–26. https://doi.org/10.1016/B978-0-08-102579-6.00001-0

Pang Y, Zeng GM, Tang L, Zhang Y, Liu YY, Lei XX, Wu MS, Li Z, Liu C (2011) Cr (VI) reduction by *Pseudomonas aeruginosa* immobilized in a polyvinyl alcohol/sodium alginate matrix containing multi-walled carbon nanotubes. Bioresour Technol 102(22):10733–10736. https://doi.org/10.1016/j.ecoleng.2017.06.023

Parshetti GK, Doong R (2009) Dechlorination of trichloroethylene by Ni/Fe nanoparticles immobilized in PEG/PVDF and PEG/nylon 66 membranes. Water Res 43:3086–3094. https://doi.org/10.1016/j.watres.2009.04.037

Parveen F, Sannakki B, Mandke MV, Pathan HM (2016) Copper nanoparticles: synthesis methods and its light harvesting performance. Sol Energy Mater Sol 144:371–382. https://doi.org/10.1016/j.solmat.2015.08.033188

Patel K, Singh N, Nayak JM, Jha B, Sahoo SK, Kumar R (2018) Environmentally friendly inorganic magnetic sulfide nanoparticles for efficient adsorption-based mercury remediation from aqueous solution. Chem Select 3(6):1840–1851. https://doi.org/10.1002/slct.201702851

Poorkarimi A, Karimi-Jashni A, Javadpour S (2017) Optimization of toluene removal over W-doped TiO_2 nano-photocatalyst under visible light irradiation. Environ Technol 39 (24):3135–3148. https://doi.org/10.1080/09593330.2017.1375021

Prasad K, Jha AK, Kulkarni AR (2007) *Lactobacillus* assisted synthesis of titanium nanoparticles. Nanoscale Res Lett 2:248–250

Qian Y, Zhou X, Zhang Y, Zhang W, Chen J (2013) Performance and properties of nanoscale calcium peroxide for toluene removal. Chemosphere 91:717–723. https://doi.org/10.1016/j.chemosphere.2013.01.049

Qiao Y, Wu J, Xu Y, Fang Z, Zheng L, Cheng W, Tsang EP, Fang J, Zhao D (2017) Remediation of cadmium in soil by biochar-supported iron phosphate nanoparticles. Ecol Eng 106:515–522. https://doi.org/10.1016/j.ecoleng.2017.06.023

Rajabairavi N, Raju CS, Karthikeyan C, Varutharaju K, Nethaji S, Hameed ASH, Shajahan A (2017) Biosynthesis of novel zinc oxide nanoparticles (ZnO NPs) using endophytic bacteria *Sphingobacterium thalpophilum*. In: Ebenezar J (ed) Recent trends in material science and applications. Springer proceedings in physics, vol 189. Springer, Cham. https://doi.org/10.1007/978-3-319-44890-9_23

Rajakumar G, Rahuman AA, Roopan SM, Khanna VG, Elango G, Kamaraj C, Abduz Zahir A, Velayutham K (2012) Fungus mediated biosynthesis and characterization of TiO2 nanoparticles and their activity against pathogenic bacteria. Spectrochimica Acta A 91:23–39. https://doi.org/10.1016/j.saa.2012.01.011

Rajendran K, Sen S (2018) Adsorptive removal of carbamazepine using biosynthesised hematite nanoparticles. Environ Nanotechnol Monit Manag 9:122–127. https://doi.org/10.1016/j.enmm.2018.01.001

Rajput S, Singh LP, Pittman CU Jr, Mohan D (2017) Lead (Pb^{2+}) and copper (Cu^{2+}) remediation from water using superparamagnetic maghemite (γ-Fe_2O_3) nanoparticles synthesised by flame spray pyrolysis (FSP). J Colloid Interface Sci 492:176–190. https://doi.org/10.1016/j.cis.2016.11.095

Raliya R, Tarafdar JC (2013) ZnO nanoparticle biosynthesis and its effect on phosphorus-mobilizing enzyme secretion and gum contents in clusterbean (*Cyamopsis tetragonoloba* L.). Agribiol Res 2(1):48–57. https://doi.org/10.1007/s40003-012-0049-z

Raliya R, Tarafdar JC (2014) Biosynthesis and characterization of zinc, magnesium and titanium nanoparticles: an eco-friendly approach. Int Nano Lett 4:93. https://doi.org/10.1007/s40089-014-0093-8

Ravikumar KVG, Kumar D, Kumar G, Mrudula P, Natarajan C, Mukherjee A (2016) Enhanced Cr (VI) removal by nanozerovalent Iron-immobilized alginate beads in the presence of a biofilm in a continuous-flow reactor. Ind Eng Chem Res 55(20):5973–5982. https://doi.org/10.1021/acs.iecr.6b01006

Reddy KJ, McDonald KJ, King H (2013) A novel arsenic removal process for water using cupric oxide nanoparticles. J Colloid Interface Sci 397:96–102. https://doi.org/10.1016/j.cis.2013.01.041

Reyes LR, Gomez I, Garza MT (2009) Biosynthesis of cadmium sulphide nanoparticles by the fungi *Fusarium sp*. Int J Green Nanotechnol Biomed 1(1):B90–B95

Rizi MSS, Emtiazi G, Sepahi AA, Maal KB, Hosseini F (2017a) Synergistic effect of nanoparticles and *Thalassospira* sp. isolated from Bahregan area in biodegradation of oil sludge. Pet Sci Technol 35(9):831–838. https://doi.org/10.1080/10916466.2016.1278386

Rizi MSS, Emtiazi G, Sepahi AA, Maal KB, Hosseini F (2017b) The effect of nanoparticles on oil sludge biodegradation by *Chromohalobacter* sp. isolated from the Bahregan area in the Persian Gulf. Pet Sci Technol 35(7):687–695. https://doi.org/10.1080/10916466.2016.1247171

Sahithya K, Das N (2015) Remediation of pesticides using nanomaterials: an overview. Int J Chem Res 8:86–91

Sakulchaicharoen N, O'Carroll DM, Herrera JE (2010) Enhanced stability and dechlorination activity of pre-synthesis stabilized nanoscale Fe/Pd particles. J Contam Hydrol 118 (3–4):117–127. https://doi.org/10.1016/j.jconhyd.2010.09.004

Sastry M, Ahmad A, Khan MI, Kumar R (2003) Biosynthesis of metal nanoparticles using fungi and actinomycete. Curr Sci 85(2):162–170

Selvarajan E, Mohanasrinivasan V (2013) Biosynthesis and characterization of ZnO nanoparticles using *Lactobacillus plantarum* VITES07. Mater Lett 112(1):180–182. https://doi.org/10.1016/j.matlet.2013.09.020

Shaban YA, El-Sayed MA, El-Maradny AA, Al-Farawati RK, Al-Zobidi MI, Khan SUM (2016) Laboratory and pilot-plant scale photocatalytic degradation of polychlorinated biphenyls in seawater using CM-n-TiO2 nanoparticles. Int J Photoenergy 2016:8471960. https://doi.org/10.1155/2016/8471960

Shan G-B, Xing J-M, Zhang H-Y, Liu H-Z (2005) Biodesulfurization of dibenzothiophene by microbial cells coated with magnetite nanoparticles. Appl Environ Microbiol 71(8):4497–4502. https://doi.org/10.1128/AEM.71.8.4497-4502.200

Shanker U, Jassal V, Rani M (2017) Green synthesis of iron hexacyanoferrate nanoparticles: potential candidate for the degradation of toxic PAHs. J Environ Chem Eng 5(4):4108–4120. https://doi.org/10.1016/j.jece.2017.07.042

Shipley HJ, Engales KE, Guettner AM (2011) Study of iron oxide nanoparticles in soil for remediation of arsenic. J Nanopart Res 13:2387–2397. https://doi.org/10.1007/s11051-010-9999-x

Shivashankarappa A, Sanjay KR (2015) Study on biological synthesis of cadmium sulphide nanoparticles by *Bacillus licheniformis* and its antimicrobial properties against food borne pathogens. Nanosci Nanotechnol Res 3(1):6–15. https://doi.org/10.12691/nnr-3-1-2

Singh BR, Dwivedi S, Al Khedhairy AA, Musarrat J (2011) Synthesis of stable cadmium sulphide nanoparticles using surfactin produced by *Bacillus amyloliquefaciens* strain KSU-109. Colloids Surf B 85(2):207–213. https://doi.org/10.1016/j.colsurfb.2011.02.030

Singh R, Manickam N, Mudiam MKR, Murthy RC, Misra V (2013) An integrated (nano-bio) technique for degradation of γ-HCH contaminated soil. J Hazard Mater 258:35–41. https://doi.org/10.1016/j.jhazmat.2013.04.016

Singh P, Kim YJ, Zhang D, Yang DC (2016) Biological synthesis of nanoparticles from plants and microorganisms. Trends Biotechnol 34(7):588–599. https://doi.org/10.1016/j.tibtech.2016.02.006

Soltani RDC, Mashayekhi M, Jorfi S, Khataee A, Ghanadzadeh MJ, Sillanpää M (2018) Implementation of martite nanoparticles prepared through planetary ball milling as a heterogeneous activator of oxone for degradation of tetracycline antibiotic: ultrasound and peroxy-enhancement. Chemosphere 210:699–708. https://doi.org/10.1016/j.chemosphere.2018.07.077

Srivastava M, Srivastava A, Yadav A, Rawat V (2019) Source and control of hydrocarbon pollution. In: Hydrocarbon pollution and its effect on the environment. Intech Open, London. https://doi.org/10.5772/intechopen.86487

Su G, Liu Y, Huang L, Lu H, Liu S, Li L, Zheng M (2014) Synthesis of hierarchal Mg-doped Fe_3O_4 micro/nano materials for the decomposition of hexachlorobenzene. Chemosphere 99:216–233. https://doi.org/10.1016/j.chemosphere.2013.10.090

Sun SP, Lemley AT (2011) p-Nitrophenol degradation by a heterogeneous Fenton-like reaction on nano-magnetite: process optimization, kinetics, and degradation pathways. J Mol Catal A 349:71–79. https://doi.org/10.1016/j.molcata.2011.08.022

Sundaram PA, Augustine R, Kannan M (2012) Extracellular biosynthesis of iron oxide nanoparticles by *Bacillus subtilis* strains isolated from rhizosphere soil. Biotechnol Bioprocess Eng 17:835–840. https://doi.org/10.1007/s12257-011-0582-9

Sweeney RY, Mao C, Gao X, Burt JL, Belcher AM, Georgiou G, Iverson BL (2004) Bacterial biosynthesis of cadmium sulfide nanocrystals. Chem Biol 11(11):1553–1559. https://doi.org/10.1016/j.chembiol.2004.08.022

Tara N, Siddiqui SI, Rathi G, Chaudhry SA, Asiri AM (2020) Nano-engineered adsorbent for the removal of dyes from water: a review. Curr Anal Chem 16(1):14–40. https://doi.org/10.2174/1573411015666190117124344

Tiwari M, Jain P, Hariharapura RC, Narayanan K, Bhat U, Udupa N, Rao JV (2016) Biosynthesis of copper nanoparticles using copper-resistant *Bacillus cereus*, a soil isolate. Process Biochem 51 (10):1348–1356. https://doi.org/10.1016/j.procbio.2016.08.008

Tomei MC, Daugulis AJ (2013) Situ bioremediation of contaminated soils: an overview of conventional and innovative technologies. Crit Rev Environ Sci Technol 43:2107–2139. https://doi.org/10.1080/10643389.2012.67205655

Tratnyek PG, Johnson RL (2006) Nanotechnologies for environmental clean-up. Nano Today 1:44–48. https://doi.org/10.1016/S1748-0132(06)70048-2

Valko M, Morris H, Cronin MTD (2005) Metals, toxicity and oxidative stress. Curr Med Chem 12:1161–1208. https://doi.org/10.2174/0929867053764635

Vardhan KH, Kumar PS, Panda RC (2019) A review on heavy metal pollution, toxicity and remedial measures: current trends and future perspectives. J Mol Liq 290:111197. https://doi.org/10.1016/j.molliq.2019.111197

Vishnu Kirthi A, Rahuman AA, Rajakumar G, Marimuthu S, Santhoshkumar T, Jayaseelan C, Elango G, Abdul Zahir A, Kamaraj C, Bagavan A (2011) Biosynthesis of titanium dioxide nanoparticles using bacterium *Bacillus subtilis*. Mater Lett 65:2745–2747. https://doi.org/10.1016/j.matlet.2011.05.077

Wan S, Ding W, Wang Y, Wu J, Gu Y, He F (2018) Manganese oxide nanoparticles impregnated graphene oxide aggregates for cadmium and copper remediation. Chem Eng J 350:1135–1143. https://doi.org/10.1016/j.cej.2018.06.068

Wang JS, Chiu K (2009) Destruction of pentachlorobiphenyl in soil by supercritical CO_2 extraction coupled with polymer-stabilized palladium nanoparticles. Chemosphere 75(5):629–633. https://doi.org/10.1016/j.chemosphere.2009.01.018

Wang X, Gai Z, Yu B, Feng J, Xu C, Yuan Y, Lin Z, Xu P (2007) Degradation of carbazole by microbial cells immobilized in magnetic gellan gum gel beads. Appl Environ Microbiol 73 (20):6421–6328. https://doi.org/10.1128/AEM.01051-07

Watanabe K (2001) Microorganisms relevant to bioremediation. Curr Opin Biotechnol 12 (3):237–241. https://doi.org/10.1016/S0958-1229(00)00205-6

Weng X, Cai W, Lan R, Sun Q, Chen Z (2018) Simultaneous removal of amoxicillin, ampicillin and penicillin by clay supported Fe/Ni bimetallic nanoparticles. Environ Pollut 236:562–569. https://doi.org/10.1016/j.envpol.2018.01.100

Windt WD, Aelterman P, Verstraete W (2005) Bioreductive deposition of palladium (0) nanoparticles on *Shewanella* oneidensis with catalytic activity towards reductive dechlorination of polychlorinated biphenyls. Environ Microbiol 7(3):314–325. https://doi.org/10.1111/j.1462-2920.2004.00696.x

Xiu ZM, Jin ZH, Li TL, Mahendra S, Lowry GV, Alvarez PJJ (2010) Effects of nano-scale zero-valent iron particles on a mixed culture dechlorinating trichloroethylene. Bioresour Technol 101 (4):1141–1146. https://doi.org/10.1016/j.biortech.2009.09.057

Yadav KK, Singh JK, Gupta N, Kumar V (2017) A review of nanobioremediation technologies for environmental cleanup: a novel biological approach. J Mater Environ Sci 8(2):740–757

Yan FF, Wu C, Cheng YY, He YR, Li WW, Yu HQ (2013) Carbon nanotubes promote Cr (VI) reduction by alginate-immobilized *Shewanella oneidensis* MR-1. Biochem Eng J 77:183–189. https://doi.org/10.1016/j.bej.2013.06.009

Yang B, Zhang Y, Deng S, Yu G, Lu Y, Wu J, Xiao J, Chen G, Cheng X, Shi L (2013) Reductive degradation of chlorinated organic pollutants-contaminated water by bimetallic Pd/Al nanoparticles: effect of acidic conditions and surfactants. Chem Eng J 234:346–353. https://doi.org/10.1016/j.cej.2013.08.079

Yaqoob AA, Parveen T, Umar K, Ibrahim MNM (2020) Role of nanomaterials in the treatment of wastewater: a review. Water 12(2):495. https://doi.org/10.3390/w12020495

Yates MD, Cusick RD, Logan BE (2013) Extracellular palladium nanoparticle production using *Geobacter sulphurreducens*. ACS Sustain Chem Eng 1(9):1165–1171. https://doi.org/10.1021/sc4000785

Zafar MN, Qamar D, Nawaz F, Zafar MN, Iqbal M, Nazar MF (2019) Effective adsorptive removal of azo dyes over spherical ZnO nanoparticles. J Mater Res Technol 8(1):713–725. https://doi.org/10.1016/j.jmrt.2018.06.002

Zanato AFS, Silva VC, Lima DA, Jacinto MJ (2017) Bimetallic magnetic Pt/Pd-nanoparticles as efficient catalyst for PAH removal from liquid media. Appl Nanosci 7:781–791. https://doi.org/10.1007/s13204-017-0612-9

Zhang W, Elliott DW (2006) Applications of iron nanoparticles for groundwater remediation. Remediat J 16(2):7–21. https://doi.org/10.1002/rem.20078

Zhang H, Hu Z (2017) Rapid production of Pd nanoparticle by a marine electrochemically active bacterium *Shewanella* sp. CNZ-1 and its catalytic performance on 4-nitrophenol reduction. RSC Adv 7:41182–41189. https://doi.org/10.1039/C7RA07438G

Zhang X, Yan S, Tyagi RD, Surampalli RY (2011) Synthesis of nanoparticles by microorganisms and their application in enhancing microbiological reaction rates. Chemosphere 82(4):489–494. https://doi.org/10.1016/j.chemosphere.2010.10.023

Zhang H, Zhang B, Liu B (2016) Integrated nanozero valent iron and biosurfactant-aided remediation of PCB-contaminated soil. Appl Environ Soil Sci 2016:5390808. https://doi.org/10.1155/2016/5390808

Bioremediation of Wastewaters

20

Oluwadara O. Alegbeleye

Abstract

Wastewater generation, handling, management, and disposal or recycling is an important issue, globally. Wastewater treatment and reuse is a critical socioeconomic issue, due to several reasons including increased strain on freshwater resources and environmental protection. This overview covers the main types and sources of wastewaters, together with their characteristics. The major alternative uses for (treated) wastewaters are highlighted, exploring the agronomic and socioeconomic intricacies and benefits of wastewater reuse. Over time, there has been extensive research and commercial optimization of suitable wastewater treatment strategies that can ensure reuse or safe environmental discharge. Bioremediation is regarded as a sustainable approach because it is relatively cheap and environmentally friendly. Activated sludge, an important precursor or driver of pollutant removal due to wide abundance and diversity of microorganisms is discussed in this chapter, as well as other technologies such as the use of membrane bioreactors, aerobic granulation technology and hybrid technologies for biological remediation of wastewater-associated pollutants. Known pollutant-degrading microbial groups including bacteria, fungi, and microalgae are discussed and finally, key research gaps are identified.

Keywords

Bioremediation · Activated sludge · Bioreactors · Microalgae · Wastewater

O. O. Alegbeleye (✉)
Department of Food Science, Faculty of Food Engineering, University of Campinas, São Paulo, Brazil

© The Author(s), under exclusive licence to Springer Nature Singapore Pte Ltd. 2021

V. Kumar et al. (eds.), *Rhizobiont in Bioremediation of Hazardous Waste*,
https://doi.org/10.1007/978-981-16-0602-1_20

20.1 Introduction

The main sources of wastewaters include domestic, agricultural, and industrial activities (such as petroleum exploration, textile production, pharmaceutical activities, as well as other chemical and manufacturing processes) (Changotra et al. 2020). Wastewaters may contain potentially hazardous biological and chemical pollutants including heavy metals, other organic and inorganic chemicals, nitrogen, phosphorous, or other nutrients, microplastics, suspended solids, dispersed oils, salts, clinically relevant pathogens, antibiotic resistance genes, radioactive substances, endocrine disrupters, and so on (Changotra et al. 2019b). Wastewaters are typically characterized based on appearance, temperature, pH, salinity, biological oxygen demand (BOD), chemical oxygen demand (COD), total nitrogen (TN), total phosphorous (TP) levels of total suspended solids (TSS), total dissolved solids (TDS), and non-biodegradable organic compounds (Fazal et al. 2018). Management and disposal of wastewaters constitute a significant technical problem for governments, industry leaders, and other relevant stakeholders since the continuous discharge of raw or poorly treated wastewaters into the natural environment may pose substantial ecological and human health risks (Ferronato and Torretta 2019). Wastewater-associated contaminants may be washed off into surface waters via runoff or seep through soils to contaminate groundwater resources (Alegbeleye and Sant'Ana 2020) and could enter into the human food chain, posing significant human health risks.

20.2 Alternative Uses of Wastewaters

First, a definition of terminologies used in this section is provided, for proper context. Graywater refers to all wastewater that does not contain sewage, i.e. water from a po
source that has been used for laundry and other domestic purposes. Urban wastewater refers to combined effluent that contains sewage. Water that has been adequately treated and is considered suitable for particular specified uses such as domestic purposes, irrigation, etc. is known as reclaimed water. Green water is reclaimed water that has been comparatively highly treated, making it suitable for general purposes, as a non-potable source in parallel with a potable source. Drinking water is very high-quality water certified suitable for human consumption.

Generally, water sources are ranked in the following order in terms of microbiological and chemical quality: rainwater or potable water, deep groundwater, shallow groundwater, surface water (e.g. rivers, lakes, and so on), and raw or poorly treated wastewaters (Alegbeleye et al. 2016; Alegbeleye et al. 2018). Wastewater recycling options depend on the amount and quality of wastewater available, but also on the intended end use (Corominas et al. 2020). For example, in residential or domestic settings, available graywater is usually comparatively limited and treating domestic wastewater generates considerably larger volume of reusable water

(Radingoana et al. 2020). Wastewater treatment however generates significant amounts of sludge (discussed in later sections), which require further management.

Globally, particularly in semi-arid, arid, and other water-stressed regions, freshwater resources are increasingly becoming scarce (Mizyed 2013). Wastewater (and graywater) reuse is thus becoming attractive, as it is technically and logistically advantageous for many reasons (Alegbeleye et al. 2018). Fundamentally, the reuse of wastewaters contributes meaningfully to the conservation of natural resources. In certain cases (such as agricultural farming), it serves as a source of nutrients and eases economic and environmental pressures, providing a suitable alternative to environmental disposal of industrial or municipal effluents (Power 2010). Some of the most popular alternative uses of wastewater include: for irrigation of non-food and food crops as well as urban green areas, domestic sanitation, in industrial cooling or other industrial processes, fire systems, recovering arid land, and so on (Englande et al. 2015; Dery et al. 2019). It is important to clarify that the unregulated reuse of graywater is not recommended, because even though graywater does not include sewage, it may contain human pathogens. Many countries, especially advanced countries have stipulated safety standards regulating the recycling and use of (treated) wastewaters. Generally, standards for effluent treatment are based on the required water quality criteria to protect the well-being and beneficial purposes of the end-user or receiving environment. This broadly cuts across the following categories: (1) protection of terrestrial and aquatic ecosystems, (2) agricultural water uses, (3) recreational water uses, (4) groundwater and soils, and (5) human consumption or food production.

While treated wastewaters are usually of slightly poorer quality compared to rainwater, most conventional treatment strategies sufficiently reduce human pathogens and other pollutants to safe levels rendering it colorless, odorless, and suitable for most domestic purposes and agricultural farming (Yadav et al. 2019). Generally, wherever possible, such as in regions with adequate rainfall such as Latin America and sub-Saharan Africa, it is better to use rainwater or potable water for higher-grade purposes such as drinking. The use of raw or poorly treated wastewater for drinking or irrigating crops that will be consumed raw or minimally processed is not recommended (Alegbeleye et al. 2018).

The unintended (or indirect) use of wastewaters, which occurs when untreated, partially treated or treated wastewater is released into environmental resources such as canals and rivers that supply agricultural water is one of the most significant problems associated with the discharge and recycling of wastewaters (Jeong et al. 2016). This is prevalent in developing countries and poses significant public health hazards as the end user is unaware. The probable human and ecological health hazards include: occupational, i.e. (risks to growers, fishermen, and others working on or within the area), residential (residents or those who otherwise have to frequently be in the contaminated area), and the risk of subsequent animal or human infection via the handling or consumption of contaminated foodstuff or contaminated animal (Narain et al. 2013). As urbanization steadily outstrips urban planning infrastructure/provisions in many parts of the developing world, indirect wastewater use is projected to rise (Satterthwaite et al. 2010; Butsch and Heinkel

Table 20.1 Pollutants that may be present in raw or ineffectively treated wastewater (Buechler and Scott 2006; Jechalke et al. 2015; Jaramillo and Restrepo 2017)

Category	Example
Biological	Pathogens Antibiotics, mobile genetic elements (MGEs), class 1 integrons
Metals (especially heavy metals)	Cadmium, nickel, chromium, arsenic, lead, mercury
Nutrients and salts	Phosphorous, nitrate
Organic chemicals	Hydrocarbons, pesticides, other toxic organic compounds
Inorganic chemicals	Fluoride Cyanide Hydrogen sulfide
Emerging contaminants	Pharmaceuticals Endocrine disrupters Other veterinary residues Detergents Other active pharmaceutical ingredients (API)
Other	Suspended matter/solids, acids, and bases

2020). Types of pollutants that are typically occurring in wastewaters are shown in Table 20.1.

The reuse of treated wastewater is also fraught in that the safety at the point of use depends not only on the source and efficaciousness of treatment, but also on the storage or holding conditions and distribution systems (Alegbeleye et al. 2018). All of these contiguous factors and systems must thus be optimized to yield the full benefits of wastewater recycling. Human perception and attitudes are also significant as people are mostly averse to consuming treated wastewaters (Murray and Ray 2010; Wester et al. 2015). For example, in Singapore wastewater is treated to drinking water standard using membrane filtration, but the water is rarely used for drinking because most people will not knowingly consume treated wastewater (Ormerod 2017; Tortajada and Nambiar 2019). The primary consideration for wastewater reuse is not the direct or indirect municipal or economic benefits, but public health protection (Janeiro et al. 2020). Therefore, the most critical goal of all wastewater reuse endeavors should be to eliminate or at best, minimize potential health risks.

20.3 Treatment of Wastewaters

Wastewaters are treated to sufficiently improve their chemical and microbiological quality such that they can be safely released into waterways or reused for agricultural farming or certain domestic purposes, without exerting any significant environmental or human health hazards (Kehrein et al. 2020). To protect public health, it is important to approach wastewater collection, treatment, and disposal (or recycling) as constructively as possible.

Table 20.2 Wastewater treatment options (Scott et al. 2002; Deegan et al. 2011)

Physicochemical	(i) Coagulation. (ii) Filtration. (iii) Sedimentation. (iv) Flocculation. (v) Chemical disinfection, e.g. chlorination.
Biological	(i) Aerobic, e.g. activated sludge (continuous, fill, and draw), membrane batch reactors (crossflow, submerged), sequence batch reactors. (ii) Anaerobic, e.g. anaerobic filters, anaerobic sludge reactors, anaerobic film reactors
Membrane processes	Nanofiltration, ultrafiltration, microfiltration, electrodialysis reversal, reverse osmosis, membrane bioreactors, combinations of membranes in series
Advanced oxidation processes	Hydrogen peroxide, ozonation, perozonation, transition metals and metal oxides, Fenton reactions, photolysis, photocatalysis, electrochemical oxidation, ultrasound irradiation, wet air oxidation
Hybrid technologies	For example, advanced oxidation processes + biological treatment
Other	(i) Phytoremediation. (ii) Bioremediation. (iii) Biosorption.

Most times, treatment strategies and sequence depend on the source and characteristics of the wastewaters. Wastewaters typically contain various particles of differing sizes categorized as supracolloidal (> 100–100 mm), settleable (> 100 μm), dissolved (< 0.08 μm), and colloidal (0.08–1 μm) (Kinyua et al. 2016). Generally, physicochemical and biological treatment strategies are popular as they are deemed cheaper and more sustainable (Barak et al. 2020). Popular wastewater treatment approaches are shown in Table 20.2.

Physicochemical treatment may represent the sole stage/phase in wastewater treatment or may be incorporated as an auxiliary strategy during treatment to improve biological degradation or secondary treatment (such as polishing). Physicochemical wastewater treatment works fundamentally based on the separation of colloidal particles (Samer 2015). Addition of chemical destabilizers such as flocculants and coagulants can alter the physical state of colloids, enhance their stability and in turn, their ability for particle or floc formation, thereby improve settling properties (Sánchez-Martín et al. 2012; Tetteh and Rathilal 2019). Examples of physicochemical or mechanical wastewater treatment processes include: filtration, clarification, dissolved air flotation, aeration, coagulation, sorption, ion exchange, sedimentation, and chlorination, among others (Table 20.2). These processes remove large particles such as fillers, coating materials, bark particles, and other suspended organic solids from wastewaters (Mohan and Pittman 2007). Passing the water through a filter or screen typically can remove large solid compounds and then the water could be passed through grinders or grit chambers to further disintegrate the residual solid wastes or sift out gravel, sand, and other inorganic materials.

For proper perspective/context, very fine particles (colloids), which are highly stable and do not aggregate and subsequently settle, cannot be efficiently separated

by flotation, settling, or filtration as they will pass through any filter. In such cases though, separation via other physicochemical treatments like activated carbon filtration and other advanced oxidation processes is possible (Kehrein et al. 2020). Comparatively large particles can be separated by settling using flotation or gravity, depending on the relative densities of water and solids. Physicochemical treatment of wastewaters is evidently not specifically suited for the elimination of microorganisms (Bello et al. 2008; Skouteris et al. 2020). Urban wastewater treatment plants typically consist of a pretreatment step (screening, oil removal, grit removal), a primary settling treatment, designed to retain suspended solids and reduce turbidity. This is followed by secondary treatment (i.e. biological treatment) using microorganisms to catalyze the oxidation of the biodegradable organic matter, which in many cases is the activated sludge (Bertrand et al. 2015).

20.4 Bioremediation of Wastewaters

Bioremediation exploits the metabolic capability of bacteria and other microorganisms to degrade organic compounds and other pollutants into less hazardous compounds, carbon dioxide, water, and minerals (Balseiro-Romero et al. 2019). Aerobic lagoons, anaerobic biological processes, activated sludge systems, and fungal treatment are some of the approaches applied to improve the overall physicochemical properties and neutralize (or at least reduce the toxicity) of chemicals and other hazardous compounds occurring in wastewaters (Pant and Adholeya 2007; Ullah et al. 2020).

Bioremediation technologies can be categorized into two: in situ and ex situ, where in situ refers to the application of bioremediation at the place or point of contamination using natural conditions and ex situ indicates the treatment of wastewater at a separate facility as in the case of centralized and/decentralized wastewater treatment (Kumar Singh et al. 2020). In situ treatment uses natural conditions at the contaminated site, is believed to be relatively cheaper but might be slower. Ex situ treatment approaches are comparatively more expensive as they require waste excavation and transport (Azubuike et al. 2016). In practice, particularly in natural habitats, in situ biodegradation of contaminants is achieved by synergistic interactions among a wide variety or consortia of microbial groups, rather than a single species with known degrading capabilities (Li et al. 2018). In any case, microorganisms with known degrading capabilities may not satisfactorily degrade contaminants in situ (Li et al. 2020a), a trend demonstrated by studies showing that microbial consortia can better degrade pollutants attributable to structural and functional co-operations among diverse members of microbial communities including direct degraders and the so-called non-direct degraders (NDDs) (Hesnawi et al. 2014). Bacterial, fungal, and microalgal species secrete unique enzymes and possess unique degrading genes, which are different in terms of substrate specificity and function over a range of pH and temperature (Roccuzzo et al. 2020). Conversely, however, there is the possibility for interrelationships other than symbiosis such as competition, antagonism, parasitism, neutralism, or commensalism to occur

potentially altering the efficacy of co-cultures. In addition, these associations are not static and can in fact evolve over time, which necessitates research on the specific and co-operative roles that the various microbial groups play, specific or co-metabolic degradation steps, and metabolic pathways to permit optimum process control (Roccuzzo et al. 2020). Several strategies including bioventing, biopiling, and bioaugmentation among others are some of the processes that have been developed for the manipulation/modulation and optimization of microbial metabolism of hazardous compounds, colorants, and nutrients occurring in contaminated wastewaters (Ruberto et al. 2009; Alegbeleye et al. 2017a).

Ex situ bioremediation uses bioreactors and there are many different types whose process parameters have been optimized, including aerobic, anaerobic, advanced aerobic, and other wastewater treatment systems (Vikrant et al. 2018; Villegas-Plazas et al. 2019). In one common approach, raw wastewater is suspended in the presence of autochthonous or exogenous microorganisms (in the case of exogenous strains, it is usually those that have been characterized as proficient degraders), thoroughly homogenized and aerated (Samer 2015; Jesus et al. 2019). In another approach, the wastewater can be sprayed over trickling filters or beds of stone covered with microbial biofilms or a cocktail of microbial slime, which act on it to break them down into less toxic byproducts (Ahmed 2007).

The highly controlled and usually conducive conditions in a bioreactor significantly enhance pollutant degradation as well as process rates and efficiency (Alegbeleye et al. 2017a). In most cases, the conditions (such as continuous agitation) in bioreactors improve contaminant bioavailability since it facilitates improved contact between inoculants and pollutants, which enhances contaminant mass transfer phenomena (Bakri et al. 2011). Treatment in bioreactors also offers a dilution effect, which may reduce the impact of pollutant toxicity on degrading microorganisms (Balseiro-Romero et al. 2019). Fundamentally, bioremediation parameters (temperature, pH, and redox conditions) can be more easily manipulated and optimized, but also electron acceptors, solvents, and surfactants can be used to enhance the bioavailability of pollutants (Robles-González et al. 2008; Alegbeleye et al. 2017).

One of the major advantages of ex situ treatment approaches is that it makes the use of exogenous strains with known degradation capacity more feasible while avoiding potential pitfalls such as ecological disruption/stress associated with in situ treatment approaches (Azubuike et al. 2016). Ex situ approaches are also useful because they can be used to assess bioremediation potential, i.e. a pre-validation approach to verify whether or not pilot or field scale remediation may be feasible.

Apart from the management or treatment approach, another critical, yet fundamental factor that influences the type and success of bioremediation is the type of wastewater (Robles-González et al. 2008). The microbial community (diversity and prevalence) depends on the type of wastewater, and this directly affects the success of bioremediation. Increased levels of novel, emerging or recently emerged contaminants such as polychlorinated biphenyls and pharmaceuticals constitutes significant public health challenge particularly because they might not be readily biodegradable. Pharmaceutical wastewaters, for example, might be relatively more

challenging to bioremediate seeing as many groups of pharmaceuticals are toxic to microbes; some are antimicrobial agents that can significantly reduce microbial populations in wastewater treatment systems (Iranzo et al. 2018; Changotra et al. 2020).

20.5 Conventional Activated Sludge Methods

Activated sludge is one of the most conventional technologies for the biological treatment of wastewater in wastewater treatment plants (WWTPs), where a suspension of bacterial biomass (i.e. the activated sludge) initiates the biological treatment of pollutants and nutrients (Salama et al. 2019). The process utilizes a dense microbial culture in suspension to aerobically biodegrade organic compounds and form a biological floc for solid separation in the settling units (Tyagi and Lo 2013; Fang et al. 2018; de Rollemberg et al. 2019). The mechanism of treatment is contingent on establishing and maintaining a population of proficient microbial degraders, assuring adequate levels of dissolved oxygen and other environmental/physicochemical parameters, as well as suitable contaminant–microbe contact (Salama et al. 2019). In some treatment systems, biomass may grow attached to a surface (broadly referred to as biofilms) as, for example, in trickling filters, rotating biological contactors/reactors, granular media biofilters, fixed media submerged biofilters, fluidized bed reactors, among others (Rusten et al. 2006). Some other types of biological suspension systems are moving bed biofilm reactors (MBBR) (discussed in subsequent section 20.4.1), and integrated fixed-film activated sludge systems (which can be regarded as a variation of the MBBR process) (Gernaey and Sin 2011).

Activated sludge treatment removes organic carbon compounds, nutrients such as nitrogen and phosphorous as well as pathogens. In some cases, further treatment (thermal or anaerobic) may be applied to efficiently denature pathogens (Wang et al. 2014). Biological decontamination of pollutants may be brought about by a combination of processes including volatilization, surface binding, and microbial decomposition (Fang et al. 2018). Crucial factors such as environmental variables (including pH, temperature, and oxygen), nutrients (usually suitable, biodegradable waste from the bulk of the "nutrients"), microbial diversity, and abundance influence the overall efficiency of activated sludge systems (Zhai et al. 2020; de Rollemberg et al. 2019). Microbial decomposition may not always proceed at a desirable rate, or effectively eliminate, or reduce hazardous compounds due to unfavorable environmental or physicochemical conditions and sub-optimal levels of proficient microbial degraders (Zhao et al. 2017a; Rastogi et al. 2020). These drawbacks can be countered by strategies such as prior acclimatization (or adaptation) of the microbes to contaminants, i.e. biostimulation (Alegbeleye et al. 2017b; Nikolopoulou et al. 2013; Yang et al. 2019). Oxygen conditions and aeration may be improved by diffused or mechanical aeration, such as in bioreactors (e.g. introducing air via agitation, in the form of bubbles, or through diffusers), or the use of models to determine, forecast,

and monitor suitable environmental factors for the elimination of respective compounds in activated sludge systems (Brdjanovic et al. 2015).

Activated sludge systems are designed depending on factors such as the ratio of the microorganisms (or activated sludge) to the substrate (waste) and other characteristics of the waste. In most systems, healthy, active microbial groups/population that will feed on new, incoming batch of organic compounds is maintained by replenishing the microbe concentration (sludge) that has drained through the tank and settled out in a secondary sedimentation tank and disposing part of the settled material. For domestic sewage, adsorption of most organic compounds by the sludge floc occurs within 15–45 min, although most conventional plants are designed to provide up to 90 min contact time to ensure adequate adsorption by the sludge floc.

The efficaciousness of activated sludge systems for pathogen inactivation or removal varies tremendously. For instance, there is some indication that despite high removal efficiency and rates, parasites can survive the activated sludge process and that the treatment does not completely inactivate them. Parasites are mostly inactivated during secondary sedimentation, where some studies have reported enhanced protozoa settling during secondary sedimentation, although this seems to vary depending on the type of protozoa. Cryptosporidium removal seems to be comparatively poorer and slower, and both primary and secondary sedimentation may be necessary for the removal of helminth eggs. Researchers have detected the presence of helminth eggs of *Ascaris* spp., *Trichuris trichiura*, Hookworm, *Taenia saginata*, *Hymenolepis* spp. and protozoan oocysts of *Giardia* spp., *Cryptosporidium*, and *Entamoeba* spp. in activated sludge effluents (Ben Ayed et al. 2009). Helminth eggs are the infective stage of a variety of intestinal worms and although not all helminths are the same, all known helminth eggs are enclosed in a strong protective membrane that consists of an internal lipoidal shell, an intermediate quitinose layer, and a proteic external shell (Robles et al. 2020). This feature makes them highly resistant to most conventional treatment protocols (Robles et al. 2020). Reported removal percentage may, however, depend on the sampling pattern (i.e. if the effluent samples were collected after aeration and sludge separation, or following activated sludge treatment (after secondary sedimentation).

Though activated sludge effectively improves sanitation and minimizes overall environmental health impacts, drawbacks such as associated complex process design, large land footprint, bad odor emissions, and management of treatment byproducts have over time created the need for advancements (Ferronato and Torretta 2019; Cichowicz and Stelęgowski 2019; Guo et al. 2019). In addition, activated sludge processes generate significant amounts of sewage sludge, which may themselves be heavily contaminated (Cichowicz and Stelęgowski 2019; Al-Gheethi et al. 2018). For example, Iranzo et al. (2018) reported sufficient degradation of pharmaceuticals in wastewaters, but elevated levels of the pharmaceuticals were detected in resultant sewage sludge. Sewage sludge can be managed, but imposes additional financial and logistical costs. Sewage sludge management practices vary depending on the type and properties and includes agricultural land application, land reclamation, land filling, anaerobic digestion,

energy recovery through incineration, and so on (Kehrein et al. 2020). In recent times, sewage sludge is to a large extent, not regarded as waste per se, but as a source of organic matter, energy, and nutrients (Lalander et al. 2016; Kehrein et al. 2020). There are several strategies for decontaminating sludge such as composting and anaerobic digestion, while composting eliminates most pathogens, as well as a wide range of environmental pollutants, it does not eradicate all pharmaceuticals.

Although several physicochemical and biological approaches such as the use of biofilters, bioscrubbers, and biotrickling filters have been developed over time to minimize the nuisance of bad odors (Barbusinski et al. 2017), odor emissions from activated sludge processes persist as a public health problem. Part of the problem is that certain challenges such as accumulation of toxic metabolites in the treatment systems, moisture control, short-circuiting of gas, media plugging, and so on have been identified as significant drawbacks in some of the intervention techniques developed (Fan et al. 2020; Wu et al. 2018). Contemporary approaches such as aqueous activated sludge biotechnologies have been proposed for end-of-pipe odor removal or prevention of odor emissions. Although they still need to be more robustly characterized and optimized, they are promising because they offer the benefit of simultaneously treating odor and decontaminating wastewater and because of associated low cost (since they can use existential WWTPs facilities).

20.5.1 Membrane Bioreactors

Membrane bioreactors combine the features of conventional activated sludge processes with membrane separation (microfiltration or ultrafiltration in the range 0.05–0.4 μm) to remediate pollutants (Barak et al. 2020). The retention of biomass within the reactor promotes the growth and action of slow-growing autotrophic bacteria, which in many cases, translates to enhanced nutrient and pollutant removal. In fact, when nutrient removal is a priority, MBRs offer a competitive advantage (Yeo et al. 2015). There are a variety of commercially available membranes for use in membrane bioreactors and the most important characteristics that determine the choice include pore size, source material, and structure (Subtil et al. 2014). Based on structural characterization, membranes are categorized as anisotropic (i.e. consists of a thin layer of membrane supported by a dense layer of porous understructure) and isotropic (homogeneous composition). The hollow fiber membrane bioreactor is the most commonly used type of membrane bioreactor (Gede Wenten et al. 2020). There are two possible cell immobilization modes in membrane bioreactors: cells are either immobilized within the membrane or on the membrane in the form of biofilms, or cells are separated from the bioreaction medium by the membrane and maintained in a separate compartment (Nemati and Webb 2011). Regardless of how the cells are immobilized, one critical advantage of MBRs is that the membrane protects the cells from existent bubble bursting and shear forces, which are detrimental to plant and mammalian cells (Nemati and Webb 2011). Generally, because MBRs prevent direct exposure of microbial cells to toxic compounds, it may be considered the preferred choice in the treatment of certain types of waste streams that contain hazardous

agents (Sun et al. 2019). There is also some research indication that MBRs may have comparatively better potential (20–50%) for removing micropollutants and other emerging contaminants (Kumar Singh et al. 2020), partly attributable to lengthier solids retention time, which permits more complete oxidation of pollutants.

With membrane pore sizes of less than 0.1 μm, MBR can mount a barrier to some chlorine resistant pathogens, an indication that it can eliminate a wider range of pathogenic bacteria and viruses (Giorno et al. 2011). Membrane reactors do not require sedimentation and media filtration for suspended solids or mixed liquor separation from treated effluent and the secondary clarifier can be eliminated. This is because aeration, clarification, and filtration are merged into a single unit, which makes the process simpler and enables the use of smaller bioreactors, saving space, and exerting low visual impact. Other advantages include reduced CO_2 footprint, high aeration rates, increased separation efficiency, decreased sludge production, and superior effluent quality compared to conventional activated sludge treatment approaches (Barak et al. 2020). The rate and efficiency of bioremediation in MBRs is hinged on controlling and monitoring operational parameters such as influent pH, organic loads, nitrogen and phosphate levels, and aeration within the bioreactors to ensure optimal conditions for microbial species (Awolusi et al. 2015). Careful selection of microbial species and the carrier material for use is also necessary to ensure high exposure area and provisions of sufficient reaction sites to avoid problems such as limited diffusion or enhanced toxicity (Roccuzzo et al. 2020). The use of MBRs offers simultaneous product separation and bioconversion, usually in form of a concentrated stream and in the last decade, their use for municipal and industrial wastewater treatment has increased. Cost-effective design and operation that has easily built on available technologies makes MBRs more attractive. For example, activated sludge models (ASMs), an important advancement in the modeling and operation of conventional activated sludge processes, though developed for use in activated sludge systems have been easily transferred and applied to MBR processes. Despite these merits however, certain disadvantages such as the need to periodically replace membranes and the need to control membrane fouling have been identified.

20.5.2 Moving Bed Biofilm Reactors (MBBR)

Moving bed bioreactor is a hybrid, advanced wastewater treatment approach that merges the features of attached growth processes/media and suspended growth in a single aerobic tank, utilizing the whole tank volume for biomass growth, which increases biomass quantity within treatment tanks (Ødegaard 2006; Marques et al. 2008). In addition to suspended biomass, attached biomass is usually grown on some specially designed biocarriers that have a high surface area, which is applied for enhanced pollutant removal. It does not require any sludge recycle since the biomass grow on carriers that move freely in the water volume of the reactors (Rusten et al. 2006). These carriers are held within the reactor volume by a sieve system fitted to the outlet of the reactor.

The media is in many cases, fluidized through aeration or by mechanical mixing. The premise is to achieve a continuous operating bioreactor with high surface for biomass growth and minimal head losses. This process has proven efficient for pollutant removal and its comparative (compared to traditional suspended growth systems) minimal footprint makes it particularly attractive (Kumar Singh et al. 2020). In addition, it is easy to retrofit existential aerated treatment processes to an MBBR process by integrating the effluent screens and plastic media into the system (Rusten et al. 2006).

20.5.3 Aerobic Granulation Technology

Aerobic granules are formed when consortia of microorganisms self-immobilize or self-aggregate in the absence of a support carrier (Liu et al. 2003). Aerobic granulation technology is a development on activated sludge technology targeted at improving among other drawbacks, sludge-water separation issues during wastewater bioremediation (Nancharaiah and Sarvajith 2019). It is a promising wastewater treatment approach because the various occurring microbial species can play different specific roles in the treatment of wastewater-associated contaminants (Li et al. 2014). Aerobic granules are regular in shape and have a dense, compact structure, which enhances settling capacity, multi-microbial functions, higher biomass retention, as well as enhanced tolerance to toxicity and shock loading (Li et al. 2020c; Maszenan et al. 2011). So many studies have explored granulation mechanisms, the extracellular polymeric substance matrix (EPS) (i.e. sticky polymers secreted by bacteria consisting of lipids, phospholipids, polysaccharides, proteins, and humic acids, which trigger cell adhesion and formation of aerobic granules), as well as other factors that contribute to the physical and chemical structure of the granules. The factors responsible for the long-term stability of AGS and other related factors that influence the rate and efficiency of wastewater remediation have also been abundantly explored (Franca et al. 2018; Alshabib and Onaizi 2019; El-sayed 2020; Li et al. 2020b; Ogura et al. 2020; Pei et al. 2020; Phong Vo et al. 2020). Granulation is according to some research (Barr et al. 2010) rooted in the formation of biofilms, i.e. aggregation of microbes (similar to that in AS), facilitated by polymeric entanglement, cations, granules shaping, and then densification and possible disintegration. The consensus, however, seems to be that four important stages: (i) intercellular interactions, (ii) microbial attachment and formation of aggregates, (iii) EPS facilitated attachment, and (iv) shaping of granules in anaerobic granulation (Lv et al. 2014) are involved in the formation of dense aggregates (AGS). The approach for AGS cultivation from activated sludge flocs, which involves operating the sequencing batch reactor with anaerobic, aerobic, and short settling phases in the cycle creates optimum growth conditions for slow-growing microbes such as glycogen accumulating organisms (GAOs), polyphosphate accumulating organisms (PAOs), and nitrifying bacteria as dense aggregates (Bengtsson et al. 2018; Wilén et al. 2018). Results of most studies suggest that the predominant microbial groups in AGS are bacteria: (such as *Dechloromonas* spp.,

Thauera sp., *Nitrospira* sp., zoogloea, among many others). There is, however, some research indication that protozoal and fungal filaments play vital roles in the initial stages of granule formulation, contributing to the development of a core for bacterial colonization (Beun et al. 1999; Weber et al. 2007).

Aerobic granulation technology has in the last several years evolved into a robust biotechnological approach that has been used commercially for full-scale industrial and municipal wastewater treatment in different parts of the world such as the UK, Netherlands, Sweden, Brazil, and South Africa (Li et al. 2020c). Several studies have described remediation of persistent hazardous pollutants including phthalates, nitroaromatics, chloroanilines, pharmaceuticals, azo dyes, phenols, organophosphorous compounds, metal chelating agents, and explosives, in AGS reactors (Sarvajith et al. 2018; Zhao et al. 2015; Ramos et al. 2015). Compared to conventional wastewater treatment strategies, aerobic granulation technology is more effective in terms of energy requirements and land use (Sarma and Tay 2017). The process design is also comparatively simpler because aerobic, anaerobic, and anoxic microenvironments are occurring within microbial granules, eliminating the need for separate aerobic and anoxic compartments for efficient biological nitrogen removal (BNR). As a consequence, it is possible to achieve both biological treatment and biomass separation from treated wastewater in a single treatment tank. Also, secondary clarifiers, key for the AS process is not required because of the good settling velocities of granules (Weber et al. 2007). Some other benefits include lower sludge production attributed to peculiar metabolism of the various involved microbial groups and resourceful utilization of excess sludge (Nancharaiah and Sarvajith 2019). Despite its advantages however, certain drawbacks such as the requirement of complex sequencing batch operation modes and the need for post-treatment to satisfy environmental standards have been identified (Liébana et al. 2018). The technique of a popular commercial brand/application (Nereda®) involves a short fill/draw timer over the cycle time ratio (e.g. 15%) of sequencing batch reactors which imposes a stringent flow requirement on its pumping systems, meaning that it can only handle small treatment demands (Zou et al. 2018).

Considering that most large-scale WWTPs are currently running under continuous-flow operation, instead of upgrading WWTPs to SBR systems like Nereda, which is logistically and financially costly, it is more practical to incorporate aerobic granulation technology into existing continuous-flow operations (Kent et al. 2018). Requirements for cultivating microorganisms in continuous-flow reactors differ significantly from that in SBRs. There are typically low substrate concentrations in CFRs due to constant substrate consumption by microorganisms. Cultivation and utilization of aerobic granulation in CFRs are thus unstable and challenging (Kent et al. 2018; Li et al. 2020c). To mitigate some of these limitations, studies have explored strategies such as the application of selective pressure into CFRs by modifying the configuration to stimulate the growth of slow-growing bacteria (Devlin and Oleszkiewicz 2018; Zou et al. 2018; Li et al. 2020c). Incorporation/implementation of AGS technology into WWTPs for full-scale, routine use requires that certain operational parameters be optimized. Bioreactor conditions such as anaerobic feeding, feast farming regime, and short settling

periods select for slow-growing bacteria that have unique metabolic traits and favor granulation (Li et al. 2020c). The maintenance of granular stability is contingent on optimization of anaerobic feeding and sludge removal strategies. In addition, it is important to further explore molecular aspects of granulation. Over time, studies have developed approaches for improved cultivation of aerobic granules. Recently, Li et al. (2020c) developed a reactor to cultivate aerobic granules under continuous-flow and identified key features and operation conditions for sludge granulation and nitrogen removal during municipal wastewater treatment. In addition to reactor configuration, the study found that dynamic feeding pattern enhanced nitrogen removal performance and nutrient removal in AGS.

20.5.4 Hybrid Technologies

Biological treatment approaches, though widely acknowledged as cheap and effective can be disadvantageous in that they are slow, they generate large amounts of sludge and in some cases, unpleasant odor (Gogate et al. 2020; Brillas 2020). In addition, direct biological treatment technologies are for the most part, suitable for the degradation of biodegradable organic pollutants only (Wang et al. 2014; Changotra et al. 2020). Many times, however, wastewater may contain a significant amount of non-biodegradable, recalcitrant compounds and there is good research evidence indicating that biological treatment may be more effective and faster when combined with other techniques such as physical, chemical, or other biological approaches (Changotra et al. 2019a; Paździor et al. 2019; Rahimi et al. 2020; Bhanot et al. 2020). Examples of pretreatment, auxiliary, or sequential approaches include those based on hydrodynamic cavitation, H_2O_2, Fenton, ozone, and other chemical oxidation approaches (Gogate et al. 2020). Of the several possible combination of technologies, advanced oxidation processes (AOPs) and biological treatment is according to several recent studies particularly promising (Ganzenko et al. 2014; Thanekar et al. 2020; Popat et al. 2019; Paździor et al. 2019). Some advanced oxidation processes such as Fenton processes offer the dual advantage of coagulation and oxidation, while more contemporary processes such as electro-Fenton aid the rapid and effective degradation of recalcitrant pollutants (Nidheesh et al. 2018). Some laboratory and field scale studies have designed dual or multi-phased chemical/biological treatment schemes for the treatment of wastewaters. For example, Changotra et al. (2019b) applied phenton (dark, solar driven photo and electro) as pretreatment for biological treatment of pharmaceutical wastewaters. These processes significantly reduced the organic load of wastewater, enhanced the BOD/COD ratio, improved biocompatibility for subsequent biological degradation, and the overall biodegradability. The study indicated that of the three applied pretreatment technologies, photofenton was the most efficient and was not toxic to the microorganisms in the biological treatment setup. A recent study by Gogate et al. (2020) corroborated these findings reporting that the application of an ultrasonic pretreatment significantly reduced biodegradation time (36 h compared to 60 h of biological oxidation without pretreatment). The pretreatment also significantly

enhanced the biodegradability index. Another recent study by Ceretta et al. (2020) coupled biological and photocatalytic treatment for decontaminating textile wastewaters. The study applied bacterial treatment first and then subsequently used photocatalytic process (ZnO/polypyrrole) and reported improved decolorization efficiency and bioremediation rates.

Some researchers have proposed integrating aerobic granular technology with membrane bioreactors for wastewater remediation (Liébana et al. 2018). This combination would yield a hybrid system known as aerobic granular sludge membrane bioreactors (AGMBRs), where the aerobic granules constitute the biomass and the water is treated via filtration (Liébana et al. 2018). Already, research has shown that utilizing granular sludge in MBRs reduced fouling likely because granular sludge has a more compact structure, higher density, as well as larger particle size compared to floccular sludge (Liébana et al. 2018). Also, the use of membranes for the separation of aerobic granules from the treated water (depending on membrane pore size) would yield high-quality effluents. In a full-scale WWTP, AGMBRs would be advantageous since it would guarantee high-quality effluent, with associated advantages including low-permeability loss, minimal space requirements, and less fouling. Some challenges such as maintaining granular stability in AGMBRs is a limitation for the technology (Li et al. 2005; Vijayalayan et al. 2014; Liébana et al. 2018).

Although hybrid processes where systems or treatment protocols are integrated and methods applied sequentially or consecutively seem promising, certain drawbacks persist. For example, AOPs are quite expensive and are inefficient in terms of energy use and sludge production. Overall, integrated treatment approaches seem promising, and it is important to optimize operational parameters that can achieve maximum degradation of organic and inorganic components of wastewaters without exerting any tangible human or ecological health impacts. It is crucial to determine the most suitable treatment sequence(s) and design standard methods for the characterization and management of byproducts.

20.6 Microbial Groups Used for Bioremediation

The rate, efficiency, and overall success of wastewater bioremediation depend to a great extent on the microbial communities in the system (Barak et al. 2020). The potential of using microorganisms: bacteria, fungi, yeasts, and algae to remediate wastewaters has been abundantly explored (Dellamatrice et al. 2017; Roccuzzo et al. 2020); and it has been determined that some microorganisms have the capacity to metabolize/mineralize toxic compounds into CO_2, methane, and other simpler compounds, while others contribute to decolorizing wastewaters (Forgacs et al. 2004; Spolaore et al. 2006). Several studies have attempted to elucidate the major microbial groups that catalyze the different processes in wastewater bioremediation streams or reactors (Costa and Duarte 2005; Maintinguer et al. 2013). This is critical, as it forms an important basis for improving overall process efficiency. Bioreactors and other biological wastewater treatment systems typically contain a tremendously

complex and diverse microbial community (Valentín-Vargas et al. 2012; Show et al. 2020; Zhang et al. 2020). The advent, advancement, and increased accessibility of molecular identification and characterization methodologies have greatly enabled our understanding of these microbial degraders (Czaplicki and Gunsch 2016; Malla et al. 2018). The microbial groups required to catalyze the bioremediation pathways, processes, and dynamics depend on whether or not the bioremediation process is aerobic or anaerobic (Juwarkar et al. 2010; Azubuike et al. 2016; Alegbeleye et al. 2017a). Where oxygen is the electron acceptor (aerobic bioremediation), aerobic microorganisms including members of the bacterial phyla Proteobacteria, Firmicutes (which include nitrogen-fixing and denitrifying bacteria), and Bacteroides are some of the most predominant bacterial groups associated with degrading or stabilizing wastewater-associated pollutants (Maintinguer et al. 2013; Zhao et al. 2017b). Some popular decomposing bacterial Genera include Pseudomonas, Bacillus, Rhodococcus, Sphingomonas, Burkholderia, and Mycobacterium (Alegbeleye et al. 2017a; Li et al. 2020a). Members of the pathogenic species Enterobacteriaceae and Enterococcus have been found predominant in some surveys, but their use for bioremediation is not recommended due to their potential health relevance (Robinson et al. 2010; Alegbeleye et al. 2017a; Drzewiecka 2016). Anaerobic bioremediation, however, is triggered and progresses through reducing electron acceptors and specific heterotrophic microorganisms. Notable anaerobic metabolic processes that contribute to biodegradation include fermentation, nitrates respiration (including denitrification), and methanogenesis. Examples of studies that have demonstrated the potential for bacterial species to improve the chemical and microbiological quality of industrial, agricultural, and domestic wastewaters abound in the literature. Paisio et al. (2014) reported that *Acinetobacter* sp. and *Rhodococcus* sp. degraded up to 1000 mg/L of tannery and chemical industry associated 2-methoxyphenol, as well as 4-chlorophenol, 2,4-dichlorophenol, and pentachlorophenol efficiently. In addition, after 7 days of treatment, BOD and COD levels had been significantly reduced. Similarly, Hesnawi et al. (2014) used *Pseudomonas aeruginosa* and *Bacillus subtilis* for the bioremediation of municipal wastewaters.

Fungi can efficiently degrade pollutants occurring in wastewaters via biosorption/bioaccumulation, adsorption, or other intra- and extracellular enzymatic mechanisms (Roccuzzo et al. 2020; Sharma et al. 2020). Their use is advantageous because they purify wastewater satisfactorily, yielding good quality effluent, they are renewable, and they produce commercially valuable biomass that can serve as animal feed, biofuel, and fertilizer (Roccuzzo et al. 2020). Examples of proficient fungal degraders are *Aspergillus ochraceus, Scedosporium apiospermum, Aspergillus fumigatus, Aspergillus niger, Aspergillus versicolor, A. terreus, A. cylindrospora Penicillium purpurogenum,* among many others (Martínez-Gallardo et al. 2020; Sharma et al. 2020).

Although several proficient and potential pollutant-degrading microorganisms have been identified and characterized, a significant percentage of possible degraders remain unexplored. Despite advances in microbial detection, identification, and characterization, several biotechnologically relevant microbial groups remain unidentified and unexploited. Certain studies have indicated that NDDs

(i.e. degradation augmenting or assistant strains) can play significant roles in in situ biodegradation and their roles or potential in replenishing contaminated sites should be further explored (Li et al. 2020a). A number of contemporary techniques are used to determine metabolic responses and identify functionality of predominant/active microorganisms in their natural environments. An example is the DNA-stable-isotope-probing (DNA-SIP) technique, a cultivation-independent approach that can be used to identify microorganisms involved in the in situ degradation of contaminants including direct and non-direct degraders in complex microbial communities (Li et al. 2020a). While these approaches are not yet scaled up for real time environmental applications, there is some recent research indicating that the so-called non-direct degraders may play critical roles in bioremediation of compounds such as biphenyl in wastewaters.

20.6.1 Microalgae

Microalgae are a group of eukaryotic or prokaryotic photosynthetic microorganisms that grow in marine and freshwater systems and even wastewater (Khan et al. 2018). Although their photosynthetic mechanism is similar to that of higher plants, microalgae's systematics is based on the type and combinations of photosynthetic pigments occurring in the different species (Moejes et al. 2017; Khan et al. 2018). Most species are, however, capable of capturing solar energy up to 10–15 times better than terrestrial plants (Mondal et al. 2017). They have a simple cellular structure, a large surface to volume body ratio, which enables nutrient uptake and comparatively high growth rates, an indication of efficient CO_2 fixation and high biomass productivity (Singh and Ahluwalia 2013). Additionally, few species can tolerate extreme environmental conditions such as high salinity.

Studies have demonstrated the potential for microalgae to phytoremediate industrial wastes such as dyes, metals, nutrients, and other toxicants in industrial wastewaters (Singh et al. 2016; Fazal et al. 2018). There is also some indication that the cultured microalgae may serve as feedstock for biodiesel production, a potentially sustainable strategy for energy generation, although that is a different subject matter and is not within the scope of this chapter. Microalgae can be cultivated in the wastewaters, which may utilize salts, nutrients, metals, and dyes (depending on the kind of wastewater) as carbon sources for growth and proliferation (Renuka et al. 2015). Some pollutants such as dyes may also adsorb onto the surface structure of microalgae, which has a large surface area and strong binding affinity for some contaminants such as azo dyes and metals, thus acting as a biosorbent (Pathak et al. 2015). Utilization of wastes as a carbon source and biosorption/bioaccumulation may according to some studies occur simultaneously, potentially accelerating the rate and efficiency of bioremediation. Examples of microalgae species capable of pollutant or nutrient biodegradation include *Chlorella vulgaris*, *Chlorella pyrenoidosa*, and *Oscillatoria tenuis* (Forgacs et al. 2004). For example, Chlorella alga isolated by Cheriaa et al. (2009) degraded textile dyes indigo, remazol brilliant orange, crystal violet, and direct blue. Studies have reported

that microalgae–microalgae and/or bacteria–microalgae mixed populations are more efficient than individual microbial strains for neutralizing nutrients and biodegradation of pollutants (Xiong et al. 2018; Roccuzzo et al. 2020). Microalgal–bacterial symbiotic consortia are potentially more sustainable since microalgae can via photosynthesis, provide oxygen for aerobic bacteria while utilizing CO_2 released from bacterial respiration. This improves aeration in the system and can potentially reduce high electricity inputs for aeration (Roccuzzo et al. 2020).

20.7 Conclusions

As agricultural and industrial activities continue to increase, it can be expected that wastewaters will continue to be generated. The handling, management, and disposal or recycling of wastewaters is an important issue, globally due to the potential public health impacts of poor management. As highlighted in this chapter and several other studies and summaries, wastewater-associated pollutants including human pathogens, endocrine disrupters, and potential carcinogens may enter into terrestrial and aquatic ecosystems, human food chains, and reach humans. Effective and readily accessible treatment technologies are required for the decontamination of wastes prior to reuse or disposal to minimize potential human health and ecological impacts. Bioremediation is widely regarded as a sustainable treatment strategy, as it is a relatively safe and effective treatment approach that degrades toxic wastes into less hazardous compounds. Some of the mechanisms, dynamics and microbial groups and processes, relevant technologies including conventional activated sludge, membrane bioreactors, and aerobic granulation technology have been summarized in this chapter. Despite significant strides, some gaps, which can further improve optimized strategies and contribute meaningfully to protection of public health have been highlighted.

20.8 Future Perspectives

Although wastewater treatment has advanced significantly over time, particularly in response to increasingly more stringent water conservation and public health requirements, there are still some research gaps.

Optimization of critical parameters such as most suitable microbial species, culturing and harvesting requirements/approaches, dynamics, suitable reactors, and other process parameters is necessary. Microorganisms and their potential for biodegradation vary substantially. Some microbes have more versatile biodegradative potential and are thus, more promising biotechnological tools for degradation of wastes. Probably more critical is that of the microbial groups with known biodegradative potential, some groups are more suitable for some types of wastewaters. Wastewaters vary in type and characteristics and some may offer unbalanced nutrient profiles for certain groups of microorganisms. Some pollutants may also be inhibitors to the growth and proliferation of some groups of

microorganisms. Adaptability to physicochemical and environmental changes also varies among different types of microbes. It is important to characterize process inhibitors; for example, microbes present in sludge may be unable to degrade the organic compounds in wastewater. Considering that the generation and accumulation of toxic byproducts have been shown to contribute to bacteria die-off and halt or slow down the remediation process, it is important that the generation of metabolites as bioremediation progresses be better characterized and modulated, if need be.

The behavior of pollutants (e.g. their susceptibility to treatment, their persistence potential, their potential for environmental partitioning, their ability to biomagnify along the food chain, their potential non-human hosts, human infection mechanisms, host response, other environmental behavior) has to be properly understood for better design of bioremediation systems/paradigms. Also, future research should evaluate and compare remediation efficiencies of the various remediation approaches in more realistic settings.

References

Ahmed SAR (2007) Fast-track evaluation of a compact chemically enhanced-trickling filter system. Braz J Chem Eng 24:171–184. https://doi.org/10.1590/S0104-66322007000200002

Alegbeleye OO, Opeolu BO, Jackson V (2017a). Bioremediation of polycyclic aromatic hydrocarbon (PAH) compounds:(acenaphthene and fluorene) in water using indigenous bacterial species isolated from the Diep and Plankenburg rivers, Western Cape, South Africa. Brazilian journal of microbiology 48(2):314–325

Alegbeleye OO, Opeolu BO, Jackson VA (2016) Investigation into the bacterial pollution levels at various sites along the Diep and Plankenburg river systems, 3 Western cape, South Africa. Water Sci Technol 73:2590–2599. https://doi.org/10.2166/wst.2016.054

Alegbeleye OO, Opeolu BO, Jackson VA (2017b). Polycyclic aromatic hydrocarbons: a critical review of environmental occurrence and bioremediation. Environmental management 60 (4):758–783

Alegbeleye OO, Sant'Ana AS (2020) Manure-borne pathogens as an important source of water contamination: an update on the dynamics of pathogen survival/transport as well as practical risk mitigation strategies. Int J Hyg Environ Health 227:113524. https://doi.org/10.1016/j.ijheh.2020.113524

Al-Gheethi AA, Efaq AN, Bala JD et al (2018) Removal of pathogenic bacteria from sewage-treated effluent and biosolids for agricultural purposes. Appl Water Sci 8:74. https://doi.org/10.1007/s13201-018-0698-6

Alshabib M, Onaizi SA (2019) A review on phenolic wastewater remediation using homogeneous and heterogeneous enzymatic processes: current status and potential challenges. Sep Purif Technol 219:186–207. https://doi.org/10.1016/j.seppur.2019.03.028

Awolusi OO, Kumari SKS, Bux F (2015) Ecophysiology of nitrifying communities in membrane bioreactors. Int J Environ Sci Technol 12:747–762. https://doi.org/10.1007/s13762-014-0551-x

Azubuike CC, Chikere CB, Okpokwasili GC (2016) Bioremediation techniques–classification based on site of application: principles, advantages, limitations and prospects. World J Microbiol Biotechnol 32:180. https://doi.org/10.1007/s11274-016-2137-x

Bakri Y, Mekaeel A, Koreih A (2011) Influence of agitation speeds and aeration rates on the Xylanase activity of Aspergillus Niger SS7. Braz Arch Biol Technol 54:659–664. https://doi.org/10.1590/S1516-89132011000400003

Balseiro-Romero M, Monterroso C, Kidd PS et al (2019) Modelling the ex situ bioremediation of diesel-contaminated soil in a slurry bioreactor using a hydrocarbon-degrading inoculant. J Environ Manag 246:840–848. https://doi.org/10.1016/j.jenvman.2019.06.034

Barak H, Brenner A, Sivan A, Kushmaro A (2020) Temporal distribution of microbial community in an industrial wastewater treatment system following crash and during recovery periods. Chemosphere 258:127271. https://doi.org/10.1016/j.chemosphere.2020.127271

Barbusinski K, Kalemba K, Kasperczyk D et al (2017) Biological methods for odor treatment – a review. J Clean Prod 152:223–241. https://doi.org/10.1016/j.jclepro.2017.03.093

Barr JJ, Cook AE, Bond PL (2010) Granule formation mechanisms within an aerobic wastewater system for phosphorus removal. Appl Environ Microbiol 76:7588–7597. https://doi.org/10.1128/AEM.00864-10

Bello ARC, de AD d F, Domingos RN (2008) Microbiological and physicochemical treatments applied to metallurgic industry aiming water reuse. Braz Arch Biol Technol 51:391–397. https://doi.org/10.1590/S1516-89132008000200020

Ben Ayed L, Schijven J, Alouini Z et al (2009) Presence of parasitic protozoa and helminth in sewage and efficiency of sewage treatment in Tunisia. Parasitol Res 105:393–406. https://doi.org/10.1007/s00436-009-1396-y

Bengtsson S, Blois M, de Wilén BM, Gustavsson D (2018) Treatment of municipal wastewater with aerobic granular sludge. Crit Rev Environ Sci Technol 48:119–166. https://doi.org/10.1080/10643389.2018.1439653

Bertrand J-C, Caumette P, Lebaron P et al (2015) Environmental microbiology: fundamentals and applications: microbial ecology. Springer, Cham

Beun JJ, Hendriks A, van Loosdrecht MCM et al (1999) Aerobic granulation in a sequencing batch reactor. Water Res 33:2283–2290. https://doi.org/10.1016/S0043-1354(98)00463-1

Bhanot P, Celin SM, Sreekrishnan TR et al (2020) Application of integrated treatment strategies for explosive industry wastewater—a critical review. J Water Process Eng 35:101232. https://doi.org/10.1016/j.jwpe.2020.101232

Brdjanovic D, Meijer SCF, Lopez-Vazquez CM et al (2015) Applications of activated sludge models. IWA Publishing, London

Brillas E (2020) A review on the photoelectro-Fenton process as efficient electrochemical advanced oxidation for wastewater remediation. Treatment with UV light, sunlight, and coupling with conventional and other photo-assisted advanced technologies. Chemosphere 250:126198. https://doi.org/10.1016/j.chemosphere.2020.126198

Buechler S, Scott C (2006) Wastewater as a Controversial, Contaminated yet Coveted Resource in South Asia. Human Development Occasional Papers (1992–2007) HDOCPA-2006-36, Human Development Report Office (HDRO), United Nations Development Programme (UNDP)

Butsch C, Heinkel S-B (2020) Periurban transformations in the global south and their impact on water-based livelihoods. Water 12:458. https://doi.org/10.3390/w12020458

Ceretta MB, Vieira Y, Wolski EA et al (2020) Biological degradation coupled to photocatalysis by ZnO/polypyrrole composite for the treatment of real textile wastewater. J Water Process Eng 35:101230. https://doi.org/10.1016/j.jwpe.2020.101230

Changotra R, Rajput H, Dhir A (2019b) Treatment of real pharmaceutical wastewater using combined approach of Fenton applications and aerobic biological treatment. J Photochem Photobiol A Chem 376:175–184. https://doi.org/10.1016/j.jphotochem.2019.02.029

Changotra R, Rajput H, Guin JP et al (2020) Techno-economical evaluation of coupling ionizing radiation and biological treatment process for the remediation of real pharmaceutical wastewater. J Clean Prod 242:118544. https://doi.org/10.1016/j.jclepro.2019.118544

Changotra R, Rajput H, Paul Guin J et al (2019a) Hybrid coagulation, gamma irradiation and biological treatment of real pharmaceutical wastewater. Chem Eng J 370:595–605. https://doi.org/10.1016/j.cej.2019.03.256

Cheriaa J, Bettaieb F, Denden I, Bakhrouf A (2009) Characterization of new algae isolated from textile wastewater plant. J Food Agric Environ 7(3&4):700–704

Cichowicz R, Stelęgowski A (2019) Effect of thermal sludge processing on selected components of air quality in the vicinity of a wastewater treatment plant. Chem Pap 73:843–849. https://doi.org/10.1007/s11696-018-0636-y

Corominas L, Byrne D, Guest JS et al (2020) The application of life cycle assessment (LCA) to wastewater treatment: a best practice guide and critical review. Water Res 184:116058. https://doi.org/10.1016/j.watres.2020.116058

Costa MC, Duarte JC (2005) Bioremediation of acid mine drainage using acidic soil and organic wastes for promoting Sulphate-reducing Bacteria activity on a column reactor. Water Air Soil Pollut 165:325–345. https://doi.org/10.1007/s11270-005-6914-7

Czaplicki LM, Gunsch CK (2016) Reflection on molecular approaches influencing state-of-the-art bioremediation design: culturing to microbial community fingerprinting to Omics. J Environ Eng 142(10):03116002

Deegan AM, Shaik B, Nolan K, et al (2011) Treatment options for wastewater effluents from pharmaceutical companies. Int J Environ Sci Technol 8:649–666. https://doi.org/10.1007/BF03326250

Dellamatrice PM, Silva-Stenico ME, de Moraes LAB et al (2017) Degradation of textile dyes by cyanobacteria. Braz J Microbiol 48:25–31. https://doi.org/10.1016/j.bjm.2016.09.012

Dery JL, Rock CM, Goldstein RR et al (2019) Understanding grower perceptions and attitudes on the use of nontraditional water sources, including reclaimed or recycled water, in the semi-arid Southwest United States. Environ Res 170:500–509. https://doi.org/10.1016/j.envres.2018.12.039

Devlin TR, Oleszkiewicz JA (2018) Cultivation of aerobic granular sludge in continuous flow under various selective pressure. Bioresour Technol 253:281–287. https://doi.org/10.1016/j.biortech.2018.01.056

Drzewiecka D (2016) Significance and roles of Proteus spp. Bacteria in natural environments. Microb Ecol 72:741–758. https://doi.org/10.1007/s00248-015-0720-6

El-sayed MEA (2020) Nanoadsorbents for water and wastewater remediation. Sci Total Environ 739:139903. https://doi.org/10.1016/j.scitotenv.2020.139903

Englande AJ, Krenkel P, Shamas J (2015) Wastewater treatment and water reclamation. In: Reference module in earth systems and environmental sciences. Elsevier, Amsterdam

Fan F, Xu R, Wang D, Meng F (2020) Application of activated sludge for odor control in wastewater treatment plants: approaches, advances and outlooks. Water Res 181:115915. https://doi.org/10.1016/j.watres.2020.115915

Fang H, Zhang H, Han L et al (2018) Exploring bacterial communities and biodegradation genes in activated sludge from pesticide wastewater treatment plants via metagenomic analysis. Environ Pollut 243:1206–1216. https://doi.org/10.1016/j.envpol.2018.09.080

Fazal T, Mushtaq A, Rehman F et al (2018) Bioremediation of textile wastewater and successive biodiesel production using microalgae. Renew Sust Energ Rev 82:3107–3126. https://doi.org/10.1016/j.rser.2017.10.029

Ferronato N, Torretta V (2019) Waste mismanagement in developing countries: a review of global issues. Int J Environ Res Public Health 16(6):1060. https://doi.org/10.3390/ijerph16061060

Forgacs E, Cserháti T, Oros G (2004) Removal of synthetic dyes from wastewaters: a review. Environ Int 30:953–971. https://doi.org/10.1016/j.envint.2004.02.001

Franca RDG, Pinheiro HM, van Loosdrecht MCM, Lourenço ND (2018) Stability of aerobic granules during long-term bioreactor operation. Biotechnol Adv 36:228–246. https://doi.org/10.1016/j.biotechadv.2017.11.005

Ganzenko O, Huguenot D, van Hullebusch ED et al (2014) Electrochemical advanced oxidation and biological processes for wastewater treatment: a review of the combined approaches. Environ Sci Pollut Res 21:8493–8524. https://doi.org/10.1007/s11356-014-2770-6

Gede Wenten I, Friatnasary DL, Khoiruddin K et al (2020) Extractive membrane bioreactor (EMBR): recent advances and applications. Bioresour Technol 297:122424. https://doi.org/10.1016/j.biortech.2019.122424

Gernaey KV, Sin G (2011) 6.25 - ecological models: wastewater treatment models. In: Moo-Young M (ed) Comprehensive biotechnology, 2nd edn. Academic Press, Burlington, NJ, pp 291–303
Giorno L, De Bartolo L, Drioli E (2011) 2.20 - membrane bioreactors. In: Moo-Young M (ed) Comprehensive biotechnology, 2nd edn. Academic Press, Burlington, NJ, pp 263–288
Gogate PR, Thanekar PD, Oke AP (2020) Strategies to improve biological oxidation of real wastewater using cavitation based pre-treatment approaches. Ultrason Sonochem 64:105016. https://doi.org/10.1016/j.ultsonch.2020.105016
Guo Z, Sun Y, Pan S-Y, Chiang P-C (2019) Integration of green energy and advanced energy-efficient technologies for municipal wastewater treatment plants. Int J Environ Res Public Health 16:1282. https://doi.org/10.3390/ijerph16071282
Hesnawi R, Dahmani K, Al-Swayah A et al (2014) Biodegradation of municipal wastewater with local and commercial Bacteria. Procedia Eng 70:810–814. https://doi.org/10.1016/j.proeng.2014.02.088
Iranzo M, Gamón M, Boluda R, Mormeneo S (2018) Analysis of pharmaceutical biodegradation of WWTP sludge using composting and identification of certain microorganisms involved in the process. Sci Total Environ 640–641:840–848. https://doi.org/10.1016/j.scitotenv.2018.05.366
Janeiro CN, Arsénio AM, Brito RMCL, van Lier JB (2020) Use of (partially) treated municipal wastewater in irrigated agriculture; potentials and constraints for sub-Saharan Africa. Phys Chem Earth Parts A/B/C 118–119:102906. https://doi.org/10.1016/j.pce.2020.102906
Jaramillo, MF, Restrepo I (2017) Wastewater reuse in agriculture: A review about its limitations and benefits. Sustainability 9(10):1734
Jechalke S, Broszat M, Lang F et al (2015) Effects of 100 years wastewater irrigation on resistance genes, class 1 integrons and IncP-1 plasmids in Mexican soil. Front Microbiol 6:163. https://doi.org/10.3389/fmicb.2015.00163
Jeong H, Kim H, Jang T (2016) Irrigation water quality standards for indirect wastewater reuse in agriculture: a contribution toward sustainable wastewater reuse in South Korea. Water 8:169. https://doi.org/10.3390/w8040169
Jesus HS, de Cassini STA, Pereira MV et al (2019) Autochthonous microalgae cultivation with anaerobic effluent: isolation of strains, survivorship, and characterization of the produced biomass. Revista Ambiente Água 14:e2362. https://doi.org/10.4136/ambi-agua.2362
Juwarkar AA, Singh SK, Mudhoo A (2010) A comprehensive overview of elements in bioremediation. Rev Environ Sci Biotechnol 9:215–288. https://doi.org/10.1007/s11157-010-9215-6
Kehrein P, Loosdrecht M, van Osseweijer P et al (2020) A critical review of resource recovery from municipal wastewater treatment plants – market supply potentials, technologies and bottlenecks. Environ Sci: Water Res Technol 6:877–910. https://doi.org/10.1039/C9EW00905A
Kent TR, Bott CB, Wang Z-W (2018) State of the art of aerobic granulation in continuous flow bioreactors. Biotechnol Adv 36:1139–1166. https://doi.org/10.1016/j.biotechadv.2018.03.015
Khan MI, Shin JH, Kim JD (2018) The promising future of microalgae: current status, challenges, and optimization of a sustainable and renewable industry for biofuels, feed, and other products. Microb Cell Factories 17:36. https://doi.org/10.1186/s12934-018-0879-x
Kinyua EM, Mwangi IW, Wanjau RN, Ngila JC (2016) Clarification of colloidal and suspended material in water using triethanolamine modified maize tassels. Environ Sci Pollut Res Int 23:5214–5221. https://doi.org/10.1007/s11356-015-5766-y
Kumar Singh N, Pandey S, Singh RP et al (2020) 11 - bioreactor and bioprocess technology for bioremediation of domestic and municipal wastewater. In: Pandey VC, Singh V (eds) Bioremediation of pollutants. Elsevier, Amsterdam, pp 251–273
Lalander C, Senecal J, Calvo MG, Ahrens L, Josefsson S, Wiberg K, Vinnerås B (2016) Fate of pharmaceuticals and pesticides in fly larvae composting. Sci Total Environ 565:279–286
Li J, Ding L-B, Cai A et al (2014) Aerobic Sludge Granulation in a Full-Scale Sequencing Batch Reactor Biomed Res Int 2014:268789. https://doi.org/10.1155/2014/268789
Li J, Luo C, Zhang D et al (2018) Autochthonous bioaugmentation-modified bacterial diversity of Phenanthrene degraders in PAH-contaminated wastewater as revealed by DNA-stable isotope probing. Environ Sci Technol 52:2934–2944. https://doi.org/10.1021/acs.est.7b05646

Li J, Peng K, Zhang D et al (2020a) Autochthonous bioaugmentation with non-direct degraders: a new strategy to enhance wastewater bioremediation performance. Environ Int 136:105473. https://doi.org/10.1016/j.envint.2020.105473

Li X, Gao F, Hua Z et al (2005) Treatment of synthetic wastewater by a novel MBR with granular sludge developed for controlling membrane fouling. Sep Purif Technol 46:19–25. https://doi.org/10.1016/j.seppur.2005.04.003

Li Y, Liu S, Chen F, Zuo J (2020c) Development of a dynamic feeding strategy for continuous-flow aerobic granulation and nitrogen removal in a modified airlift loop reactor for municipal wastewater treatment. Sci Total Environ 714:136764. https://doi.org/10.1016/j.scitotenv.2020.136764

Li Y-S, Tian T, Li B-B, Yu H-Q (2020b) Longer persistence of quorum quenching bacteria over quorum sensing bacteria in aerobic granules. Water Res 179:115904. https://doi.org/10.1016/j.watres.2020.115904

Liébana R, Modin O, Persson F, Wilén B-M (2018) Integration of aerobic granular sludge and membrane bioreactors for wastewater treatment. Crit Rev Biotechnol 38:801–816. https://doi.org/10.1080/07388551.2017.1414140

Liu Y, Xu H-L, Yang S-F, Tay J-H (2003) Mechanisms and models for anaerobic granulation in upflow anaerobic sludge blanket reactor. Water Res 37:661–673. https://doi.org/10.1016/S0043-1354(02)00351-2

Lv Y, Wan C, Lee D-J et al (2014) Microbial communities of aerobic granules: granulation mechanisms. Bioresour Technol 169:344–351. https://doi.org/10.1016/j.biortech.2014.07.005

Maintinguer SI, Sakamoto IK, Adorno MAT, Varesche MBA (2013) Evaluation of the microbial diversity of denitrifying bacteria in batch reactor Brazilian. J Chem Eng 30:457–465. https://doi.org/10.1590/S0104-66322013000300004

Malla MA, Dubey A, Yadav S et al (2018) Understanding and designing the strategies for the microbe-mediated remediation of environmental contaminants using omics approaches. Front Microbiol 9:1132. https://doi.org/10.3389/fmicb.2018.01132

Marques JJ, Souza RR, Souza CS, Rocha ICC (2008) Attached biomass growth and substrate utilization rate in a moving bed biofilm reactor. Braz J Chem Eng 25:665–670. https://doi.org/10.1590/S0104-66322008000400004

Martínez-Gallardo MR, López MJ, Jurado MM et al (2020) Bioremediation of olive mill wastewater sediments in evaporation ponds through in situ composting assisted by bioaugmentation. Sci Total Environ 703:135537. https://doi.org/10.1016/j.scitotenv.2019.135537

Maszenan AM, Liu Y, Ng WJ (2011) Bioremediation of wastewaters with recalcitrant organic compounds and metals by aerobic granules. Biotechnol Adv 29:111–123. https://doi.org/10.1016/j.biotechadv.2010.09.004

Mizyed NR (2013) Challenges to treated wastewater reuse in arid and semi-arid areas. Environ Sci Policy 25:186–195. https://doi.org/10.1016/j.envsci.2012.10.016

Moejes FW, Matuszyńska A, Adhikari K et al (2017) A systems-wide understanding of photosynthetic acclimation in algae and higher plants. J Exp Bot 68:2667–2681. https://doi.org/10.1093/jxb/erx137

Mohan D, Pittman CU (2007) Arsenic removal from water/wastewater using adsorbents—a critical review. J Hazard Mater 142:1–53. https://doi.org/10.1016/j.jhazmat.2007.01.006

Mondal M, Goswami S, Ghosh A et al (2017) Production of biodiesel from microalgae through biological carbon capture: a review. 3 Biotech 7:99. https://doi.org/10.1007/s13205-017-0727-4

Murray A, Ray I (2010) Wastewater for agriculture: a reuse-oriented planning model and its application in peri-urban China. Water Res 44:1667–1679. https://doi.org/10.1016/j.watres.2009.11.028

Nancharaiah YV, Sarvajith M (2019) Aerobic granular sludge process: a fast growing biological treatment for sustainable wastewater treatment. Curr Opin Environ Sci Health 12:57–65. https://doi.org/10.1016/j.coesh.2019.09.011

Narain V, Khan MSA, Sada R et al (2013) Urbanization, peri-urban water (in)security and human well-being: a perspective from four south Asian cities. Water Int 38:930–940. https://doi.org/10.1080/02508060.2013.851930

Nemati M, Webb C (2011) 2.24 - immobilized cell bioreactors. In: Moo-Young M (ed) Comprehensive biotechnology, 2nd edn. Academic Press, Burlington, NJ, pp 331–346

Nidheesh PV, Zhou M, Oturan MA (2018) An overview on the removal of synthetic dyes from water by electrochemical advanced oxidation processes. Chemosphere 197:210–227. https://doi.org/10.1016/j.chemosphere.2017.12.195

Nikolopoulou M, Pasadakis N, Kalogerakis N (2013) Evaluation of autochthonous bioaugmentation and biostimulation during microcosm-simulated oil spills. Mar Pollut Bull 72:165–173. https://doi.org/10.1016/j.marpolbul.2013.04.007

Ødegaard H (2006) Innovations in wastewater treatment: –the moving bed biofilm process. Water Sci Technol 53:17–33. https://doi.org/10.2166/wst.2006.284

Ogura S, Hamza RA, Tay JH (2020) Dried aerobic granules for fast startup of aerobic granular sludge reactors: reactivation and performance. J Water Process Eng 36:101298. https://doi.org/10.1016/j.jwpe.2020.101298

Alegbeleye OO, Singleton I, Sant'Ana AS (2018) Sources and contamination routes of microbial pathogens to fresh produce during field cultivation: a review. Food Microbiol 73:177–208. https://doi.org/10.1016/j.fm.2018.01.003

Ormerod KJ (2017) Common sense principles governing potable water recycling in the southwestern US: examining subjectivity of water stewards using Q methodology. Geoforum 86:76–85. https://doi.org/10.1016/j.geoforum.2017.09.004

Paisio CE, Quevedo MR, Talano MA et al (2014) Application of two bacterial strains for wastewater bioremediation and assessment of phenolics biodegradation. Environ Technol 35:1802–1810. https://doi.org/10.1080/09593330.2014.882994

Pant D, Adholeya A (2007) Biological approaches for treatment of distillery wastewater: a review. Bioresour Technol 98:2321–2334. https://doi.org/10.1016/j.biortech.2006.09.027

Pathak VV, Kothari R, Chopra AK, Singh DP (2015) Experimental and kinetic studies for phycoremediation and dye removal by Chlorella pyrenoidosa from textile wastewater. J Environ Manag 163:270–277. https://doi.org/10.1016/j.jenvman.2015.08.041

Paździor K, Bilińska L, Ledakowicz S (2019) A review of the existing and emerging technologies in the combination of AOPs and biological processes in industrial textile wastewater treatment. Chem Eng J 376:120597. https://doi.org/10.1016/j.cej.2018.12.057

Pei Y, Tao C, Ling Z et al (2020) Exploring novel Cr(VI) remediation genes for Cr(VI)-contaminated industrial wastewater treatment by comparative metatranscriptomics and metagenomics. Sci Total Environ 742:140435. https://doi.org/10.1016/j.scitotenv.2020.140435

Phong Vo HN, Ngo HH, Guo W et al (2020) Poly-and perfluoroalkyl substances in water and wastewater: a comprehensive review from sources to remediation. J Water Process Eng 36:101393. https://doi.org/10.1016/j.jwpe.2020.101393

Popat A, Nidheesh PV, Anantha Singh TS, Suresh Kumar M (2019) Mixed industrial wastewater treatment by combined electrochemical advanced oxidation and biological processes. Chemosphere 237:124419. https://doi.org/10.1016/j.chemosphere.2019.124419

Power AG (2010) Ecosystem services and agriculture: tradeoffs and synergies. Philos Trans R Soc Lond Ser B 365:2959–2971. https://doi.org/10.1098/rstb.2010.0143

Radingoana MP, Dube T, Mazvimavi D (2020) Progress in greywater reuse for home gardening: opportunities, perceptions and challenges. Phys Chem Earth Parts A/B/C 116:102853. https://doi.org/10.1016/j.pce.2020.102853

Rahimi S, Modin O, Mijakovic I (2020) Technologies for biological removal and recovery of nitrogen from wastewater. Biotechnol Adv 43:107570. https://doi.org/10.1016/j.biotechadv.2020.107570

Ramos C, Suárez-Ojeda ME, Carrera J (2015) Long-term impact of salinity on the performance and microbial population of an aerobic granular reactor treating a high-strength aromatic wastewater. Bioresour Technol 198:844–851. https://doi.org/10.1016/j.biortech.2015.09.084

Rastogi M, Nandal M, Khosla B (2020) Microbes as vital additives for solid waste composting. Heliyon 6(2):e03343. https://doi.org/10.1016/j.heliyon.2020.e03343

Renuka N, Sood A, Prasanna R, Ahluwalia AS (2015) Phycoremediation of wastewaters: a synergistic approach using microalgae for bioremediation and biomass generation. Int J Environ Sci Technol 12:1443–1460. https://doi.org/10.1007/s13762-014-0700-2

Robinson CJ, Bohannan BJM, Young VB (2010) From structure to function: the ecology of host-associated microbial communities. Microbiol Mol Biol Rev 74:453–476. https://doi.org/10.1128/MMBR.00014-10

Robles I, Becerra E, Barrios JA et al (2020) Inactivation of helminth eggs in an electro-Fenton reactor: towards full electrochemical disinfection of human waste using activated carbon. Chemosphere 250:126260. https://doi.org/10.1016/j.chemosphere.2020.126260

Robles-González IV, Fava F, Poggi-Varaldo HM (2008) A review on slurry bioreactors for bioremediation of soils and sediments. Microb Cell Factories 7:5. https://doi.org/10.1186/1475-2859-7-5

Roccuzzo S, Beckerman AP, Trögl J (2020) New perspectives on the bioremediation of endocrine disrupting compounds from wastewater using algae-, bacteria- and fungi-based technologies. Int J Environ Sci Technol 18:89–106. https://doi.org/10.1007/s13762-020-02691-3

de Rollemberg SLS, de Barros AN, Lira VNSA et al (2019) Comparison of the dynamics, biokinetics and microbial diversity between activated sludge flocs and aerobic granular sludge. Bioresour Technol 294:122106. https://doi.org/10.1016/j.biortech.2019.122106

Ruberto L, Dias R, Lo Balbo A et al (2009) Influence of nutrients addition and bioaugmentation on the hydrocarbon biodegradation of a chronically contaminated Antarctic soil. J Appl Microbiol 106:1101–1110. https://doi.org/10.1111/j.1365-2672.2008.04073.x

Rusten B, Eikebrokk B, Ulgenes Y, Lygren E (2006) Design and operations of the Kaldnes moving bed biofilm reactors. Aquac Eng 34(3):322–331

Salama E-S, Saha S, Kurade MB et al (2019) Recent trends in anaerobic co-digestion: fat, oil, and grease (FOG) for enhanced biomethanation. Prog Energy Combust Sci 70:22–42. https://doi.org/10.1016/j.pecs.2018.08.002

Samer M (2015) Biological and chemical wastewater treatment processes. In: Wastewater treatment engineering. Intechopen, New York. https://doi.org/10.5772/61250

Sánchez-Martín J, Beltrán-Heredia J, Peres JA (2012) Improvement of the flocculation process in water treatment by using moringa oleifera seeds extract. Braz J Chem Eng 29:495–502. https://doi.org/10.1590/S0104-66322012000300006

Sarma SJ, Tay JH (2017) Aerobic granulation for future wastewater treatment technology: challenges ahead. Environ Sci: Water Res Technol 4:9–15. https://doi.org/10.1039/C7EW00148G

Sarvajith M, Reddy GKK, Nancharaiah YV (2018) Textile dye biodecolourization and ammonium removal over nitrite in aerobic granular sludge sequencing batch reactors. J Hazard Mater 342:536–543. https://doi.org/10.1016/j.jhazmat.2017.08.064

Satterthwaite D, McGranahan G, Tacoli C (2010) Urbanization and its implications for food and farming. Philos Trans R Soc Lond Ser B 365:2809–2820. https://doi.org/10.1098/rstb.2010.0136

Scott, T. M., Rose, J. B., Jenkins, T. M., Farrah, S. R., Lukasik, J. (2002). Microbial Source Tracking: Current Methodology and Future Directions. Appl. Environ. Microbiol., 68 (12):5796–5803. https://doi.org/10.1128/AEM.68.12.5796-5803.2002

Sharma R, Talukdar D, Bhardwaj S et al (2020) Bioremediation potential of novel fungal species isolated from wastewater for the removal of lead from liquid medium. Environ Technol Innov 18:100757. https://doi.org/10.1016/j.eti.2020.100757

Show K-Y, Yan Y, Yao H et al (2020) Anaerobic granulation: a review of granulation hypotheses, bioreactor designs and emerging green applications. Bioresour Technol 300:122751. https://doi.org/10.1016/j.biortech.2020.122751

Singh UB, Ahluwalia AS (2013) Microalgae: a promising tool for carbon sequestration. Mitig Adapt Strateg Glob Change 18:73–95. https://doi.org/10.1007/s11027-012-9393-3

Singh V, Tiwari A, Das M (2016) Phyco-remediation of industrial waste-water and flue gases with algal-diesel engenderment from micro-algae: a review. Fuel 173:90–97. https://doi.org/10.1016/j.fuel.2016.01.031

Skouteris G, Rodriguez-Garcia G, Reinecke SF, Hampel U (2020) The use of pure oxygen for aeration in aerobic wastewater treatment: a review of its potential and limitations. Bioresour Technol 312:123595. https://doi.org/10.1016/j.biortech.2020.123595

Spolaore P, Joannis-Cassan C, Duran E, Isambert A (2006) Commercial applications of microalgae. J Biosci Bioeng 101:87–96. https://doi.org/10.1263/jbb.101.87

Subtil EL, Mierzwa JC, Hespanhol I (2014) Comparison between a conventional membrane bioreactor (C-MBR) and a biofilm membrane bioreactor (BF-MBR) for domestic wastewater treatment. Braz J Chem Eng 31:683–691. https://doi.org/10.1590/0104-6632.20140313s00002890

Sun Y, Wang D, Tsang DCW et al (2019) A critical review of risks, characteristics, and treatment strategies for potentially toxic elements in wastewater from shale gas extraction. Environ Int 125:452–469. https://doi.org/10.1016/j.envint.2019.02.019

Tetteh EK, Rathilal S (2019) Application of organic coagulants in water and wastewater treatment. Organ Polym. https://doi.org/10.5772/intechopen.84556

Thanekar P, Garg S, Gogate PR (2020) Hybrid treatment strategies based on hydrodynamic cavitation, advanced oxidation processes, and aerobic oxidation for efficient removal of naproxen. Ind Eng Chem Res 59:4058–4070. https://doi.org/10.1021/acs.iecr.9b01395

Tortajada C, Nambiar S (2019) Communications on technological innovations: potable water reuse. Water 11:251. https://doi.org/10.3390/w11020251

Tyagi VK, Lo S-L (2013) Sludge: a waste or renewable source for energy and resources recovery? Renew Sust Energ Rev 25:708–728. https://doi.org/10.1016/j.rser.2013.05.029

Ullah A, Hussain S, Wasim A, Jahanzaib M (2020) Development of a decision support system for the selection of wastewater treatment technologies. Sci Total Environ 731:139158. https://doi.org/10.1016/j.scitotenv.2020.139158

Valentín-Vargas A, Toro-Labrador G, Massol-Deyá AA (2012) Bacterial community dynamics in full-scale activated sludge bioreactors: operational and ecological factors driving community assembly and performance. PLoS One 7:e42524. https://doi.org/10.1371/journal.pone.0042524

Vijayalayan P, Thanh BX, Visvanathan C (2014) Simultaneous nitrification denitrification in a batch granulation membrane airlift bioreactor. Int Biodeterior Biodegrad 95:139–143. https://doi.org/10.1016/j.ibiod.2014.05.020

Vikrant K, Giri BS, Raza N et al (2018) Recent advancements in bioremediation of dye: current status and challenges. Bioresour Technol 253:355–367. https://doi.org/10.1016/j.biortech.2018.01.029

Villegas-Plazas M, Sanabria J, Junca H (2019) A composite taxonomical and functional framework of microbiomes under acid mine drainage bioremediation systems. J Environ Manag 251:109581. https://doi.org/10.1016/j.jenvman.2019.109581

Wang D, Ji M, Wang C (2014) Degradation of organic pollutants and characteristics of activated sludge in an anaerobic/anoxic/oxic reactor treating chemical industrial wastewater. Braz J Chem Eng 31:703–713. https://doi.org/10.1590/0104-6632.20140313s00002748

Weber SD, Ludwig W, Schleifer K-H, Fried J (2007) Microbial composition and structure of aerobic granular sewage biofilms. Appl Environ Microbiol 73:6233–6240. https://doi.org/10.1128/AEM.01002-07

Wester J, Timpano KR, Çek D et al (2015) Psychological and social factors associated with wastewater reuse emotional discomfort. J Environ Psychol 42:16–23. https://doi.org/10.1016/j.jenvp.2015.01.003

Wilén B-M, Liébana R, Persson F et al (2018) The mechanisms of granulation of activated sludge in wastewater treatment, its optimization, and impact on effluent quality. Appl Microbiol Biotechnol 102:5005–5020. https://doi.org/10.1007/s00253-018-8990-9

Wu H, Yan H, Quan Y et al (2018) Recent progress and perspectives in biotrickling filters for VOCs and odorous gases treatment. J Environ Manag 222:409–419. https://doi.org/10.1016/j.jenvman.2018.06.001

Xiong J-Q, Kurade MB, Jeon B-H (2018) Can microalgae remove pharmaceutical contaminants from water? Trends Biotechnol 36:30–44. https://doi.org/10.1016/j.tibtech.2017.09.003

Yadav M, Gupta R, Sharma RK (2019) Chapter 14 - green and sustainable pathways for wastewater purification. In: Ahuja S (ed) Advances in water purification techniques. Elsevier, Amsterdam, pp 355–383

Yang C-F, Liu S-H, Su Y-M et al (2019) Bioremediation capability evaluation of benzene and sulfolane contaminated groundwater: determination of bioremediation parameters. Sci Total Environ 648:811–818. https://doi.org/10.1016/j.scitotenv.2018.08.208

Yeo BJ, Goh S, Zhang J et al (2015) Novel MBRs for the removal of organic priority pollutants from industrial wastewaters: a review. J Chem Technol Biotechnol 90:1949–1967. https://doi.org/10.1002/jctb.4782

Zhai W, Qin T, Li L et al (2020) Abundance and diversity of microbial arsenic biotransformation genes in the sludge of full-scale anaerobic digesters from a municipal wastewater treatment plant. Environ Int 138:105535. https://doi.org/10.1016/j.envint.2020.105535

Zhang Y, Hsu H-H, Wheeler J et al (2020) Emerging investigator series: emerging biotechnologies in wastewater treatment: from biomolecular engineering to multiscale integration. Environ Sci Water Res Technol 6(8):1967–1985. https://doi.org/10.1039/D0EW00393J

Zhao J, Wu J, Li X et al (2017a) The denitrification characteristics and microbial community in the cathode of an MFC with aerobic denitrification at high temperatures. Front Microbiol 8:9. https://doi.org/10.3389/fmicb.2017.00009

Zhao K, Xu R, Zhang Y et al (2017b) Development of a novel compound microbial agent for degradation of kitchen waste. Braz J Microbiol 48:442–450. https://doi.org/10.1016/j.bjm.2016.12.011

Zhao X, Chen Z, Wang X et al (2015) Remediation of pharmaceuticals and personal care products using an aerobic granular sludge sequencing bioreactor and microbial community profiling using Solexa sequencing technology analysis. Bioresour Technol 179:104–112. https://doi.org/10.1016/j.biortech.2014.12.002

Zou J, Tao Y, Li J et al (2018) Cultivating aerobic granular sludge in a developed continuous-flow reactor with two-zone sedimentation tank treating real and low-strength wastewater. Bioresour Technol 247:776–783. https://doi.org/10.1016/j.biortech.2017.09.088

Occurrence and Attenuation of Antibiotics in Water Using Biomass-Derived Materials

21

Nhamo Chaukura, Courtie Mahamadi, Edmore Muzawazi, and Tendai Sveera

Abstract

Annually, large quantities of pharmaceuticals are consumed globally. The presence of pharmaceutical compounds in water bodies is concerning because these compounds are recalcitrant bioaccumulative toxins. Surface water is contaminated by pollutants from storm water overflows, wastewater treatment plants, and run off from non-point sources such as concrete surfaces in urban areas and agricultural land. Depending on the hydrology, antibiotics (Abs) can also permeate into ground water. Among the various pharmaceutical compounds, antibiotics are widely used globally, consequently, water pollution due to Abs has received widespread attention. Because they are weakly absorbed by the human and animal bodies, a significant proportion of Abs are excreted untransformed or as metabolites depending on their physicochemical characteristics. Consequently, a large quantity of Abs enter the aquatic environment directly through aquaculture or effluents from wastewater treatment facilities or landfills. Wastewater treatment plants are not capable of efficiently removing pharmaceuticals in wastewater, thus these pollutants reach the receiving media, which is usually drinking water. In the environment, Abs residues are poorly biodegradable, and can result in antibiotic resistant genes (ARGs) in animals and humans from prolonged exposure at low concentrations. The existence of Abs, antibiotic

N. Chaukura (✉)
Department of Physical and Earth Sciences, Sol Plaatje University, Kimberley, South Africa
e-mail: nhamo.chaukura@spu.ac.za

C. Mahamadi
Research and Postgraduate Centre, Bindura University of Science Education, Bindura, Zimbabwe

E. Muzawazi · T. Sveera
Materials Research (MatRes) group, Chemistry Department, Bindura University of Science Education, Bindura, Zimbabwe

© The Author(s), under exclusive licence to Springer Nature Singapore Pte Ltd. 2021

V. Kumar et al. (eds.), *Rhizobiont in Bioremediation of Hazardous Waste*,
https://doi.org/10.1007/978-981-16-0602-1_21

resistant bacteria (ARB), and ARGs in the environment, particularly in wastewater and drinking water and the food chain, is a serious public health concern, and has thus generated significant interest. Antibiotic resistance arising from the intensive usage of Abs compromises their effectiveness in the management of diseases and upsets native microbes in the ecosystem.

Methods that have been used to remove Abs, ARBs, and ARGs from contaminated water include bioreactors, membrane filtration, advanced oxidation processes, and adsorption. Adsorption is an effective method which is simple to operate, with the adsorbent being key to the pollutant removal efficiency. Moreover, numerous studies have used adsorbents produced from readily available biowaste making the method cost effective. One such adsorbent is biochar (BC), which is an environmentally friendly carbon-rich adsorbent with a highly porous structure. Consequently, a number of studies have reported high Abs removal capacities using BC. In this chapter, the removal of Abs from wastewater using BC is explored and compared to other methods. The mechanisms of adsorption, and research gaps were evaluated.

Keywords

Adsorption · Biochar · Emerging pollutants · Microbes

21.1 Introduction

Emerging contaminants represent a new challenge to water quality through potentially severe environmental and human health impacts. Pharmaceutical compounds are emerging contaminants, and their presence in aquatic systems is concerning. A wide range of pharmaceuticals for human and veterinary use are excreted untransformed or as metabolites, and are constantly introduced into aquatic environments (Fekadu et al. 2019). Among the various pharmaceutical compounds, antibiotics (Abs) are a distinct category with selective antimicrobial activity which does not affect cells and tissues (Ahmed et al. 2015; Xiang et al. 2019). Owing to the intensive use of Abs as prescription drugs for humans and animals, their discharge may pollute the aquatic environment and cause ecological harm (Fig. 21.1).

Moreover, Abs are not efficiently removed in wastewater treating plants (WWTPs), as a result, Abs residues have been reported in a range of matrices especially in the water bodies such as drinking water, groundwater, and wastewater (Azanu et al. 2018; Xiang et al. 2019). The situation is compounded by water reuse which is practiced in some communities (Iakovides et al. 2019; Santos et al. 2019). As a result, antibiotic resistance has been reported in many countries around the world (Table 21.1). The discharge of Abs into the aquatic environment occurs via numerous routes such as aquaculture, pharmaceutical production processes, municipal effluent, farmland runoff, hospital effluent, irrigation with water contaminated with Abs, landfills, and inappropriate disposal of unused or expired medicines (Xiang et al. 2019).

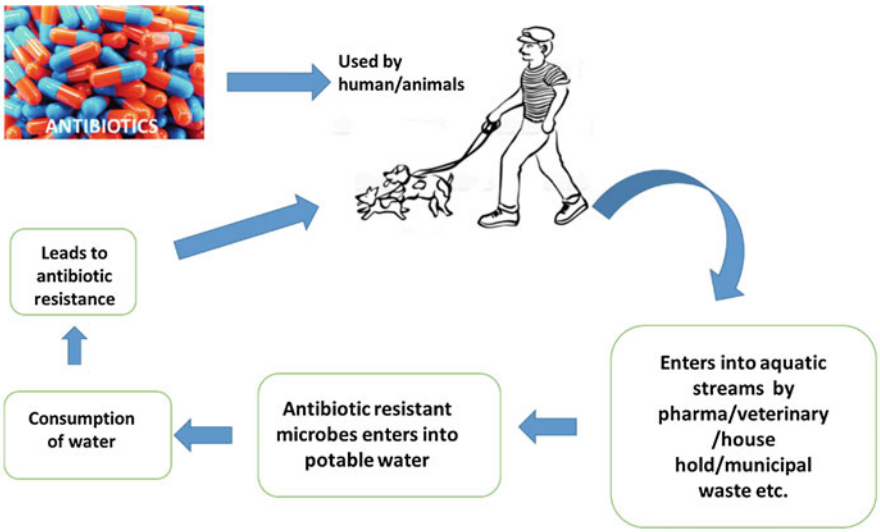


Fig. 21.1 The role of humans and animals in antibiotic resistance development

Table 21.1 Recent studies on the prevalence of antibiotic resistance

Pathogenic organisms	Human health risk	Antibiotic resistant recommended	Country	Observation	References
Acinetobacter spp	Wound infections	Tetracyclines	China	13% ($n = 23$), resistant ESBL isolates reported	Zhang et al. (2016)
Klebsiella pneumoniae	Urinary tract infections	Levofloxacin or ciprofloxacin	Ethiopia	66.6% ($n = 6$) resistant isolates reported	Abera et al. (2016)
Salmonella	Enteric fever	Levofloxacin	India	100% ($n = 36$) resistant isolates reported	Kumar et al. (2013)
Escherichia Coli	Urinary tract infections	Cotrimoxazole	China	25.5% ($n = 99$) isolates were resistant	Chen (2018)

The effects of Abs exposure to animals and humans are varied. Several studies revealed that prolonged exposure to Abs even at relatively low concentrations (μg/L-mg/L) may significantly influence the body weight and growth of biota (Xiang et al. 2019). Other adverse impacts include inducing antibiotic resistant bacteria (ARB) and antibiotic resistant genes (ARGs) owing to: (1) sub-inhibitive Abs concentrations in wastewater, (2) horizontal transfer of ARGs to Ab sensitive microbials, and (3) endocrine disruptive and other harmful ecotoxicological effects (Fekadu et al. 2019; Stange et al. 2019). As a result, the existence of ARB and ARGs in aquatic systems has become the major concern due to their ecotoxicity. Previous

studies reported that ARB could be transmitted to consumers from livestock through meat and milk products, causing infections and other adverse effects in humans. Generally, exposure to high concentrations of Abs can compromise the immune system, while some Abs are carcinogenic, mutagenic, teratogenic, and may even inhibit hormonal functions (Sanganyado and Gwenzi 2019; Xiang et al. 2019).

Current WWTPs are designed for removing pollutants such as suspended solids, nutrients, organic matter, and, to some extent, pathogens. They cannot, however, efficiently remove Abs, ARB, and ARGs (Stange et al. 2019). While chlorination, UV radiation, and ozonation as tertiary wastewater treatment methods can effectively remove bacteria, their capacity to remove Abs, ARBs, and ARGs is limited. Thus, ARGs can be potentially transferred to pathogenic microorganisms in the environment following the emission of treated effluent into freshwater or seawater environments. In this regard, effective and sustainable treatment technologies are needed (Stange et al. 2019). A number of methods to remove Abs have been investigated. These include biological processes, filtration, advanced oxidation processes, chlorination, ozonation, adsorption, membrane processes, and a combination of these (Jiang et al. 2018). Among these methods, adsorption is a commonly used method because it is efficient, simple, environmentally friendly, sensitive, cost effective, and easy to scale-up (Chaukura et al. 2016). Moreover, it does not generate secondary pollution. Consequently, adsorption processes have been used for the removal of organics from contaminated streams.

The characteristics of adsorbate, adsorbent, and the chemical composition of the wastewater influence the adsorption efficiency (Xiang et al. 2019). Adsorption using carbon nanostructured materials is a promising and thus commonly used method for removing low pharmaceutical concentrations in aquatic systems (Rostamian and Behnejad 2017; Sarker et al. 2019). One such material is biochar (BC), a carbonaceous material fabricated via biomass pyrolysis under an oxygen-depleted environment. The adsorptive performance of BC is due to its superior physicochemical characteristics such as functional groups, high surface area, high porosity, and surface charge (Teixeira et al. 2019). Although the surface of BC is largely hydrophobic, it also has a variety of polar functional groups from heteroatoms such as O, N, and S. The nature of these functional groups is influenced by the activation conditions and determines the acidity of the surface and, subsequently, to interactions with pollutants. In addition to the properties of BC, the capacity to sorb organics is influenced by the ion strength, pH, and temperature of the aqueous system, along with the properties of the pollutant. The surface charge of BC and the speciation of pollutants are dependent on solution pH, and this subsequently affects hydrophobicity and solubility properties (Teixeira et al. 2019). The physicochemical characteristics of BC, in turn, are influenced by the type of precursor material, and the pyrolysis conditions such as pyrolysis temperature, contact time, heating rate, and reactor design. The feedstock for BC is primarily derived from biowastes such as agrowaste, industrial and municipal solid waste (Jiang et al. 2018). Owing to these properties, BC has found application in the sequestration of Abs in aquatic systems.

21.2 The Occurrence of Antibiotics in Aquatic Systems

The manufacture and consumption of Abs for the prevention and management of bacterial infections in animals and humans have increased. The release of Abs into the environment occurs through a number of pathways including effluents from households, medical practices, agricultural activities, sewage, surface runoff and pharmaceutical industry effluents, and inappropriate disposal of unused or expired medicines (Adegoke et al. 2018; Dires et al. 2018; Anjali and Shanthakumar 2019; Hou et al. 2019; Xiang et al. 2019). In dairy farming, for instance, Abs are generally used to treat a range of diseases and as growth agents to quicken food production and improve the quality of products. A small fraction of the consumed Abs is metabolized while the rest is excreted with little transformation (Cha and Carlson 2019). Thus effluents emanating from animal husbandry activities are a key source of Abs in the environment (Alsager et al. 2018). High concentrations of Abs, ARBs, and ARGs in aquatic systems can be traced back to anthropogenic activities such as the discharge of Abs in wastewater (Huang et al. 2019b). Due to the large disease burden, the quantity of Abs prescribed in low-income countries is increasing, and drug abuse in the developed world contributes to the prevalence of Abs, ARBs, and ARGs in the aquatic environment (Adegoke et al. 2018). Moreover, the release of wastewater contaminants into the environment with little or no treatment is commonly practiced in low-income countries, thus contaminating water bodies (Dires et al. 2018). Although WWTPs are key in reducing and removing Abs, they also act as hot-spots for the accumulation and propagation of Abs, ARBs, and ARGs from a variety of sources (Hu et al. 2019). This way, they enhance the proliferation of ARBs by facilitating the horizontal gene transfer via conjugation, transduction, and transformation, enabling the Abs resistance to spread rapidly to hosts such as animals and humans (Dires et al. 2018; Hu et al. 2019; Huang et al. 2019a; Ma et al. 2019).

Previous studies have predicted the uptake of Abs by crops, and their subsequent entry into the food chain (Azanu et al. 2018). Toxicity in crops can arise when they are irrigated with polluted water, and the cultivars may uptake Abs in the irrigation water. Some of the effects of Abs, ARBs, and ARGs on plants include the inhibition of root elongation (Adegoke et al. 2018). Generally, exposure to Abs may retard growth and reduce the body weight of aquatic organisms (Ahmed et al. 2015). Antibiotics such as fluoroquinolones and sulfonamides interfere with the nitrogen cycle in the environment, resulting in an accumulation of nitrogen, and causing toxicity to living organisms (Larsson et al. 2018).

On transmission into pathogenic bacteria, ARGs express in harmful pathogens which will compromise the efficacy to treat bacterial infections and threaten human health (Dires et al. 2018; Hu et al. 2018). Antibiotics bioaccumulate in living organisms and up the food chain where it causes feminization of male fish, reducing the reproduction process (Anjali and Shanthakumar 2019).

21.3 Removal Strategies of Antibiotics

Residues of Abs have to be removed before discharging wastewater into the environment, but this is usually expensive (Ahmed et al. 2015). Several methods have been used to remove Abs, ARB, and ARGs from wastewater. These include absorption, biodegradation, coagulation, flocculation, sedimentation, membrane processes, and advanced oxidation processes (AOPs) (Pirsaheb et al. 2019; Hiller et al. 2019). However, physical methods like coagulation, flocculation, filtration, and sedimentation are ineffective since they only transfer contaminants from one medium to another requiring follow-up treatment (Alsager et al. 2018). Moreover, membrane technologies such as advanced microfiltration combined with reverse osmosis and UV irradiation cannot adequately remove Abs from wastewater (Alsager et al. 2018).

Conventional WWTPs do not efficiently remove Abs, resulting in the persistence of the pollutants in drinking water sources (Adegoke et al. 2018). While chemical disinfectants destroy pathogens through oxidative impairment of the cell wall, UV radiation can penetrate the water and deactivate pathogens. The antimicrobial effect of UV radiation is however limited to the region in close proximity to the radiation source, and the presence of suspended solids and dissolved organic matter in the water increases the chances of survival of pathogens (Stange et al. 2019).

AOPs have great promise owing to the complete mineralization and non-selectivity for treating a variety of organic pollutants (Kang et al. 2016; Anjali and Shanthakumar 2019). The efficiency of a variety of AOPs in removing Abs, ARGs, and inactivate ARB in wastewater have been widely studied (Iakovides et al. 2019). The major limitation of AOPs is that the generation of radicals requires combinations of reagents, use of toxic elements, or use of secondary sources of energy such as electricity or radiation (Alsager et al. 2018). However, AOPs have become an emerging and promising technique for removing Abs in contaminated water. The AOP techniques include UV irradiation, ozonation, Fenton reactions, persulfate oxidation, and various combinations of these.

Ultraviolet light is commonly integrated into tertiary treatment in WWTPs. However, bacterial regrowth in the distribution system may interfere with the original bacterial culture or encourage the persistence of ARB. Furthermore, previous studies have reported the inefficiency of UV in removing Abs from aqueous media. To circumvent this, catalysts in combination with oxidants such as H_2O_2, $Fe^{2+}/^{3+}$, and TiO_2 have been included to improve removal performance (Saitoha and Shibayama 2016). These technologies constitute AOPs. Due to the environmental friendliness compared to Hg-based lamps, more efficient light conversion, irradiance adjusting capabilities, and a long life span, UV light emitting diodes have attracted significant attention in water treatment. The almost instantaneous switching of the sources of radiation mean pulsed light can now be used in water treatment (Biancullo et al. 2019).

Recently, ozonation has gained wide usage in the treatment of wastewater to enhance pollutant degradation (Anjali and Shanthakumar 2019). It is a strong oxidant that reacts selectively with organic pollutants by directly reacting with

molecular ozone, or via an indirect pathway with hydroxyl radical species in alkaline media, which result from the degradation of ozone in aqueous solution. Ozonation can oxidize a range of Abs and inactivate pathogens in water (Alsager et al. 2018; Iakovides et al. 2019; Sanganyado and Gwenzi 2019). The benefits of ozonation include being less energy intensive and ability to achieve high water recovery with minimal waste generation. It, however, has the potential disadvantage of high implementation cost (Anjali and Shanthakumar 2019).

The Fenton reaction depends on the generation of reactive oxygen species (ROS), and is effective for the oxidative treatment of Abs (Kang et al. 2016). In the homogeneous Fenton process, stoichiometric Fe^{2+} and H_2O_2 are used to produce ROS, while heterogeneous systems use iron bearing minerals, iron oxy-hydroxides, or a variety of iron immobilized matrices. Heterogeneous systems have the advantage of limited sludge formation, no ion leaching, operation at circum-neutral pH, and easy catalyst recovery (Kang et al. 2016; Kamagate et al. 2018).

Persulfate oxidation is an emerging AOP with good oxidant stability and strong oxidizing capacity. When subjected to heating, UV radiation, transition metal, or ultrasound, $S_2O_8^{2-}$ can be activated to form $SO_4\bullet^-$, a reactive radical that can attack and degrade Abs (Peng et al. 2019). Consequently, persulfate oxidation has been used to degrade organics in contaminated environmental media.

While AOPs can effectively remove Abs from polluted water, intermediate degradation byproducts can potentially result in secondary pollution of the water. Moreover, AOP methods are expensive and most are still on laboratory scale with limited field application data. In view of these challenges, there is need for alternative low-cost and efficient treatment methods.

21.4 Biomass-Derived Removal Materials

Apart from AOPs, adsorption is the most efficient technology for the removal of Abs from polluted aquatic environments. Adsorption, as a method for the removal of Abs from aquatic systems, is well established, more cost effective, ecofriendly, and more efficient compared to other methods (Chaukura et al. 2016; Guo et al. 2019). However, large-scale application of adsorption is limited by the challenge associated with separating and recovering spent adsorbents from the treated water (Li et al. 2017). A number of adsorbents for Abs removal have been studied. These include raw biomass activated carbon, activated hydrochars, BC, carbon nanotubes, graphene-based materials, metal oxides, porous silica, and organic carbon frameworks (Guo et al. 2019; Liu et al. 2019; Mourid et al. 2019; Peng et al. 2019).

21.4.1 Raw Biomass

Low-cost adsorbents can be fabricated from readily available and abundant feedstock including biowastes from forestry, timber processing, fermentation processes, crop residues, and aquatic weeds (Gwenzi et al. 2015). Aquatic plants such as water

hyacinth and algae show rapid growth in nutrient-laden tropical aquatic systems posing significant ecological and public health risks (Gwenzi et al. 2014). Other biomaterials include animal waste and microorganisms which can also be used as biosorbents. Several studies have reported the ability of both live and dead biomass for removal of organic contaminants. The commonly reported live biomass types are bacteria, fungi. and yeast, of which species of the genera *Aspergillus*, *Candida,* and S*accharomyces*, among others have a high sorption capacity for organics. A kind of ectomycorrhizal fungi, *Gomphidius viscidus*, was reported in the phytoremediation of anthracene in soil (Huang et al. 2010). The biosorbent acts as a linker between the plant and the soil. This biosorption process involves several metabolism-independent routes, including physisorption and chemisorption, chelation, and microprecipitation in the cell wall (Aksu 2005). High adsorption capacity (105–419 mg/g) for organic dyes has also been reported for *Corynebacterium glutamicum* (Vijayaraghavan and Yun 2007). Biosorptive components in microbial biomass include peptidoglycan carboxyl groups, sulfonated polysaccharides, glycoproteins, and extracellular polymeric substances.

Dead biomass including crop residues, sludge, sawdust, sea shells, chitosan, and poultry feathers with high adsorption affinities for organic compounds has also been explored as alternatives to live biomass. Commonly used dead biomasses include saw dust, sea shells, and agro-wastes including rice husks (Toniazzo et al. 2013), sugarcane bagasse (Noreen and Bhatti 2014), seed portion of *Abelmoschus esculentus* (lady's finger) (Le et al. 2018), and nonliving alga *Nostoc comminutum* (Gupta et al. 2014). Although most previous studies have focused on organic dyes, it is possible that such biosorbents may also be effective for the removal of Abs. Despite a considerable number of studies reporting high affinity of dead biomass for inorganic pollutants, raw dead biomass often lacks thermal and chemical stability and the desired specificity towards organic contaminants. To overcome these limitations, activated or engineered biosorbents have been developed and tested.

21.4.2 Biochar as a Low-Cost Alternative

Owing to its porosity, large specific surface area, and surface functional groups, commercial activated carbon (AC) has excellent removal capabilities for a variety of pollutants including Abs (Bardalai and Mahanta 2018). However, it is expensive and unaffordable to low-income countries (Xiang et al. 2019). Therefore, a low-cost adsorbent with fast adsorption kinetics and high adsorption capacity is required (Liu et al. 2019; Mourid et al. 2019; Peng et al. 2019). There are reagent and plant costs associated with the preparation processes of the precursor material, from which the total cost of BC (T_c) can be determined Eq. (21.1) (Ahmed et al. 2015):

$$T_c = P_c + R_c + PL_c \tag{21.1}$$

where P_c is the cost of production, R_c is the cost of regenerating spent BC, and PL_c is the cost of process loss.

Usually, the cost of feedstock is low, depending on local abundance. Overall, the cost of BC depends on the local supply of feedstock, the extent of processing, type of reactor used, pyrolysis conditions, the production of value added byproducts, and reusability (Ahmed et al. 2015). In order to keep T_c low, there is need to establish large-scale supply chains for producing high yield feedstock at low cost.

Several studies have used BC to remove Abs from wastewater (Sun et al. 2018; Liu et al. 2019; Xu et al. 2019; Zhao et al. 2019). Biochar can be produced from a range of biowastes under a range of process conditions, such as temperature and heating rate (Gwenzi et al. 2015). The particle size of biomass plays an important role in the structural transformation of the BC during the rearrangement of the solid phase. During the pyrolysis process, the biomass is heated between 300 and 700 °C in a low oxygen environment (Bardalai and Mahanta 2018). The pyrolysis process can be performed using a range of reactors which include the ablative, auger, fluidized-bed, fixed-bed, vacuum pyrolysis, rotating cone, plasma, solar, and screw type reactors. In addition, rotary kilns, drum kilns, pyrolytic cook stoves, and drum pyrolysers have also been used (Bardalai and Mahanta 2018). Other modification methods include hydrothermal synthesis. While pyrolysis involves carbonization of dry biomass under a limited oxygen atmosphere, low-temperature hydrothermal carbonization involves the treatment of a biomass-water mixture at temperatures in the range of 170–300 °C in a pressurized reactor (Fuertes et al. 2010). Various feedstocks can be used in the production of BC (Table 21.2). These include sludge, municipal solid waste, forest residues, agro-processing wastes, and aquatic weeds. Due to the high temperatures of pyrolysis a variety of chemical reactions occur within the biomass resulting in its conversion into a solid residue and gaseous product.

The characteristics of BC are primarily determined by the preparation temperature and biomass. High pyrolysis temperatures often result in high surface area leading to high sorption capacity for pollutants (Bardalai and Mahanta 2018). Biochar derived from different source materials show varying surface area, ash content, electrical conductivity, porosity, and functional groups (Bardalai and Mahanta 2018). The adsorption capacity of BC can therefore be enhanced via structural and chemical modification, which can be effected through various facile activation techniques such as acid/base treatment, amination, biological modification, impregnation with metal salts, microwave treatment, ozone treatment, and plasma treatment, and introduction of functional groups have been used (Xiang et al. 2019). This produces BC with many desirable properties, making it very effective in sequestering Abs (Liu et al. 2019).

Functionalization alters the surface characteristics such as the surface functional groups, charge, and textural properties of BC. Furthermore, acid modification removes inherent inorganic impurities in the BC, providing additional active sites for the binding of pollutants. This also increases the acidity, and changes the pore structure by oxidizing the water molecules in the pores to produce oxygen-carrying moieties. Adsorption efficiency is determined by the surface chemistry of the BC (Roy et al. 2018). While amination introduces amine moieties on BC surface, modification using $KMnO_4$ via the Hummer's method has been used to increase

Table 21.2 Examples of biomass and the properties of biochar

Biomass source	Pyrolysis conditions	Chemical modification %C %H %O			Characteristics pH EC % ash %moisture				References
Paper and pulp sludge	750 °C under N_2 for 2 h	–	–	–	8.5	0.16	36.2	1.4	Narzari et al. (2017)
Corn stem	600 °C at 10 °C/min under N_2 atmosphere for 1 h	–	–	–	8.9	–	–	16.8	Liu et al. (2019)
Pongamia glabra	350 °C under N_2 for 2 h	61.72	2.24	29.65	8.6	0.76	9.1	13.5	Narzari et al. (2017)
Areca catechu tree dust	450 °C under N_2	54.03	42.14	2.90	8.9	–	24.2	0.1	Bardalai and Mahanta (2018)
Maize	500 °C under N_2 for 2 h	–	–	–	10.5	–	–	0.2	Bogusz et al. (2017)

the number of oxygenated groups such as C=O, C-O, COOH, and phenolics on the BC surface (Jiang et al. 2018; Roy et al. 2018; Yanyan et al. 2018). These functional groups enhance the adsorption of pollutants such as Abs.

Because of its excellent adsorptive properties, BC has been used in water treatment to remove a variety of pollutants including Abs from water bodies (Gwenzi et al. 2014). The capacity of BC fabricated from burcucumber (*Sicyos angulatus* L.) to retain sulfamethazine in loamy sand and sandy loam soils has been investigated (Vithanage et al. 2014). The mobility of sulfamethazine was increasingly retarded with increasing proportions of BC, implying the analyte was progressively retained by BC. Yao et al. (2013) demonstrated the effectiveness of BC derived from various wastewater sludges in removing fluoroquinolone Abs from water. In another study, benzo(a)anthracene, β-estradiol, and bisphenol were bioadsorbed onto chitin, which has attractive features due to its unique molecular structure, physicochemical characteristics, and chemical stability (Krupadam et al. 2011). Two chemically activated BCs fabricated under oxygen-rich and oxygen-starved environments were effectively used for the sequestration of sulfamethoxazole (Jung et al. 2013). A summary of the capacities of a range of biomass-derived adsorbents for the sequestration of Abs is shown in Table 21.3.

21.5 Mechanisms of Removal of Abs Using BC

The sorptive interactions between BC and Abs can be physical adsorption, chemisorption, or electrostatic interactions. These molecular-level interactions include electrostatic, hydrogen bonding, hydrophobic, Lewis acid-base, π-π electron donor-acceptor (EDA), π–π interactions, and van der Waals interactions (Fig. 21.2). Surface functionalities such as -COOH, -OH, -NH_2 in BC also influence the mechanism and efficacy of adsorption. The primary interaction between BC and Abs is electrostatic interaction, which usually occur in the adsorption of Abs. For example, previous studies reported that electrostatic interactions and hydrophobic attraction were the major sorption mechanisms of fluoroquinolone on BC (Tan et al. 2016; Gwenzi et al. 2018; Jiang et al. 2018). Hydrophobic interactions are mainly responsible for the adsorption of Abs in aqueous systems, culminating in enhanced removal. In another study, the sorption of quinolone onto powdered activated carbon was reported to be mainly due to electrostatic interactions, hydrophobic interactions, and π–π dispersion forces (Xiang et al. 2019).

The primary mechanisms for the adsorption of Abs onto the BC are largely electrostatic interactions, hydrophobic interactions, hydrogen bonding, partitioning into non-carbonized fractions, pore-filling, π–π interactions, and surface precipitation (Tan et al. 2016). Generally, the adsorption process occurs in four stages: (1) the transportation of Abs in the bulk medium, (2) film diffusion of Abs, (3) pore diffusion of Abs, and (4) the interaction between Abs and the BC matrix. Compared to physisorption, these interactions are strong and more specific, and are confined to the monolayer. The surface chemistry of BC plays a key role in the sorption of Abs since BC has heterogeneous surfaces due to the presence of carbonized and

Table 21.3 Antibiotic removal capacities of biomass-derived materials

Adsorbent	Antibiotic	Adsorption capacity /Removal (%)	Remarks	References
Biochar-derived from swine manure digestate	Sulfadimidine and Tylosin	83.76, and 77.34%	Co-adsorption of abs in the presence of arsenic	Jiang et al. (2018)
Metal organic frameworks	Norfloxacin, Ofloxacin, and Enoxacin	408.2, 450.4, and 425.5 mg/g	Electrostatic interaction between charged functional groups key in adsorption mechanism	Guo et al. (2019)
Activated carbon from walnut shells	Metronidazole, Sulfamethoxazole	107.4 mg/g 93.5 mg/g	pH 8 at 30 °C pH 5.5 at 30 °C	Teixeira et al. (2019)
Aerobic granular sludge	Kanamycin Tetracycline Ciprofloxacin Ampicillin Erythromycin	88.4 ± 4.5%	High protein content from tightly bound extracellular polymeric substances facilitated aerobic granulation.	Peng et al. (2019)
Combinations of up-flow Anaerobic sludge bed, anoxic-oxic tank, and advanced oxidation technologies	Tetracyclines, Sulfamethoxazole, and ampicillin enrofloxacin	62.5–80.9% 73.9%	All antibiotics fully eliminated during the 180 d-operation	Hou et al. (2019)
Drinking water treatment processes	Sulfonamides, sulfamethoxazole		The removal efficiency of advanced process for each antibiotic was higher than that of conventional process, except for sulfameter	Hu et al. (2018)
UVC-activated peroxymonosulfate, UVC irradiation, and PMS oxidation	(ARB) HLS-6, intracellular *sul1* and *intI1*	Reduction rates reached up to 2.9 log and 3.4 log	Reduction rates at pH 5 reached up to 3.1 log (*sul1*) and 3.3 log (*intI1*)	Hu et al. (2019)
Ozonation	Ampicillin, azithromycin, erythromycin, clarithromycin, Ofloxacin, Sulfamethoxazole trimethoprim, and tetracycline	Not stated	Efficiency was mainly ozone dose and contact time dependent. Levels below detection limits were achieved with	Iakovides et al. (2019)

			retention time of 40 min and specific ozone dose of 0.125 gO_3 $gDOC^{-1}$	
Biochar-derived from swine manure digestate	As (III), sulfadimidine and tylosin	83.98, 83.76, 77.34%	Mn-BC was observed as the promising adsorbent	Jiang et al. (2018)
Laterite soil	Flumequine	94%	Laterite exhibited no deactivation of surface sites and an excellent catalytic stability	Kamagate et al. (2018)
Membrane bioreactor systems	Amoxicillin, azithromycin, ciprofloxacin, chloramphenicol, Meropenem, minocycline, Oxytetracycline, Sulfamethazine, and Vancomycin	Mean removal efficiency >70%	Membrane bioreactor outperformed conventional activated sludge in the removal of ARB, ARGs and most targeted antibiotics	Le et al. (2018)
Eggshell membrane-derived $MgFe_2O_4$	Doxycycline	308 mg/g	Adsorbent can be reused after magnetic separation from water and acid treatment	Li et al. (2017)
Graphene and graphene-based nanocomposites			Factors affecting absorbance include pH, temperature, dosage of adsorbent and co-existing ions. Photocatalytic degradation affected by contact time, pH, graphene concentration, and light irradiation condition	Li et al. (2019)
3D hierarchical porous-structured biochar aerogel	Phenicol abs	>90%	Highest efficiency reached in 10 min even with high initial antibiotic concentrations	Liu et al. (2019)
Calcined layered double hydroxide	Sulfamethoxazole	93%	Adsorption is governed by physisorption	Mourid et al. (2019)
MIL-101(Cr) (materials Institute Lavoisier-101(Cr)	Sulfadimethoxine, Sulfamonomethoxine, and Sulfachloropyridazine	100 mg/L.	pH 5–7 adsorption reach maximum and decrease with increasing salt concentration. Oxidation capacity	Peng et al. (2019)

(continued)

Table 21.3 (continued)

Adsorbent	Antibiotic	Adsorption capacity /Removal (%)	Remarks	References
			decrease with increase of oxidation times	

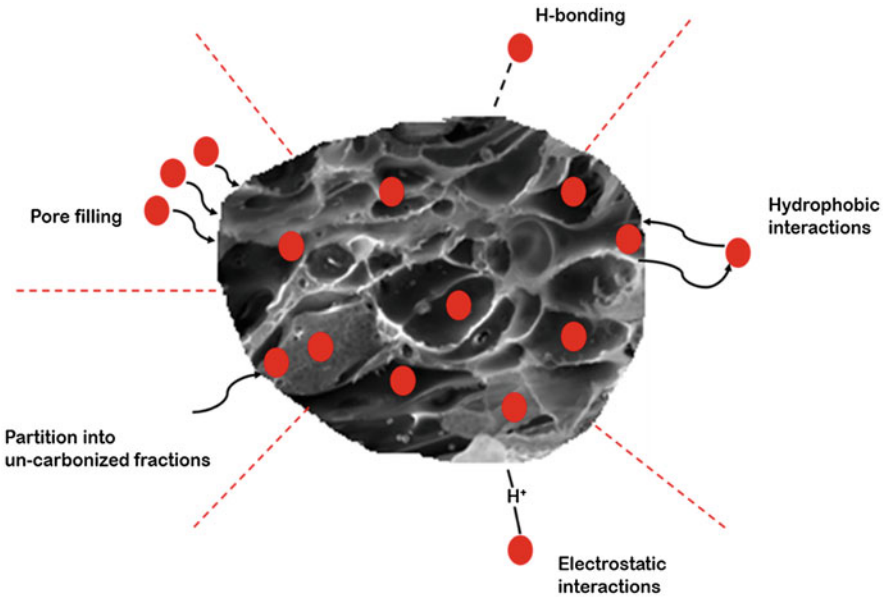


Fig. 21.2 Mechanisms involved in the sorption of Abs on BC

non-carbonized regions, which have different functional groups. For instance, the adsorption of sulfonamides on different BCs depended on the extent of graphitization, indicating π–π EDA interactions between the Abs molecules and the aromatic BC surfaces was the primary mechanism. Similarly, the sorption of sulfamethoxazole on BC under acidic conditions was predominantly through π–π EDA interactions between the protonated aniline rings with the π-electron dense graphitic BC surface, as opposed to cation exchange (Jiang et al. 2018). Under alkaline conditions, the sorption of anionic sulfamethoxazole species enhanced and was regulated by hydrogen bonding. The adsorption kinetics revealed that the predominant sorption mechanism of Abs on BC was chemisorption. The electron density of nitroimidazoles with their aromatic moieties increased π-π Abs-BC dispersion interactions and enhanced their sorption on BC (Ahmed et al. 2015).

21.6 Challenges and Future Outlook

Owing to increasing Abs discovery and usage due to the increasing disease burden, the concentration and variety of Abs, ARB, and ARGs in the aquatic environment are likely to increase. Antibiotics do not only affect aquatic ecosystems, they also compromise the human immune system and inhibit physiological processes. This requires rapid development and up-scaling of removal technologies that will effectively abate these pollutants. A number of promising methods have been explored in this chapter. Of these, the use of biomass-derived materials has been presented as a

cost-effective and efficient alternative. Owing to its high porosity and easily modified surface chemistry, BC has great promise in the sequestration of Abs from aquatic systems. With proper modification, the adsorption efficiency of BC can be improved considerably. The properties of BC and the physicochemical characteristics of Abs significantly influence the adsorption processes. Besides, understanding of the interactions between BC and Abs is still lacking. Thus the adsorption mechanisms need further study. Moreover, there is need to study the removal of individual Abs in a multi-component Abs solution, and the influence of competing co-solutes in solution on Abs removal. Use can be made of novel materials, such as nanoparticles, in modifying BC to enhance the Abs removal performance.

Although widely researched on a laboratory scale, the large-scale application of biomass-derived sorbents such as BC is limited by lack of data on reactor design for pilot- and field-scale application. Researchers in various disciplines including chemistry, engineering, environmental sciences, and water engineering need to collaborate to increase the knowledge base and generate unit processes that can be retrofitted and integrated into existing water treatment processes. There is need for state-of-the-art analytical facilities to continuously monitor the concentrations of different Abs in aquatic systems. Another challenge is associated with the disposal of spent adsorbent, which can potentially cause secondary pollution. The cost of the technology can be reduced by establishing large-scale supply chains for producing high yield feedstock at low cost, and using low-cost techniques to regenerate spent BC for multiple reuse. However, at the end of its lifecycle, and with adequate environmental impact assessment, spent BC can be used for such applications as road surfacing and construction (Chaukura et al. 2016). Because of the rich nutrients, other researchers have developed slow-release fertilizers from spent adsorbents (Gwenzi et al. 2018). However, owing to the risk of leaching organics into the soil, spent biomass loaded with organic pollutants will need a thorough characterization before being applied as a fertilizer or any other application.

21.7 Conclusion

This chapter has demonstrated that BC and other biomass-derived materials can be effectively used to remove various Abs from the aquatic environment. Biochar is fabricated through pyrolysis or hydrothermal synthesis of biomass, and the production conditions determine the properties of the resulting product. Adsorption using biomass-derived materials is an attractive technique because: (1) it uses readily available materials, making it cost effective and thus usable even in low-income countries, (2) it effectively removes Abs, (3) it can be regenerated for repeated use, and thus reduce its carbon footprint, and (4) the pollutant-laden material has potential applications as a slow-release fertilizer and soil conditioner. Although experimental studies have been extensively reported, the large-scale use of BC is still lacking. This is mainly because, while there is a lot of data on batch experiments,

little data exists on column studies that generate process design parameters for large-scale application.

References

Abera B, Kibret M, Mulu W (2016) Extended-spectrum beta (β)-lactamases and antibiogram in enterobacteriaceae from clinical and drinking water sources from Bahir Dar city, Ethiopia. PLoS One 11(11):e0166519. https://doi.org/10.1371/journal.pone.0166519

Adegoke AA, Faleye AC, Stenstrom TA (2018) Residual antibiotics, antibiotic resistant superbugs and antibiotic resistance genes in surface water catchments: public health impact. Phys Chem Earth Parts A/B/C 105:177–183

Ahmed MB, Zhou JL, Ngo HH, Guo W (2015) Adsorptive removal of antibiotics from water and wastewater: progress and challenges. Sci Total Environ 532:112–126

Aksu Z (2005) Application of biosorption for the removal of organic pollutants: a review. Process Biochem 40(3–4):997–1026

Alsager OA, Alnajrani MN, Abuelizz HA, Aldaghmani IA (2018) Removal of antibiotics from water and waste milk by ozonation: kinetics, byproducts, and antimicrobial activity. Ecotoxicol Environ Saf 158:114–122

Anjali R, Shanthakumar S (2019) Insights on the current status of occurrence and removal of antibiotics in wastewater by advanced oxidation processes. J Environ Manag 46:51–62

Azanu D, Styrishave B, Darko G, Weisser JJ, Abaidoo RC (2018) Occurrence and risk assessment of antibiotics in water and lettuce in Ghana. Sci Total Environ 622-623:293–305

Bardalai M, Mahanta DK (2018) Characterisation of biochar produced by pyrolysis from areca catechu dust. Mater Tod: Proc 5:2089–2097

Biancullo F, Moreira NFF, Ribeiro AR, Manaia CM, Faria JL, Nunes OC, Castro-Silva SM, Silva AMT (2019) Heterogeneous photocatalysis using UVA-LEDs for the removal of antibiotics and antibiotic resistant bacteria from urban wastewater treatment plant effluents. Chem Eng J 367:304–313

Bogusz A, Nowak K, Stefaniuk M, Dobrowolski R, Oleszczuk P (2017) Synthesis of biochar from residues after biogas production with respect to cadmium and nickel removal from wastewater. J Environ Manag 201:268–276

Cha J, Carlson KH (2019) Biodegradation of veterinary antibiotics in lagoon waters. Process Saf Environ Prot 127:306–313

Chaukura N, Gwenzi W, Tavengwa N, Manyuchi M (2016) Biosorbents for the removal of synthetic organics and emerging pollutants: opportunities and challenges for developing countries. Environ Dev 19:84–89

Chen BW (2018) Complex pollution of antibiotic resistance genes due to beta-lactam and aminoglycosidic use in aquaculture farming. Water Res 134:200–208

Dires S, Birhanu T, Ambelu A, Sahilu G (2018) Antibiotic resistant bacteria removal of subsurface flow constructed wetlands from hospital wastewater. J Environ Chem Eng 6:4265–4272

Fekadu S, Alemayehu E, Dewil R, Van der Bruggen B (2019) Pharmaceuticals in freshwater aquatic environments: a comparison of the African and European challenge. Sci Total Environ 654:324–337

Fuertes AB, Arbestain MC, Sevilla M, Macia-Agullo JA, Fiol S, Lopez R, Smernik RJ, Aitkenhead WP, Arce F, Macias F (2010) Chemical and structural properties of carbonaceous products obtained by pyrolysis and hydrothermal carbonisation of corn Stover. Aust J Soil Res 48:618–626

Guo X, Kang C, Huang H, Chang Y, Zhong C (2019) Exploration of functional MOFs for efficient removal of fluoroquinolone antibiotics from water. Microporous Mesoporous Mater 286:84–91

Gupta VK, Bhushan R, Nayak A, Singh P, Bhushan B (2014) Biosorption and reuse potential of a blue green alga for the removal of hazardous reactive dyes from aqueous solutions. Biorem J 18:179–191

Gwenzi W, Chaukura N, Mukome FND, Machado S, Nyamasoka B (2015) Biochar production and applications in sub-Saharan Africa: opportunities, constraints, risks and uncertainties. J Environ Manag 150:250–261

Gwenzi W, Musarurwa T, Nyamugafata P, Chaukura N, Chaparadza A, Mbera S (2014) Adsorption of Zn^{2+} and Ni^{2+} in a binary aqueous solution by biosorbents derived from sawdust and water hyacinth (*Eichhornia crassipes*). Water Sci Technol 70:1419–1427

Gwenzi W, Nyambishi TJ, Chaukura N, Mapope N (2018) Synthesis and nutrient release patterns of a biochar based N-P-K slow-release fertilizer. Int J Environ Sci Technol 15:405–414

Hiller CX, Hübner U, Fajnorova S, Schwartz T, Drewes JE (2019) Antibiotic microbial resistance (AMR) removal efficiencies by conventional and advanced wastewater treatment processes: a review. Sci Total Environ 685:596–608

Hou J, Chen Z, Gao J, Xie Y, Li L, Qin S, Wang Q, Mao D, Luo Y (2019) Simultaneous removal of antibiotics and antibiotic resistance genes from pharmaceutical wastewater using the combinations of up-flow anaerobic sludge bed, anoxic-oxic tank, and advanced oxidation technologies. Water Res 159:511–520

Hu Y, Jiang L, Zhang T, Jin L, Han Q, Zhang D, Lin K, Cui C (2018) Occurrence and removal of sulfonamide antibiotics and antibiotic resistance genes in conventional and advanced drinking water treatment processes. J Hazard Mater 360:364–372

Hu Y, Zhang T, Jiang L, Luo Y, Yao S, Zhang D, Lin K, Cui C (2019) Occurrence and reduction of antibiotic resistance genes in conventional and advanced drinking water treatment processes. Sci Total Environ 669:777–784

Huang H, Zeng S, Dong X, Li D, Zhang Y, He M, Du P (2019b) Diverse and abundant antibiotics and antibiotic resistance genes in an urban water system. J Environ Manag 231:494–503

Huang Y, Liu Y, Du P, Zeng L, Mo C, Li Y, Lu H, Cai Q (2019a) Occurrence and distribution of antibiotics and antibiotic resistant genes in water and sediments of urban rivers with black-odor water in Guangzhou, South China. Sci Total Environ 670:170–180

Huang Y, Zhang S, Lv M, Xie S (2010) Biosorption characteristics of Ectomycorrhizal fungal mycelium for Anthracene. Biomed Environ Sci 23:378–383

Iakovides IC, Michael-Kordatou I, Moreira NFF, Ribeiro AR, Fernandes T, Pereira MFR, Nunes OC, Silva CM, Fatta-Kassinos D (2019) Continuous ozonation of urban wastewater: removal of antibiotics, antibiotic-resistant Escherichia coli and antibiotic resistance genes and phytotoxicity. Water Res 159:333–347

Jiang B, Lin Y, Mbog JC (2018) Biochar derived from swine manure digestate and applied on the removals of heavy metals and antibiotics. Bioresour Technol 270:603–611

Jung C, Park J, Lim KH, Park S, Heo J, Her N, Oh J, Yun S, Yoon Y (2013) Adsorption of selected endocrine disrupting compounds and pharmaceuticals on activated biochars. J Hazard Mater 263:702–710

Kamagate M, Assadi AA, Kone T, Giraudet S, Coulibaly L, Hanna K (2018) Use of laterite as a sustainable catalyst for removal of fluoroquinolone antibiotics from contaminated water. Chemosphere 195:847–853

Kang J, Duan X, Zhou L, Sun H, Tade MO, Wang S (2016) Carbocatalytic activation of persulfate for removal of antibiotics in water solutions. Chem Eng J 288:399–405

Krupadam RJ, Sridevi P, Sakunthala S (2011) Removal of endocrine disrupting chemicals from contaminated industrial groundwater using chitin as a biosorbent. J Chem Technol Biotechnol 86:367–374. https://doi.org/10.1002/jctb.2525

Kumar S, Tripathi VR, Garg SK (2013) Antibiotic resistance and genetic diversity in water-borne Enterobacteriaceae isolates from recreational and drinking water sources. Int J Environ Sci Technol 10:789–798. https://doi.org/10.1007/s13762-012-0126-7

Larsson DGJ, Antoine Andremont A, Bengtsson-Palme J, Brandt KK, Husman AMR, Fagerstedt P, Fick J, Flach C, Gaze WH, Kuroda M, Kvint K, Laxminarayan R, Manaia CM, Nielsen KM,

Plant L, Ploy M, Segovia C, Simonet P, Smalla K, Snape J, Topp E, van Hengel AJ, Verner-Jeffreys DW, Virta MPJ, Wellington EM, Wernersson A (2018) Critical knowledge gaps and research needs related to the environmental dimensions of antibiotic resistance. Environ Int 117:132–138

Le T, Ng C, Tran NH, Chen H, Gin KY (2018) Removal of antibiotic residues, antibiotic resistant bacteria and antibiotic resistance genes in municipal wastewater by membrane bioreactor systems. Water Res 145:498–508

Li J, Ng DHL, Ma R, Zuo M, Song P (2017) Eggshell membrane-derived $MgFe_2O_4$ for pharmaceutical antibiotics removal and recovery from water. Chem Eng Res Des 126:123–133

Li M, Liu Y, Zeng G, Liu N, Liu S (2019) Graphene and graphene-based nanocomposites used for antibiotics removal in water treatment: a review. Chemosphere 226:360–380

Liu H, Wei Y, Luo J, Li T, Wang D, Luo S, Crittenden JC (2019) 3D hierarchical porous-structured biochar aerogel for rapid and efficient phenicol antibiotics removal from water. Chem Eng J 368:639–648

Ma L, Li B, Zhang T (2019) New insights into antibiotic resistome in drinking water and management perspectives: a metagenomic based study of small-sized microbes. Water Res 152:191–201

Mourid EH, Lakraimi M, Benaziz L, Elkhattabi EH, Legrouri A (2019) Wastewater treatment test by removal of the sulfamethoxazole antibiotic by a calcined layered double hydroxide. Appl Clay Sci 168:87–95

Narzari R, Bordoloi N, Sarma B, Gogoi L, Gogoi N, Borkotoki B, Kataki R (2017) Fabrication of biochars obtained from valorization of biowaste and evaluation of its physicochemical properties. Bioresour Technol 242:324–328

Noreen S, Bhatti HN (2014) Fitting of equilibrium and kinetic data for the removal of Novacron Orange P-2R by sugarcane bagasse. J Ind Eng Chem 20:1684–1692

Peng J, Wu E, Wang N, Quan X, Sun M, Hu Q (2019) Removal of sulfonamide antibiotics from water by adsorption and persulfate oxidation process. J Mol Liq 274:632–638

Pirsaheb M, Moradi S, Shahlaei M, Wang X, Farhadian N (2019) A new composite of nano zero-valent iron encapsulated in carbon dots for oxidative removal of bio-refractory antibiotics from water. J Clean Prod 209:1523–1532

Rostamian R, Behnejad H (2017) A unified platform for experimental and quantum mechanical study of antibiotic removal from water. J Water Process Eng 17:207–215

Roy S, Sengupta S, Manna S, Das P (2018) Chemically reduced tea waste biochar and its application in treatment of fluoride containing wastewater: batch and optimization using response surface methodology. Process Saf Environ Prot 116:553–563

Saitoh T, Shibayama T (2016) Removal and degradation of β-lactam antibiotics in water using didodecyldimethylammonium bromide-modified montmorillonite organoclay. J Hazard Mater 317:677–685. https://doi.org/10.1016/j.jhazmat.2016.06.003. Epub 2016 Jun 5. PMID: 27339949

Sanganyado E, Gwenzi W (2019) Antibiotic resistance in drinking water systems: occurrence, removal, and human health risks. Sci Total Environ 669:785–797

Santos F, de Almeida CMR, Ribeiro I, Ferreira AC, Mucha AP (2019) Removal of veterinary antibiotics in constructed wetland microcosms - response of bacterial communities. Ecotoxicol Environ Saf 169:894–901

Sarker M, Shin S, Jhung SH (2019) Adsorptive removal of nitroimidazole antibiotics from water using porous carbons derived from melamine-loaded MAF-6. J Hazard Mater 378:120761. https://doi.org/10.1016/j.jhazmat.2019.120761

Stange C, Sidhu JPS, Toze S, Tiehm A (2019) Comparative removal of antibiotic resistance genes during chlorination, ozonation, and UV treatment. Int J Hyg Environ Health 222:541–548

Sun P, Li Y, Meng T, Zhang R, Song M, Ren J (2018) Removal of sulfonamide antibiotics and human metabolite by biochar and biochar/H_2O_2 in synthetic urine. Water Res 147:91–100

Tan X, Liu Y, Gu Y, Xu Y, Zeng G, Hu X, Liu S, Wang X, Liu S, Li J (2016) Biochar-based nano-composites for the decontamination of wastewater: a review. Bioresour Technol 212:318–333

Teixeira S, Delerue-Matos C, Santos L (2019) Application of experimental design methodology to optimize antibiotics removal by walnut shell based activated carbon. Sci Total Environ 646:168–176

Toniazzo L, Fierro V, Braghiroli F, Amaral G, Celzard A (2013) Biosorption of model pollutants in liquid phase on raw and modified rice husks. J Phys Conf Ser 416:012026

Vijayaraghavan K, Yun Y (2007) Utilization of fermentation waste (Corynebacterium glutamicum) for biosorption of reactive black 5 from aqueous solution. J Hazard Mater 141:45–52

Vithanage M, Rajapaksha AU, Tang X, Thiele-Bruhn S, Kim KH, Lee S, Ok YS (2014) Sorption and transport of sulfamethazine in agricultural soils amended with invasive-plant-derived biochar. J Environ Manag 141:95–103

Xiang Y, Xu Z, Wei Y, Zhou Y, Yang X, Yang Y, Yang J, Zhang J, Luo L, Zhou Z (2019) Carbon-based materials as adsorbent for antibiotics removal: mechanisms and influencing factors. J Environ Manag 237:128–138

Xu J, Cao Z, Wang Y, Zhang Y, Gao X, Ahmed MB, Zhang J, Yang Y, Zhou JL, Lowry GV (2019) Distributing sulfidized nanoscale zerovalent iron onto phosphorus-functionalized biochar for enhanced removal of antibiotic florfenicol. Chem Eng J 359:713–722

Yanyan L, Kurniawan TA, Zhu M, Ouyang T, Avtar R, Othman MHD, Mohammad BT, Albadarin AB (2018) Removal of acetaminophen from synthetic wastewater in a fixed-bed column adsorption using low-cost coconut shell waste pretreated with NaOH, HNO_3, ozone, and/or chitosan. J Environ Manag 226:365–376

Yao H, Lu J, Wu J, Lu Z, Wilson PC, Shen Y (2013) Adsorption of Fluoroquinolone antibiotics by wastewater sludge biochar: role of the sludge source. Water Air Soil Pollut 224:1370

Zhang S, Lin W, Yu X (2016) Effects of full-scale advanced water treatment on antibiotic resistance genes in the Yangtze Delta area in China. FEMS Microbiol Ecol 92(5):fiw065. https://doi.org/10.1093/femsec/fiw065. Epub 2016 Mar 27. PMID: 27020061

Zhao J, Liang G, Zhang X, Cai X, Li R, Xie X, Wang Z (2019) Coating magnetic biochar with humic acid for high efficient removal of fluoroquinolone antibiotics in water. Sci Total Environ 688:1205–1215

Mangrove Forest Pollution and Remediation in the Rhizosphere

22

Ali Ranjbar Jafarabadi, Elham Lashani, and Hamid Moghimi

Abstract

Mangroves are the dominant ecosystems that are lined in transitional regions between the freshwater, seawater, and land around the World, well known for most productive estuarine and marine settings, which support numerous communities and associations, particularly animal and plants. One of the most endangered environments in particular tropical regions is the mangrove ecosystem since these vital ecosystems have an overwhelming role in a productive and complicated food web in the coastal marine environments (subtropical and tropical). At a perturbing and alarming rate, these areas have been swiftly vanishing on the earth since 23% of mangrove ecosystems have been disappeared in the past two decades. These unique natural systems are menaced by both natural (sea-level rise, tropical cyclones, and coastal erosion) and human activities (organic and inorganic pollution, over-harvesting, industrialization, urbanization, aquaculture, and agriculture) factors. Bioremediation is an environment-friendly and efficient technology to *remediat*e organic and inorganic pollutants. In other words, microbial degradation is a potent approach to eliminate organic pollutants from the mangrove areas by uptaking them into the microbial cells and degrading by their active enzymes. This review discusses the vital importance and services and the most threats of mangrove habitats. Also, primary

A. R. Jafarabadi
Department of Environmental Sciences, Faculty of Natural Resources and Marine Sciences, Tarbiat Modares University, Tehran, Iran

E. Lashani · H. Moghimi (✉)
Department of Microbiology and Biotechnology, School of Biology, College of Science, University of Tehran, Tehran, Iran
e-mail: hmoghimi@ut.ac.ir

© The Author(s), under exclusive licence to Springer Nature Singapore Pte Ltd. 2021

V. Kumar et al. (eds.), *Rhizobiont in Bioremediation of Hazardous Waste*,
https://doi.org/10.1007/978-981-16-0602-1_22

organic and inorganic contaminants and the role of the microbial population in mangrove ecosystems for bioremediation have been discussed.

Keywords

Bioremediation · Ecosystem · Hydrocarbons · Mangrove · Metals · Microbes

22.1 Introduction

Mangrove ecosystems are critical coastal ecosystems located in transitional regions between the freshwater, seawater, and land (Barbier et al. 2011). These ecosystems are subject to tidal variations (Ghizelini et al. 2019) in the subtropical and tropical areas of the World (Barbier et al. 2011; Li et al. 2015; Snedaker and Saenger 1993; Viswanathan 2016; Wang et al. 2018) and globally covering approximately 1.7×10^5 km^2 of the coastlines in the World (Li et al. 2015; Snedaker and Saenger 1993; Sandilyan and Kathiresan 2012), it is being reported that 20% of the World's mangrove is located in Indonesia.

Mangrove ecosystems are taxonomically differing groups of tree species in tropical areas. These species have evolved parallel and have developed particular adaptations such as physiological and morphological ones to grow in intertidal settings, like salt regulation strategies and aerial roots (Ellison 2019; Polidoro et al. 2014). Because of intertidal habitat preferences, these ecosystems situate most immensely on low-gradient sedimentary coastlines, among high tide elevations and Mean Sea Level (MSL) (Ellison 2019).

Mangrove construction is specified by "zones" of tree species, in designs that run vertically to the coastline or river margins. Mangrove habitats are also open structures that exchange both matter and energy with offshore coastal ecosystems and upland terrestrial (Ellison 2019). These coastal intertidal wetland forests are composed of different mangrove species that grow with shrub species, submerged bases, and halophytic trees in areas between land and sea interface (Arumugam et al. 2018). Mangrove trees contain relatively 70 vegetation species in 40 genera that are shared characteristics of the sheltered coasts in subtropical and tropical regions (Hamdan et al. 2012; Hogarth 1999). Moreover, it is well documented that fairly 59 mangrove species are wide-spreading global. *Avicennia marina* and *Rhizophora* sp., are cosmopolitan species that are broadly ubiquitous in various coastal habitats like Sri Lanka, Indonesia, India, Australia, Brazil, Eastern Africa, and Persian Gulf (MacFarlane et al. 2003).

22.2 Mangrove Contribution to Ecosystem

The number of contributions these mangrove ecosystems offer to human, plant, and animal populations is undeniable. More importantly, a broad spectrum of ecosystem services profits innumerable human people in different scales from local to regional

levels since they are ecologically, environmentally, and economically prominent (Ghizelini et al. 2019; Spalding et al. 2010).

They generally have highly considerable biodiversity and phytoplankton are the prominent flora in the ecosystems that play a part in the primary production, carbon fixation (Gao et al. 2018), and feeds for organisms (especially juveniles and larvae) in mangrove ecosystems directly or indirectly (Alikunhi and Kathiresan 2012; Arumugam et al. 2016; Biswas et al. 2009; Gao et al. 2018). Various studies have confirmed that these unique ecosystems have high biomass of phytoplankton and biodiversity (Aké-Castillo and Vázquez 2008; Al-Hashmi et al. 2013; Arumugam et al. 2016; Aziz et al. 2012; Biswas et al. 2009; Canini et al. 2013; Choudhury et al. 2015; Kannan and Vasantha 1992; Mwashote et al. 2005).

Mangrove ecosystems are very efficient in retaining a broad spectrum of fauna and flora and steading food chains on the coastline (Truong and Do 2018). This coastal area prepares direct economic profits to local communities like charcoal, timber, non-timber forest products, and shellfish/fish (Wang et al. 2018). Also, they provide numerous indirect profits, comprising protecting coastal area (e.g., wave attenuation and controlling coastal erosion), nutrient cycling, water purification, carbon sequestration, research, and education (Wang et al. 2018). Mangrove is also life-support ecosystems in maintaining several aquatic species (Rönnbäck 1999). The mangrove's vast roots could prepare natural trenches and valuable food source for marine organisms. Also, mangrove roots are a shelter for animals above the seawater (e.g., birds and snakes) (Nagelkerken et al. 2002). Molluscs, particularly mussels and oysters, could utilize the roots of mangrove as a shelter. It is well proved that these highly productive zones are having an overwhelming effect as breeding and nursery grounds for several keys and prominent species (Ingole et al. 2009; Lotfinasabasl et al. 2018). These vegetation are extremely significant to estuarine fisheries due to their role in preparing detritus and organic carbon into the food chain and tree roots that make a habitat for fish and microorganisms such as fungi and bacteria (Holguin et al. 2001).

They also regulate substantial processes like hydrodynamic wave attenuation. In the pond and the mining areas, with a high concentration of metal elements, mangrove also can function as a buffer region (Arumugam et al. 2018), purvey coastal buffer area to protect coastal shelters from the natural calamity (Tamin et al. 2011). These ecosystems have a discernable and overwhelming ecological role in stabilizing and keeping balancing within coastal landforms and marine shelters (Arumugam et al. 2018; Sarika and Chandramohanakumar 2008).

Additionally, the natural food generation in these areas is the highest and essential role that mangroves have in aquaculture. They have a pivotal role in aquaculture due to the natural generation of fry and seeds. Entering shrimp seeds can happen in aquaculture settings naturally or artificially (Rönnbäck 1999). The presence of plankton mostly supports the mangrove food web, microphytobenthos, and detritus (Nagelkerken et al. 2002). A study by Larsson et al. (1994) indicated that mangrove habitat coverage of 25% prepares about 70% of the feed necessity.

Besides, mangroves are regarded as critical ecosystems in reduction programs aimed at declines in nitrogen (N) contamination (Mitsch et al. 2015). Compared to

Table 22.1 The ecological and economic services of mangroves (mean economic value)

Ecosystem service valuations of mangrove ecosystems		The global advantage of ecosystem services	
Average economic value (2007 Int$/ha/yr)		Mangrove ecosystem services	
1. Fisheries (nursery and aquaculture)	17,090	1. Waste treatment	1,62,125
2. Ecotourism and recreation	14,072	2. Habitat/Refugia	17,138
3. Coastal protection	8459	3. Disturbance regulation	5351
4. Pollution abatement	7859	4. Erosion control	3929
5. Food (for wild animals)	1535	5. Recreation	2193
6. Protection from sedimentation	579	6. Water supply	1217
7. Energy resources	306	7. Food production	1111
8.Wood and timber	247	8. Raw materials	358
9. Carbon sequestration	195	9. Genetic resources	311
10. Honey	4.23	10. Climate regulations	65
11. Fodder		11. Nutrient cycling	45
12. Water bioremediation			
13. Protection from salt intrusion			
14. Aesthetic value			
15. Pharmaceuticals			
16. Environmental risk indicators			
Total value per ha (2007 Int$/ha/yr)	50,349	Total value per ha (2007 Int$/ha/yr)	193,843

most terrestrial ecosystems, mangroves sequester more nitrogen per area (Adame et al. 2015; Donato et al. 2011). Mangroves, despite terrestrial woodlands, can store the more substantial part of their nitrogen (Adame and Fry 2016).

Many investigations have tried to evaluate the economic value of mangrove areas services globally (Salem and Mercer 2012; Wang et al. 2018). Table. 22.1 demonstrates a summary of the ecological and economic services and values of these ecosystems (Mukherjee et al. 2014).

22.3 Threats to Mangrove Ecosystem

The degradation of ecosystems is an environmental issue that diminishes the capability of abiotic and biotic compartments of ecosystems. This degradation could occur in invaluable sensitive marine ecosystems, and this degradation is continually accelerating (Jafarabadi et al. 2018a, b; Jafarabadi et al. 2017a, b, c; Jafarabadi et al. 2019a, b, c). Although the mangroves are considered as one of the most menaced tropical ecosystems (Lotfinasabasl et al. 2018), at a perturbing and alarming rate, these areas have been swiftly vanishing on the earth since 23% of these systems have been disappeared in the last 20 years (Giri et al. 2011; Spalding et al. 2010). These ecosystems are persistently perturbed by natural agents, like tropical storms, which can do a great disservice to trees and peat collapse (Kauffman and Cole 2010). The

remaining woodlands are under permanent menace from demographic pressure and human activities, like tourism, agriculture, and aquaculture, occurring at or near these woodlands (Duke et al. 2007; Ishtiaque et al. 2016).

Nonetheless, despite its invaluable socio-ecological value, these unique natural systems are menaced by both human activities (i.e., pollution, agriculture) and natural (i.e., coastal erosion, tropical hurricane/cyclones, and sea-level rise) agents (Bhowmik and Cabral 2013; Ishtiaque et al. 2016). Because of the detrimental effects of human activities like aquaculture, globalization, industrialization, and urbanization, the mangrove area has lessened by 30–50% globally across the past few decades (Chen et al. 2009; Feng et al. 2017). These ecosystems have negatively been affected by human activities (i.e., heavy agriculture and wastewater), and these ecosystems biodiversity has altered due to these activities in last years (Gao et al. 2018).

One of the most prominent compartments of mangrove ecosystems is sediment. A significant supply for these areas flexibility to the sea level rise assumptions that are forecasted is mangrove sediment, which depends on the physiographic environments of these ecosystems (Nitto et al. 2014). In mangroves, the sediment supply proceeds from internal and external processes, comprising interactions among both mangrove plants and environments. Moreover, the most variable component of mangrove environments is allochthonous sediment supply, which depends on discrepancies in the current processes operating and geomorphic settings.

22.4 Causes of Mangrove Destruction

The destruction of these ecosystems has been somewhat due to climate change, which increased sea-level, as well as by human activities like shifts of land use for coastal expansion, comprising aquaculture and agriculture activities (Jusoff and Taha 2008). Jayanthi et al. 2018 studied the Sundarbans of West Bengal, mangrove ecosystems of Gujarat, and mangrove forests of Odisha. Their results demonstrated that 8% of mangrove conversion caused by driver's human activities, and the degree of deforestation was lower than that of mangroves grown in India (Jusoff and Taha 2008). In the Sundarbans region, significant mangrove loss occurred mainly due to the inundation of seawater and coastline shifts. Natural factors including changes in rainfall, hypersaline condition, sea-level rise, lack of freshwater supply, sediment supply, and topography played a substantial role than human activities such as agriculture, aquaculture, and deforestation for the general mangrove ecosystems shifts (Jusoff and Taha 2008). Our literature review demonstrated that the main actions, which made deterioration of these vital ecosystems, are as a following (Fig. 22.1).

Detrimental influences have been formerly observed and reported by climate change on these ecosystems (Alongi 2015; Gilman et al. 2008). Elevated salinity (Eslami-Andargoli et al. 2009) has been demonstrated to decrease the growth and generation of mangroves and also augment the vulnerability of them due to the effects of climate change (Ball 2002). Projected results of climate change, like

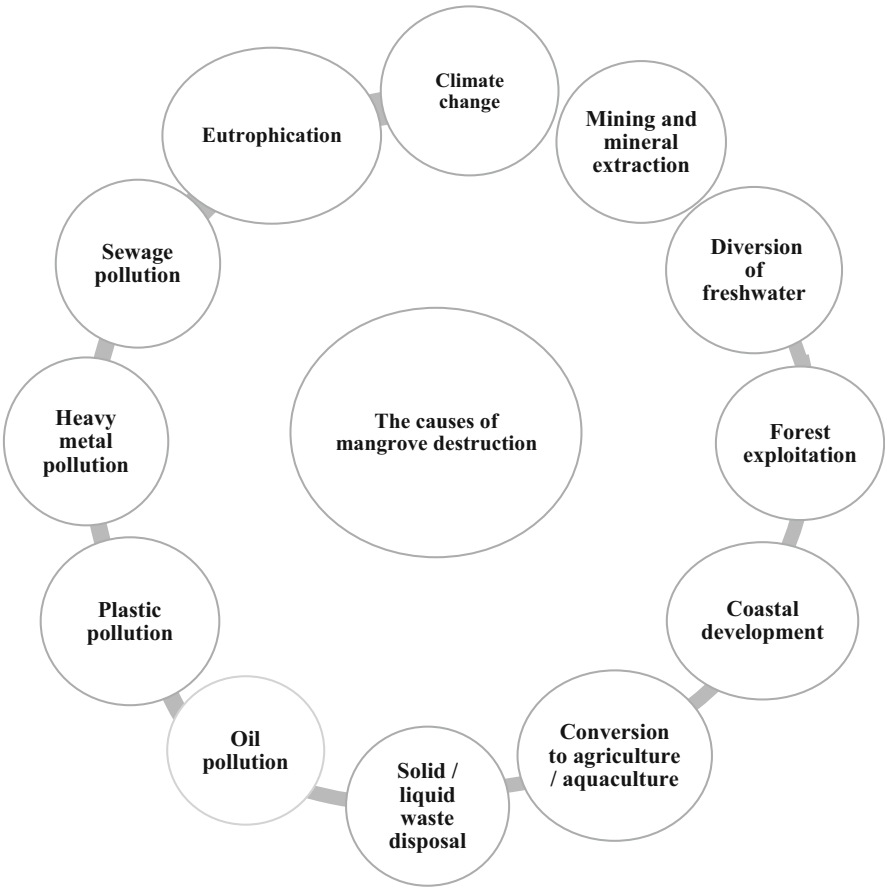


Fig. 22.1 Causes of mangrove forest degradation due to several factors

alterations in increased average temperatures, rainfall patterns, sea-level rise, increased concentration of carbon dioxide, changes in ocean circulation patterns, and increased storm activities formerly seem to have a considerable effect on the growth and expansion of mangroves across the World (Alongi 2015; Galeano et al. 2017; Urrego et al. 2013). Due to a nearby association between rainfall and mangrove habitat situations, any shifts in patterns of rainfall and surface water in watersheds will considerably affect the spatial distribution and growth of these ecosystems. Increasing in the sea level is a chiefly imperceptible menace to these ecosystems, though it is expected to have main effects on the existence of this coastal vegetation in the future (Ellison 2000; Field 1996). Besides, the vulnerability caused by sea-level rise may be exasperated by decision-makers on management decisions like damming on rivers. These choices could decrease external sediment input from fluvial sources like rivers in Vietnam (the Mekong River), in Thailand (Chao Phraya River), and Myanmar (the Ayeyarwady River).

22.4.1 Mining Activities

As the shortage of minerals in industrial sections, there is a parallel augment in mining alluvial mineral sediments. There are rich alluvial sediments of chromium, tin, and other minerals like titanium associated with them in different coastal zone sections. The utilization of ore bodies in the coastline area occurs in different parts of mangrove systems like upstream and downstream. Mining in adjacent regions of mangrove vegetation causes variable destructive effects. In mangrove ecosystems, sedimentation has a remarkable delaying impress in the exchanges of water, gases, and nutrients within the substrate. The loss of mangroves takes place within a period determined in days when this exchange is generally blocked (Saenger 2013) (Fig. 22.2).

22.4.2 Forest Exploitation

Around the World, although domestic fuel and firewood are reducing in supply, the market is swiftly ascending simultaneously. In India and Africa, mangrove vegetation is directly used for firewood. In some mangrove areas, the tree is turned into charcoal for small industrial or domestic usage (Kauffman and Cole 2010). In those areas, the annual regrowth of wood is higher than the annual extraction. In many mangrove regions, the pressure of anthropogenic activities is too much so that the woodlands are swiftly being degraded or are vanishing and more importantly, the extraction far exceeds the annual regrowth (Kauffman and Cole 2010). In some cases, mostly due to the high request for the change to other forms of land use and unsuccessful natural regeneration, exploitation in large-scale has led to a thorough loss of certain regions (Fig. 22.3).

22.4.3 Coastal Development

In high-income countries, a significant problem is a destruction and the exchange of mangrove lands to industrial and domestic expansion. In developing countries, it is beginning to become an issue of consequence. Industry and coastal tourism facilities, like small port development, and housing and residential development, are the most common forms of conversion. Urban, industrial, and airport are the three substantial types of development. Industry and airports are two developments that tend to be nearby to chief population centers (Jusoff and Taha 2008) (Fig. 22.3).

22.4.4 Conversion to Agriculture and Aquaculture

Traditionally, for agricultural and/or aqua cultural generation, coastal woodlands in anaerobic and saline settings have been regarded to be marginal, or inappropriate. Nonetheless, with considerable advancements in cultigen hybridization and



Fig. 22.2 Effects of human activities on mangrove forest destructions (Sources: Little et al. 2018; Dahdouh-Guebas et al. 2005; Duke 2016)

conversion of acidic soils, saline and augmenting demand for arable land, a substantial option for the global rise in agricultural generations is considered the mangrove areas.

Although these ecosystems are broadly recognized for their high economic values, deforestation has dramatically mounted during the last decades; predictions exhibit that if current deforestation rates persist, mangrove coverage will be lost within the next 100 years (Tanner et al. 2019). Deforestation in mangrove lands results in alterations in N and C fluxes to the beach (Lee 2016) and the release of high C quantities (Lovelock et al. 2011). Recovery of these lands can offset these N and C losses (Alongi 2012; Ouyang and Guo 2016).

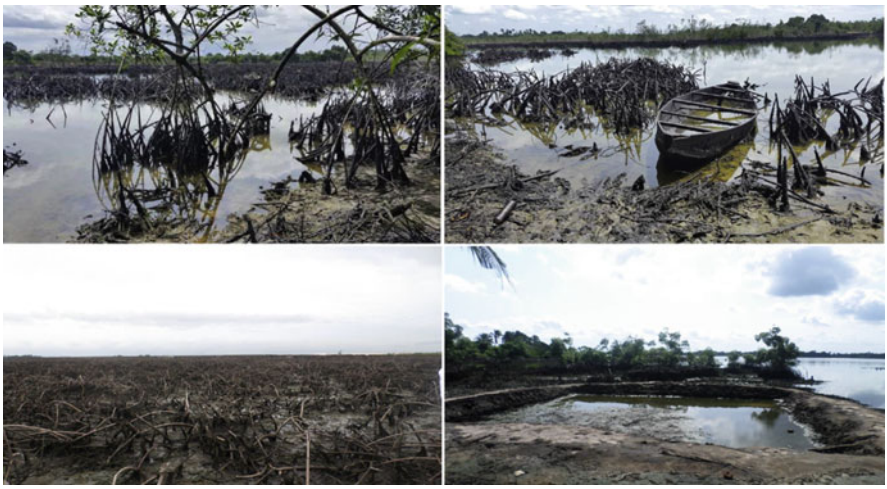


Fig. 22.3 Oil spillage and destructive effects on the mangrove environment (Sources: Onyena and Sam 2020; Sam and Zabbey 2018)

22.4.5 Solid and Liquid Waste Disposal

In the urban areas in most countries, the human populations have been doubled, and it has resulted in a considerable increase in the garbage and solid by three to four times. Additionally, these wastes have been conveyed and discarded where it would not be extremely observable to people. They have been put in the fovea or on flatlands. Much solid waste and garbage refuse have been disposed into these ecosystems. The most significant urban centers in tropical and subtropical regions are placed on estuaries or coasts, and these regions have traditionally been noted as a wasteland. Moreover, disposal of waste so close to waterways has created many unforeseen issues, which can be clearly seen in Fig. 22.2.

22.4.6 Eutrophication

Hypertrophication or eutrophication is a significant and effective factor in coastal areas. When a water body becomes excessively enriched with nutrients and minerals, the excessive growth of algae could happen. This process may lead to deleterious impacts on these forests, comprising oxygen depletion, and mangrove mortality, even killing benthos and fish in the water body (Gao et al. 2018). The swift response to this contamination of coastal areas makes considerable shifts of phytoplankton sensitive bio-indicators in aquatic ecosystems (Sathicq et al. 2017). Manna et al. (2012) studied a tidal creek of Sundarbans estuary, southern Bengal, India. They demonstrated that eutrophication, as well as the existence of toxic Cyanophyceae and Dinoflagellates, has been resulted in deterioration of water quality and consequently menacing the mangrove forests.

As mentioned above, coastal ecosystems, particularly mangrove forests are vital systems and need the supportive efforts of mangrove conservation since it is well reported that these unique trees can apply for phytoremediation for eradication contaminants in the mangrove areas (Moreira et al. 2013).

22.5 Oil Pollutants in the Mangrove Habitats

Impacts of oil spills on shorelines, particularly sensitive habitats such as mangrove are covered in more detail in the International Petroleum Industry Environmental Conservation Association (IPIECA) (Owens and Sykes 2005). Coastal habitats contain plenty of various types of habitats, each of which is characterized by various communities of animals, plants, and microbial associations. Coastal habitats and species will be vulnerable to any coastal oil spill but the scale of the effect and the rate of recovery will be defined mainly by the persistence and condition of the stranded oil, which is itself extremely correlated with wave exposure (Mittal and Singh 2009). Hereupon, effects on coastal habitats such as mangroves are typical could be short/long term since water movement usually removes oil rapidly. However, the natural removal of oil from these habitats is slower. In locations where the intertidal substrate is muddy and dominated by marsh or mangroves, oil residues can persist for years, making long-term effects/impacts (Owens and Sykes 2005).

When the oil is releasing into the environment, such as coastal settings, it becomes subject to some natural processes, known as "weathering," that quickly and progressively shift its character and redistribute much of it into other parts of the environment. The significance of each process on the fate of the oil depends on where the spill occurs, the type of oil, and environmental conditions, such as the chemical and physical (Mittal and Singh 2009; Owens and Sykes 2005). The mechanism and scale of ecological effects are greatly affected by the fate of the oil. Nevertheless, petroleum hydrocarbon contaminants such as PAHs, *n*-alkanes, hopanes, and steranes can be eliminated from the environment via fundamental actions such as natural attenuation, biological, physical, or chemical processes. Hereupon, making a deep understanding of the fate of oil compounds in the ecosystem, particularly these sensitive and productive habitats, is substantially required (Owens and Sykes 2005). When oil spills occur in the environment, several processes happen, such as sedimentation, evaporation, sinking, photo-oxidation, spreading and movement, emulsification, dissolution, dispersion, and biodegradation (Fig. 22.3).

Among coastal ecosystems, rocky coasts have an excellent self-cleaning ability via extremely energetic wave action. Conversely, mangrove habitats are appropriate traps for drifting oil slicks, and this is a fundamental problem of crude oil spillages in mangrove areas. The first is acute and immediate effects. It relates to the physical smothering effect of oil on the plant surfaces responsible for gas exchange (e.g., oxygen and carbon dioxide). It is confirmed that mangrove trees can be killed within 48–72 h via circumstances of a heavy oil spill (Moreira et al. 2013; Souza et al. 2018). The second group of effects pertinent to the long-term chronic poisoning of

trees and related fauna by the toxic components of residual oil (Moreira et al. 2013; Souza et al. 2018). Studying petroleum compounds in mangrove environments (biota and abiota) has been recently received more attention because of the toxic effects of oil pollutants. Dadashi et al. (2018) were chosen three sites along with mangrove forests of Iran. Their results demonstrated a main biogenic source of n-alkanes in marginal Qeshm Island stations, which varied from biogenic to petrogenic origins in the Khamir Port areas. In the Khamir Port, sediment samples revealed the significant existence of petroleum pollutants. This investigation indeed indicated that the Hara Protected Area in the Persian Gulf, Iran, was already contaminated by background petroleum contamination as an effect of continuous oil spills and war conflicts in the Persian Gulf.

22.6 Plastic Pollution

Recently, several investigations have been demonstrated that these coastal ecosystems are dramatically vulnerable to natural environmental shifts and anthropogenic perturbations; particularly, micro-plastic contamination. Plastic contamination in the mangrove is receiving great concern. Scientific communities suspect that due to their unique geographical characterizations, the micro-plastic contamination of semi-enclosed seas is considerably discrepant from that of other seaside types. These plastics could be surrounded by pneumatophores and prop roots of mangrove trees. This absorption may lead to a physical barrier affecting the tree itself and the associated fauna through inhibiting exchanging gas and releasing toxic chemicals absorbed by or industrially added to plastic materials (Martin et al. 2019). Moreover, only a few investigations have reported plastic contamination in mangrove areas, which mostly concentrating on micro-plastic in their surrounding sediments (Barasarathi et al. 2014; Lima et al. 2014; Lourenço et al. 2017; Martin et al. 2019; Naji et al. 2017; Nor and Obbard 2014). Recently, many investigations have been directed on micro-plastic in mangrove environments, and the majority of them confirmed that this issue is deteriorating the mangrove environment (both biota and abiota) (Fig. 22.4). Li et al. (2019) studied a typical semi-enclosed sea, the Maowei Sea. Their results demonstrated that the micro-plastic abundances at the oceanic entrance zones were much higher than those of the river estuaries (between 520 ± 8 and 940 ± 17 items/kg). In the observed mangrove sediments, polyethylene (PE), polypropylene (PP), and polystyrene (PS) were the dominant type, color, and size of the micro-plastics, respectively (Li et al. 2019).

22.7 Heavy Metal Pollution

Even though, mangrove ecosystem is involved in the impelling of industrial and domestic pollutant releases (Arumugam et al. 2018). No integrated and practical management has been implemented on these coastal ecosystems, and heavy metal has a significant concern outright of anthropogenic effects, specifically in



Fig. 22.4 Plastic pollution in mangrove habitats (Source: Martin et al. 2019)

contaminated mangrove coastlines (Arumugam et al. 2018; Qiu et al. 2011; Tam et al. 1995; Tam and Wong 2000). These metallic elements could deposit in ambient sediment in mangrove areas and finally bind with oxides such as iron ones and transferred to these trees/plants (Arumugam et al. 2018). Globally, in many places, such as China, Australia, India, and Vietnam (Nath et al. 2013), these kind of inorganic pollutants in mangroves ambient sediments have been reported. Table 22.2 shows some heavy metal polluted areas all around the world. Overall, mangrove contamination with heavy metals can be classified into two-point and non-point sources, and most of this contamination is pertinent to anthropogenic processes via municipal effluent, surface run-off, and untreated industrial wastewater (Bodin et al. 2011). Toxic minerals from tidal waters and riverine sources can be swiftly eliminated from the waterbody and placed in the ambient sediments, eventually causing it to be a depository media for these metals. It is related to the anoxic essence of mangrove sediment. Nonetheless, two major processes, biological and chemical ones, may allow the deposited toxic minerals to be desorbed from mangrove sediments, upon which they are unleashed into the waterbody (Hill et al. 2013; Wang et al. 2013).

In an interesting study, the concentration, partitioning, distribution, and ecological risks of seven metals (Ni, Fe, As, Co, Cu, Cr, and Mn) in ambient sediments and pore-waters were investigated by Thanh-Nho et al. (2019) in the Can Gio Mangrove. They collected three cores within a mudflat, beneath *Avicennia alba* and *Rhizophora apiculata* stands.

Table 22.2 Some of the toxic metal polluted regions in mangrove environments

Contamination site	Metal	Concentration	References
Shenzhen, China	W	377 mg kg^{-1}	Xu et al. (2015)
	Co	129 mg kg^{-1}	
Zambales, Philippines	Pb	Undetectable levels	Paz-Alberto et al. (2014)
Hong Kong	Cu	80 μg/g	McDonald et al. (2006), Tam and Wong (2000)
	Zn	240 μg/g	
	Cr	40 μg/g	
	Ni	30 μg/g	
	Cd	3 μg/g	
	Pb	80 μg/g	
South China	Cr	28.5–86.6 mg kg^{-1}	Liu et al. (2017), McDonald et al. (2006)
	Cu	10.3–30.9 mg kg^{-1}	
	Zn	24.8–87 mg kg^{-1}	
	As	2.44–20.1 mg kg^{-1}	
	Pb	25.6–86.4 mg kg^{-1}	
	Cd	0.07–0.39 mg kg^{-1}	
	Hg	0.061–0.24 mg. Kg^{-1}	
French Guiana	Cu	0.06–0.61 μmol/g	Al-Hashmi et al. (2013), Marchand et al. (2006)
	Co	0.12–0.68 μmol/g	
	Pb	0.08–0.18 μmol/g	
	Ni	0.32–0.76 μmol/g	
	Cr	0.61–1.4 μmol/g	
	Zn	1.25–5.94 μmol/g	
	Mn	4.36–45.4 μmol/g	
	Fe	441–1128 μmol/g	
Brazil, Rio de Janeira state, Guanabara Bay	Hg	0.7–9.78 mg kg^{-1} dry weight	Kehrig et al. (2003), McDonald et al. (2006), McDonald et al. (2006)
	Zn	78–707 mg kg^{-1} dry weight	
	Cr	3.5–480 mg kg^{-1} dry weight	

(continued)

Table 22.2 (continued)

Contamination site	Metal	Concentration	References
	Cu	2.4–300 mg kg^{-1} dry weight	
	Pb	3.6–110 mg kg^{-1} dry weight	
	Cd	0.02–2.6 mg kg^{-1} dry weight	
Brazil, Rio de Janeira state, Sepetiba Bay	Hg	0.017–0.16 mg kg^{-1} dry weight	
	Zn	18.1–795 mg kg^{-1} dry weight	
	Cr	23.9–121 mg kg^{-1} dry weight	
	Cu	2.1–166 mg kg^{-1} dry weight	
	Pb	6.5–85.7 mg kg^{-1} dry weight	
	Cd	0.5–8.7 mg kg^{-1} dry weight	

22.8 Biological Approaches for Remediation in Mangrove Habitats

Ecological parameters affecting microbial hydrocarbon bioremediation include temperature, electron acceptors, pressure, salinity, substrates, type of microorganisms, inoculum size, nutrient accessibility, biosurfactant, and bioavailability of pollutants (Varjani et al. 2017). Several techniques applied for bioremediation of polluted areas listed in Fig. 22.5.

There are two strategies for bioremediation of polluted regions, including biostimulation and bioaugmentation. Bioaugmentation refers to the addition of exogenous strains/mixed cultures to polluted environments to improve or accelerate the degradation of specific compounds. This method can effectively transform the contaminants into less complicated compounds. The genetically engineered bacteria, pre-adapted microorganisms, and a vector containing genes involved in bioremediation are applied in microbial bioaugmentation (Herrero and Stuckey 2015). In contrast, biostimulation is a bioremediation strategy that consists of the optimization of some factors (such as the addition of nutrients, trace elements, electron acceptors or donors) to induce indigenous microbial communities to remove environmental pollutants (Chen et al. 2012).

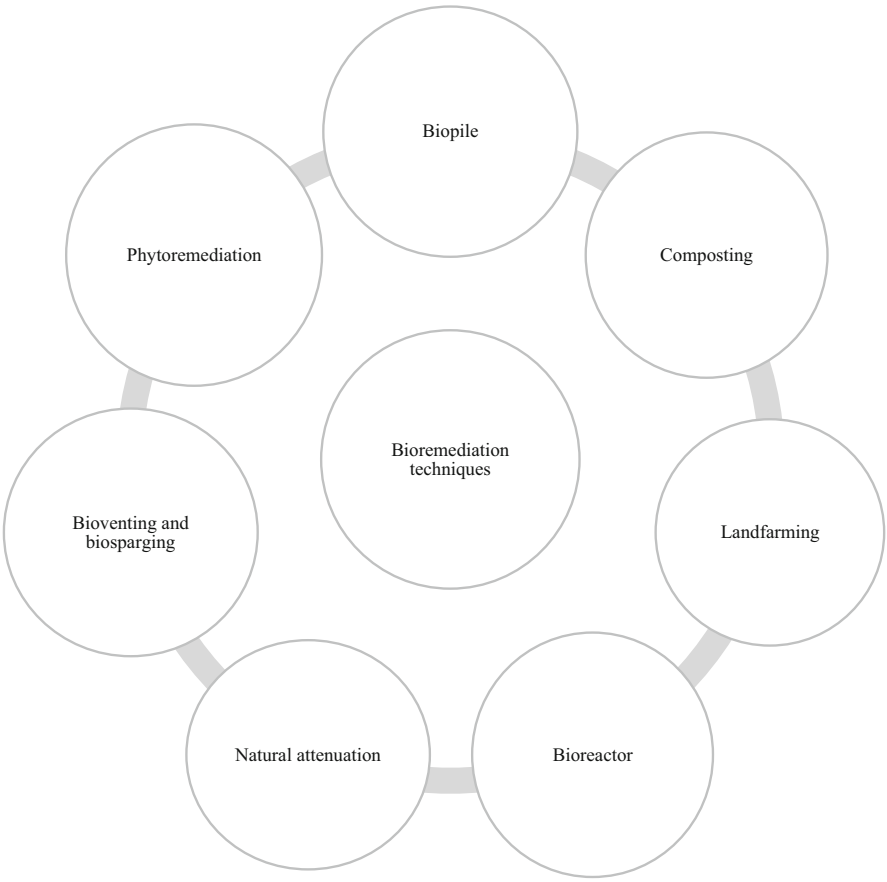


Fig. 22.5 Bioremediation strategies used in polluted environments (Gaur et al. 2018)

These strategies are classified into three groups: In situ, prepared bed/on-site (ex situ), and bioreactor (Wilson and Jones 1993). In situ-bioremediation is a simple, economical, highly efficient technique and without any secondary waste production. In this process, degrading organic pollutants and producing inorganic compounds such as methane and carbon dioxide contamination are treated in place and without excavation and transport (Farhadian et al. 2008; Wilson and Jones 1993). In contrast, ex-situ bioremediation is a costly and challenging technique that requires transportation of contaminated soil or water and can be applied in severe pollution (Tomei and Daugulis 2013).

Natural attenuation is an intrinsic bioremediation process in which diminution of pollutant adverse effects can occur with both physical or biological methods such as biodegradation by natural microorganisms, volatilization, chemical conversion, dispersion, precipitation, sorption, stabilization of contaminants, and dilution (Scow and Hicks 2005).

Bioventing is another technique of the in situ bioremediation techniques that used to aerate the polluted sites to promote microbial eradication of organic compounds. In addition to the oxygenation of the vadose zone, this process involves adding nutrients and moisture to contaminated sites for improvement of indigenous microbial activity. Biosparging is similar to bioventing with this exception that air injection is performed at the saturated area. As a result, volatile organic compounds migrate upward to the unsaturated region and undergo biodegradation (Azubuike et al. 2016).

Phytoremediation is a bioremediation technique that can be applied in large scales and is used for improving soil fertility. In this process, plants are used instead of microorganisms for the treatment of contaminated environments. There are several types of phytoremediation in which rhizofiltration, phytovolatilization, phytoextraction, and phytostabilization are remarkable (Sruthi et al. 2017).

22.9 Microbial Degradation of Organic Pollutants in Mangrove Habitats

Persistent organic pollutants (POPs) are hydrophobic compounds that accumulate in fatty tissues of vertebrates and induce cell apoptosis by producing reactive oxygen species (ROS). These compounds include dioxins, polychlorinated biphenyls (PCB), organochlorine pesticides (OCPs), PAHs, and dibenzofurans and have anthropogenic and natural sources (Gaur et al. 2018). According to the Agency for Toxic Substances and Disease Registry (ATSDR) report, PAH and PCB are, respectively, in the ninth and fifth ranks of 2017 priority list of hazardous substances, which includes metal/metalloid pollutants (Agency for Toxic Substances and Disease Registry 2017, Priority List of Hazardous Substances https://www.atsdr.cdc.gov/SPL). The amount of anthropogenic activity for PAH production in the USA, Sweden, and Norway is 9406 metric tons/year, according to Chan et al. (2006) (Chan et al. 2006). These compounds are composed of two or more attached benzene groups, and as the number of aromatic rings elevates, its carcinogenic effects increase (Ghosal et al. 2016). The remediation strategy must be employed because of the various adverse effects of contaminants such as genotoxicity, mutagenicity, and toxicity on the human health and ecosystem. Some of the microbial enzymes that take part in this process include oxygenases, peroxidases, reductases, hydroxylases, and dehydrogenases. alkA (alkane monooxygenase), alkM (alkane monooxygenase), alkB (alkane monooxygenase), ladA (alkane monooxygenase), assA1,2 (alkylsuccinate synthase alpha-subunit A), nahA-M (Naphthalene dioxygenase reductase), napA (Nitrate reductase), amoA (Ammonia mono oxygenase), dsrAB (Dissimilatory sulfate reductase), and mcrA (A-subunit of Methyl –coenzyme M reductase) are the central genes involved in biodegradation of organic pollutants (Varjani et al. 2017). Table 22.3 listed different enzymes involved in the microbial degradation of the hydrocarbon compounds.

Pure culture of bacteria may degrade few hydrocarbons, while microbial consortia may be capable of eradicating a wide range of contaminants because of synergism observed between its microorganisms (Cerniglia and Sutherland 2010; Uad et al.

Table 22.3 Microbial enzymes identified for degrading hydrocarbon compounds

Enzyme	Name of microorganism	Petroleum hydrocarbon/pollutant compound	References
Dioxygenases	*Acinetobacter sp.*	C10-C30 alkanes	Abbasian et al. (2015)
Bacterial P450 oxygenase system (CY153)	*Acinetobacter, Caulobacter Mycobacterium*	C5-C16 alkanes, cycloalkanes	Abbasian et al. (2015)
Eukaryotic P450 (CYP52)	*Candida maltose, Candida tropicalis, Yarrowia lipolytica*	C10-C16 alkanes, fatty acids	Abbasian et al. (2015), Salleh et al. (2003)
AlkB related alkane hydroxylases	*Pseudomonas, Burkholderia, Rhodococcus, Mycobacterium*	C5-C16 alkanes, alkyl benzenes, Cycloalkanes, fatty acids	Abbasian et al. (2015)
Monooxygenases	*Oxyfera*		Abbasian et al. (2015)
Soluble/ particulate methane	*Methylocystis, Methylomonas, Methylocella, Methylobacter, Methylococcus, Geobacillus thermodenitrificans, Methylomirabilis Oxyfera*	C1-C8 alkanes, C1-C5 (halogenated) Alkanes, alkenes, cycloalkanes	Abbasian et al. (2015), McDonald et al. (2006)

2010; Varjani 2017; Kumar et al. 2018). The first step of the relation between oil contaminants and the microbial community includes direct interaction between them (Souza et al. 2018) and it eventuates on the cell wall structure and its hydrophobicity. Hydrophobicity and surfactant activity favor interaction between microorganisms and hydrophobic substrate (Kavitha et al. 2014). Microorganisms having ability in degradation of oil with biosurfactant generation and anoxic conditions growth ability are more effectual for in situ methanogenesis in oil reservoirs (Zhao et al. 2016).

Similar to bacteria, fungi are potent organisms to possess the capability of biodegradation of persistent organic pollutants (Ramanathan et al. 2008). Mold and yeast can metabolize a variety of hydrocarbon compounds via their active enzymes (Reddy 1995). Mangrove inhabited fungi also involved in the remediation of contaminants in estuarine ecosystems that often exposed to a broad spectrum of organic contaminants.

Yeasts are the most dominant fungal taxon in contaminated ecosystems (Berdicevsky et al. 1993), and they can degrade PAH by consuming of other carbon sources. *Rhodotorula glutinis* is a yeast isolated from a hydrocarbon-polluted stream and can oxidize phenanthrene as well as the rate of degradation by *Pseudomonas aeruginosa* as a bacterium (Romero et al. 1998). Table 22.4 demonstrates some fungi species for biodegradation of petroleum compounds.

Table 22.4 Microbial species able to degrade petro-organic compounds

Target petroleum hydrocarbon/pollutant	Microbial species	References
Aliphatic hydrocarbon	*Acinetobacter sp.*	Foght (2008), Mittal and Singh (2009)
	Alcanivorax sp.	Brooijmans et al. (2009), Harayama et al. (2004)
	Azoarcus sp.	Widdel and Rabus (2001)
	Bacillus sp.	Ghazali et al. (2004)
	Brevibacterium	Leahy and Colwell (1990)
	Desulfosarcina sp.	Jaekel et al. (2013)
	Desulfococcus sp.	Jaekel et al. (2013)
	Marinobacter sp.	Yakimov et al. (2007)
	Micrococcus sp.	Ghazali et al. (2004), Roy et al. (2002)
	Ochrobactrum sp.	Varjani et al. (2015)
	Oleispira sp.	Harayama et al. (2004)
	Pseudomonas sp.	Mittal and Singh (2009), Rocha et al. (2011), Sajna et al. (2015), Varjani et al. (2015)
Aromatic hydrocarbons (poly−/mono-hydrocarbons)	*Acinetobacter sp.*	Batista et al. (2006)
	Archaeoglobus fulgidus	Wilkes et al. (2016)
	Aromatoleum aromaticum	Wilkes et al. (2016)
	Bacillus sp.	Janbandhu and Fulekar (2011)
	Halomonas sp.	Widdel and Rabus (2001)
	Pseudomonas sp.	Meckenstock et al. (2016), Mittal and Singh (2009)
	Rhodococcus sp.	Leahy and Colwell (1990), Salleh et al. (2003)
	Achromobacter insolitus	Janbandhu and Fulekar (2011)
	Bacillus sp.	Mittal and Singh (2009)
	Cycloclasticus sp.	Harayama et al. (2004)
	Phanerochaete chrysosporium	Salleh et al. (2003)
	Pseudomonas sp.	Meckenstock et al. (2016), Widdel and Rabus (2001)
	Vibrio sp.	Widdel and Rabus (2001)
	Penicillium janthinellum	Boonchan et al. (2000)
	Alcaligenes faecalis	Kim et al. (2009)
	Arthrobacter gandavensis	Kim et al. (2009)
	Arthrobacter sp. P1–1	Isaac et al. (2015)
	Mycobacterium fluoranthenivorans	Seo et al. (2006)
	Mycobacterium PYR-1	Hormisch et al. (2004)
	Pseudomonas fluorescens	Ramirez et al. (2001)
	Pseudomonas monteilii	Kim et al. (2009)
	Pseudomonas aeruginosa	Isaac et al. (2015)
	Ochrobactrum anthropi	Varjani et al. (2015)

(continued)

Table 22.4 (continued)

Target petroleum hydrocarbon/pollutant	Microbial species	References
	Rhodococcus wratislaviensis	Ortega-González et al. (2015))
	Sphingomonas formosensis	Isaac et al. (2015)
	Stenotrophomonas maltophilia	Lin et al. (2012)
	Anthracophyllum discolor	Acevedo et al. (2011)
	Aspergillus flavus and Paecilomyces farinosus	Romero et al. (2010)
	Aspergillus sclerotiorum	Passarini et al. (2011)
	Aspergillus terreus	Reyes-César et al. (2014)
	Byssochlamys spectabilis	Rosales et al. (2012)
	Cladophialophora psammophila	Badali et al. (2011)
	Cyclothyrium sp.	da Silva et al. (2004)
	Fusarium oxysporum	Ortega-González et al. (2015)
	Phanerochaete chrysosporium	Bhattacharya et al. (2013)
	Trichoderma asperellum	Zafra et al. (2015)
	Trichoderma longibrachiatum	Rosales et al. (2012)
Resins	*Pseudomonas sp.*	Leahy and Colwell (1990)
	Members of *Vibrionaceae* and *Enterobacteriaceae*, *Moraxella sp.*	Chandra et al. (2013)

22.10 Symbiosis Between Microbes and Mangrove Plants

Diverse groups of organisms can be associated with mangrove-specific species, like *Avicennia marina,* and help in some essential ecological processes such as N_2 fixation, organic sulfate mineralization, phosphate solubilization and providing soluble iron for these species. One of the pivotal ecological relationships is the association of N_2 fixers and mangrove roots. Bacteria and fungi can degrade biopolymers and benefit roots by changing pH, the redox potential of environments, and increasing bioavailability of nutrients. Instead, plants can provide nutrients for bacteria and fungi. Some microorganisms can produce organic acids and solubilize phosphates called phosphate solubilizing microorganisms (Alongi 2005). Because of nitrogen and phosphate limitation in mangrove ecosystems, the cooperation of N_2 fixing and phosphate solubilizing microorganisms can be crucial. Rojas et al. (2001) studied the effect of a co-culture composed of *Phyllobacterium* sp. (an N_2-fixing bacterium) and *Bacillus licheniformis* (a phosphate-solubilizing bacterium) on the development of mangrove tree leaves. The synergism observed between the two

species increased the number of leaves and nitrogen incorporation of plants (Rojas et al. 2001).

Effect of several mangrove rhizosphere bacteria and *Azospirillum* sp. on oilseed halophyte *Salicornia bigelovii* was investigated by Bashan et al. (2000). The height and dry weight of S. bigelovii increased in response to the inoculation of a mixture of two *Vibrio* strains. In addition to mentioned effects, a mixture of phosphate solubilizing bacterium (*Phyllobacterium* sp.) and N_2- fixing bacterium (*Bacillus licheniformis*) enhanced the length of spikes while inoculation of the cyanobacterium *Microcoleus chthonoplastes* decreased spike size and had no effect on plant foliage (for more details see Table 22.5) (Bashan et al. 2000).

The symbiosis between mangrove plant species and Arbuscular Mycorrhizal Fungi (AMF) is an exciting subject in Microbial ecology. AMF benefits plants by supporting growth and increasing plant biomass levels and absorption of nitrogen, phosphate, and potassium (5). In this regard, Wang et al. 2010 investigated the symbiosis between six AMF species (*Glomus* and *Acaulospora*) and *Sonneratia apetala* B. Ham (plant species). They suggested that phosphate level and hydrological conditions such as moisture content of rhizosphere soil and flooding duration are the most important abiotic factors influencing arbuscular mycorrhizal fungi colonization of mangrove plants. Survival of AMF, as aerobic microorganisms in flooded conditions (low oxygen), depends on oxygen provided by aerenchyma developed in adult mangrove species. Hence, the AMF colonization rates were increased in the dry and aerobic zones compared to wet and hypoxic regions. Furthermore, a very low or high level of phosphate limits AMF colonization to mangrove species (Wang et al. 2010).

22.11 Microbial Biodiversity in Mangrove Ecosystems

The reaction of mangrove environments to various pollutants is essential for controlling contaminants in this environment. Therefore, the study of microbial diversity of these ecosystems has involved the attention of many studies. Understanding the impacts of pollution on the microbial diversity (such as the fungi) that associated with mangrove ecosystem is of substantial importance for the maintenance of renewable resources in an effective way (Tsui et al. 1998). Microorganisms can also degrade contaminants such as PAHs or other organic pollutants from domestic effluent (Holguin et al. 2001; Jones 2000; Santos et al. 2011). Different studies accompanied by the microbial community structure of contaminated mangrove habitats (Maciel-Souza et al. 2006). Different studies investigated the microbial diversity such as bacteria (Grativol et al. 2017) and fungi (they are well known to be highly potent in the eradication of several contaminants) (D'Annibale et al. 2006).

Microorganisms with petroleum hydrocarbon metabolizing activity are broadly dispersed in the environment (Brooijmans et al. 2009; Lamichhane et al. 2016). For a better evaluating of microbial distribution and abundance in natural ecosystems such as mangrove habitats, the tools are well developed (Varjani et al. 2015).

Table 22.5 Effect of bacteria on mangrove plants growth parameters

Factors	*A. halopraeferens* AU10		*A. brasilense* strains	*Vibrio* strains	*B. licheniformis* + *Phyllobacterium* sp.	*Microcoleus chthonoplastes*
Total phosphate	+		+	+	+	−
The total lipid of seeds	−		+	−	+	+
Total N of seeds	+		+	+	+	+
Total N of plants	−		−	−	−	−
Plant height	+		+	+	+	+
Plant dry weight	+		+	+	+	+
Number of branches	+		−	+	No effect	+
Length of spikes	+		+	+	+	−

Table 22.6 Taxonomic classes on the four different microhabitats

Location	More abundant classes	Less abundant classes
Immersed *A. marina*	*Sordariomycetes Dothideomycetes*	*Leotiomycetes*
Emerged *A. marina*	*Dothideomycetes*	*Leotiomycetes*
Immersed *R. stylosa*	*Dothideomycetes*	*Leotiomycetes*
Emerged *R. stylosa*	*Lecanoromycetes Dothideomycetes*	*Leotiomycetes*

The effects of hydrocarbon pollutants on three Brazilian mangrove forests were investigated by Marcial Gomes et al. (2008). DNA was extracted from samples and 16S rDNA gene fragments denaturing gradient gel electrophoresis (DGGE) was done as a culture-independent method. Despite other natural sites that harbor *Alphaproteobacteria*, *Actinobacteria*, and *Pseudomonads* taxa as predominant groups, the dominant species of these samples like other hydrocarbon polluted sites species have belonged to *Pseudomonadales*, *Burkholderiales*, *Alteromonadales*, *Rhodocyclales*, and *Rhodobacterales* orders (Marcial Gomes et al. 2008).

Metagenomic analysis of Sundarbans mangrove (India) bacterial diversity revealed that *Proteobacteria*, *Firmicutes*, *Chloroflexi*, *Bacteroidetes*, *Acidobacteria*, *Nitrospirae*, and *Actinobacteria* are the dominant taxa of this ecosystem, respectively. Only 5% of sequences are related to a poorly characterized taxon (Basak et al. 2015).

Illumina sequencing method was employed to determine the bacterial diversity of sediments in Mai Po Ramsar mangrove wetland, Hong Kong. The results showed that *Actinobacteria*, *Verrucomicrobia*, *Acidobacteria*, and *Nitrospirae* comprised the dominant phyla in the inner sediments. *Proteobacteria* and *Defferibacteria* were prevalent in the surface sediments. In this ecosystem, *Gammaproteobacteria* and *Deltaproteobacteria* were the abundant taxa among *Proteobacteria* (Jiang et al. 2013).

Arfi et al. (2012) studied the fungal diversity of two mangrove trees (*A. marina* and *R. stylosa*) at Saint Vincent Bay, New Caledonia, by pyrosequencing method. *Ascomycota*, with 82%, was the dominant phyla, and *Basidiomycetes* comprise only 3% of the community. 15% of sequences were related to unknown taxa. *Dothideomycetes* with 25–55% were predominant on emerged and immersed surfaces of these two mangrove trees. The details are presented in Table 22.6 (Arfi et al. 2012).

Molecular tools were applied for characterization of the Cyanobacterial community of mangrove environments of south-east Brazil and showed 19 different genera of cyanobacteria and unidentified taxa. *Nostocales* and *Oscillatoriales* were dominant orders which included N2 fixing cyanobacteria such as *Anabaena*, *Brasilonema*, *Scytonema*, *Symphyonemopsis*, *Fischerella*, *Rivularia*, and *Nostoc* that highlighted the importance of nitrogen-fixing bacteria and nitrogen cycle for decreasing nitrogen limitation in ecosystems (Rigonato et al. 2012).

22.12 Biotechnological Importance of Mangrove Microorganisms

Mangroves are the desired place for isolating cellulase producing microorganisms because of the frequent amount of lignocellulosic substrate for carbon turnover in these environments (Gao et al. 2010). There are three types of cellulase, including exoglucanase (EXG), endoglucanase (EG), and β-glucosidase (BGL), which both bacteria and fungi can produce (Behera et al. 2017). Castro et al. (2014) isolated plant-associated endophytic bacteria of two mangrove environments by culture-dependent methods. *Bacillus* was the most dominant genus isolated from both environments, and the other genera include *Enterobacter*, *Pantoea*, *Brevundimonas*, *Microbacterium*, *Chryseobacterium*, *Novosphingobium*, *Xanthomonas*, *Erwinia*, *Alcaligenes*, *Ochrobactrum*, *Curtobacterium*, *Stenotrophomonas*, and *Sphingopyxis*. Amylase, protease, lipase, endoglucanase, and esterase were produced by 45%, 75%, 52.5%, 62.5%, and 17.5% of these microorganisms, respectively. The highest rate of amylolytic, estrasic, and endocellulolytic activity was observed in *Bacillus*. This finding emphasized the ability of mangrove inhabiting microorganisms for biotechnological applications (Castro et al. 2014).

In addition to bacteria isolated from mangrove ecosystems, yeasts are also capable of producing metabolites such as extracellular hydrolytic enzymes. In this regard, Jiang et al. (2016) isolated 300 yeast strains from mangrove ecosystems and screened them for inulin hydrolyzing activity. This enzyme called β-Fructofuranosidase (FFase) and has two types: extracellular and intracellular. The substrates of FFase are sucrose, raffinose, and inulin, which can be degraded to glucose and fructose. FFase has immense biotechnological applications and can be used in food and beverage, cosmetic, pharmaceutical, fermentation, and paper industries. After screening, the highest insulin-degrading activity (30.98 ± 0.8 U. ml^{-1} after 108 h) was observed in *Aureobasidium* sp. P6 strain (Jiang et al. 2016).

22.13 Heavy Metal Removal in Mangrove Sediments

Heavy metal is referred to as any metal between groups 3 and 16 (Hawkes 1997) with a specific gravity of 5 g/cm^3 or over. These elements have atomic weights between 63.5 and 200.6. Heavy metal pollutions occur by some anthropogenic activities such as paper industries, tanneries, batteries, fertilizers. These elements accumulate in living organisms and promote toxic or carcinogenic reactions. The most major heavy metals with adverse effects on the environment include Cu, Zn, Ni, Hg, Cr, Pb, and Cd (Fu and Wang 2011).

The effect of heavy metal on the microbial community composition of Xiangjiang River was investigated by Zhu et al. (2013). In this study, the microbial diversity of four samples polluted by different heavy metals analyzed by PCR-RFLP as a culture-independent method. As shown in Fig. 22.6, *Proteobacteria* (55%) was the dominant phylum in this environment. *Alphaproteobacteria*, *betaproteobacteria*, *Gammaproteobacteria*, *Deltaproteobacteria*, *Epsilonproteobacteria* comprised

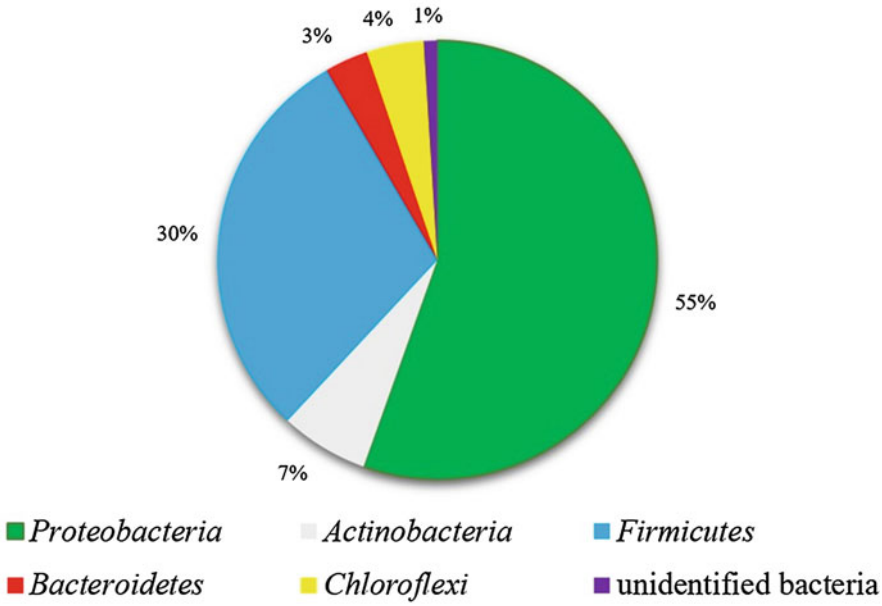


Fig. 22.6 Different operational taxonomical units (OTU) in Xiangjiang river

23.4%, 22.6%, 3.6%, 5.5%, and 0.4% of microbial diversity, respectively. As heavy metal concentration raised, the percentage of *Alphaproteobacteria* elevated (Zhu et al. 2013).

Microbial diversity of two hydrocarbon and heavy metal polluted regions of Brazil (Santos and Itanhaem estuaries) was studied by Pinto et al. (2015). Heavy metal pollutants include Cd, As, Cu, Cr, Hg, Zn, and Pb. Direct counting method applied for quantification of heterotrophic bacteria, cyanobacteria, and yeasts. Because of less pollution of Itanhaem estuary than Santos estuary, the total density of microorganisms (heterotrophic bacteria, yeasts, and cyanobacteria) of Itanhaem estuary was more. Nevertheless, the count of cyanobacteria in sediments of Santos was higher than Itanhaem estuary. It can be for the immense potential of these microorganisms in hydrocarbon biodegradation (Pinto et al. 2015).

Mallick et al. (2018) isolated *Bacillus vietnamensis* AB403 and *Kocuria flava* AB402 from the mangrove rhizosphere of Sundarbans. These halophilic strains were arsenite resistant and can eradicate arsenite from environments by biosorption to their exopolysaccharides and accumulation intracellularly. These mechanisms lead to diminished concentration of arsenite and have some impacts on plants in arsenite polluted sites such as plant growth promotion and decrease of arsenite accumulation (Mallick et al. 2018).

22.14 Conclusion

Mangroves are unique ecosystems in subtropical and tropical areas and represent significant productive habitats for many living things. Despite their great ecological, biological, and economical importance, mangroves ecosystems are exposed to many natural and human-made pollutants. In this review, we suggest that organic and inorganic pollution may be the most threatened in mangrove ecosystems. Bioremediation is an environment-friendly and economical method to reduce the toxic effect of pollutants in terrestrial and aquatic ecosystems. Microbial groups perform the central role in bioremediation. Microorganisms have evolved too many mechanisms that allow them to utilize organic pollutants as an energy source or biotransform inorganic contaminants to a less or non-toxic form. The use of prevention strategies for mangrove ecosystem protection and bioremediation of pollutants by a diverse group of microorganisms, especially in mangrove plant rhizosphere, could help to reduce the risk of mangrove extinction.

References

Abbasian F, Lockington R, Mallavarapu M, Naidu R (2015) A comprehensive review of aliphatic hydrocarbon biodegradation by bacteria. Appl Biochem Biotechnol 176:670–699

Acevedo F, Pizzul L, del Pilar Castillo M, Cuevas R, Diez MC (2011) Degradation of polycyclic aromatic hydrocarbons by the Chilean white-rot fungus *Anthracophyllum discolor*. J Hazard Mater 185:212–219

Adame M, Fry B (2016) Source and stability of soil carbon in mangrove and freshwater wetlands of the Mexican Pacific coast. Wetl Ecol Manag 24:129–137

Adame M, Hermoso V, Perhans K, Lovelock C, Herrera-Silveira J (2015) Selecting cost-effective areas for restoration of ecosystem services. Conserv Biol 29:493–502

Agency for Toxic Substances and Disease Registry (2017) Priority list of hazardous substances. https://www.atsdr.cdc.gov/SPL

Aké-Castillo JA, Vázquez G (2008) Phytoplankton variation and its relation to nutrients and allochthonous organic matter in a coastal lagoon on the Gulf of Mexico. Estuar Coast Shelf Sci 78:705–714

Al-Hashmi K, Al-Azri A, Claereboudt MR, Piontkovski S, Amin S (2013) Phytoplankton community structure of a mangrove habitat in the arid environment of Oman: the dominance of Peridinium quinquecorne. J Fish Aqua Sci 8:595–606

Alikunhi NM, Kathiresan K (2012) Phytoplankton productivity in interlinked mangroves, seagrass and coral reefs and its ecotones in gulf of Mannar biosphere reserve south East India. Mar Biol Res 8:61–73

Alongi DM (2005) Mangrove-microbe-soil relations. In: Interactions between macro- and microorganisms in marine sediments, vol 60. Wiley, New York, pp 85–103

Alongi DM (2012) Carbon sequestration in mangrove forests. Carbon Manag 3:313–322

Alongi DM (2015) The impact of climate change on mangrove forests. Curr Clim Change Rep 1:30–39

Arfi Y, Buee M, Marchand C, Levasseur A, Record E (2012) Multiple markers pyrosequencing reveals highly diverse and host-specific fungal communities on the mangrove trees a vicennia marina and R hizophora stylosa. FEMS Microbiol Ecol 79:433–444

Arumugam G, Rajendran R, Ganesan A, Sethu R (2018) Bioaccumulation and translocation of heavy metals in mangrove rhizosphere sediments to tissues of Avicenia marina–a field study from tropical mangrove forest. Environ Nanotechnol Monit Manag 10:272–279

Arumugam S, Sigamani S, Samikannu M, Perumal M (2016) Assemblages of phytoplankton diversity in different zonation of Muthupet mangroves. Reg Stud Mar Sci 3:234–241

Aziz A, Rahman M, Ahmed A (2012) Diversity, distribution and density of estuarine phytoplankton in the Sundarban mangrove forests, Bangladesh. Bangladesh J Bot 41:87–95

Azubuike CC, Chikere CB, Okpokwasili GC (2016) Bioremediation techniques–classification based on site of application: principles, advantages, limitations and prospects. World J Microbiol Biotechnol 32:180

Badali H, Prenafeta-Boldu FX, Guarro J, Klaassen CH, Meis JF, De Hoog GS (2011) Cladophialophora psammophila, a novel species of Chaetothyriales with a potential use in the bioremediation of volatile aromatic hydrocarbons. Fungal Biol 115:1019–1029

Ball MC (2002) Interactive effects of salinity and irradiance on growth: implications for mangrove forest structure along salinity gradients. Trees 16:126–139

Barasarathi J, Agamuthu P, Emenike C, Fauziah S (2014) Microplastic abundance in selected mangrove forest in Malaysia. In: Proceeding of the ASEAN Conference on Science and Technology, pp. 1–5

Barbier EB, Hacker SD, Kennedy C, Koch EW, Stier AC, Silliman BR (2011) The value of estuarine and coastal ecosystem services. Ecol Monogr 81:169–193

Basak P, Pramanik A, Roy R, Chattopadhyay D, Bhattacharyya M (2015) Cataloguing the bacterial diversity of the Sundarbans mangrove, India in the light of metagenomics. Genom Data 4:90–92

Bashan Y, Moreno M, Troyo E (2000) Growth promotion of the seawater-irrigated oilseed halophyte Salicornia bigelovii inoculated with mangrove rhizosphere bacteria and halotolerant Azospirillum spp. Biol Fertil Soils 32:265–272

Batista S, Mounteer A, Amorim F, Totola M (2006) Isolation and characterization of biosurfactant/bioemulsifier-producing bacteria from petroleum contaminated sites. Bioresour Technol 97:868–875

Behera B, Sethi B, Mishra R, Dutta S, Thatoi H (2017) Microbial cellulases–diversity & biotechnology with reference to mangrove environment: a review. J Genet Eng Biotechnol 15:197–210

Berdicevsky I, Duek L, Merzbach D, Yannai S (1993) Susceptibility of different yeast species to environmental toxic metals. Environ Pollut 80:41–44

Bhattacharya SS, Syed K, Shann J, Yadav JS (2013) A novel P450-initiated biphasic process for sustainable biodegradation of benzo [a] pyrene in soil under nutrient-sufficient conditions by the white rot fungus Phanerochaete chrysosporium. J Hazard Mater 261:675–683

Bhowmik AK, Cabral P (2013) Cyclone Sidr impacts on the Sundarbans floristic diversity. J Earth Sci 2:62

Biswas SR, Mallik AU, Choudhury JK, Nishat A (2009) A unified framework for the restoration of southeast Asian mangroves—bridging ecology, society and economics. Wetl Ecol Manag 17:365–383

Bodin N, Ka RG, Le Loc'h F, Raffray J, Budzinski H, Peluhet L, de Morais LT (2011) Are exploited mangrove molluscs exposed to persistent organic pollutant contamination in Senegal, West Africa? Chemosphere 84:318–327

Boonchan S, Britz ML, Stanley GA (2000) Degradation and mineralization of high-molecular-weight polycyclic aromatic hydrocarbons by defined fungal-bacterial cocultures. Appl Environ Microbiol 66:1007–1019

Brooijmans RJ, Pastink MI, Siezen RJ (2009) Hydrocarbon-degrading bacteria: the oil-spill clean-up crew. Microb Biotechnol 2:587–594

Canini ND, Metillo EB, Azanza RV (2013) Monsoon-influenced phytoplankton community structure in a Philippine mangrove estuary. Trop Ecol 54:331–343

Castro RA et al (2014) Isolation and enzyme bioprospection of endophytic bacteria associated with plants of Brazilian mangrove ecosystem. Springer Plus 3:382

Cerniglia C, Sutherland J (2010) Degradation of polycyclic aromatic hydrocarbons by fungi. In: Handbook of hydrocarbon and lipid microbiology. Springer, Berlin, pp 2079–2110

Chan SMN, Luan T, Wong MH, Tam NFY (2006) Removal and biodegradation of polycyclic aromatic hydrocarbons by Selenastrum capricornutum. Environ Toxicol 25:1772–1779

Chandra S, Sharma R, Singh K, Sharma A (2013) Application of bioremediation technology in the environment contaminated with petroleum hydrocarbon. Ann Microbiol 63:417–431
Chen L, Wang W, Zhang Y, Lin G (2009) Recent progresses in mangrove conservation, restoration and research in China. Plant Ecol 2:45–54
Chen M, Shih K, Hu M, Li F, Liu C, Wu W, Tong H (2012) Biostimulation of indigenous microbial communities for anaerobic transformation of pentachlorophenol in paddy soils of southern China. J Agric Food Chem 60:2967–2975
Choudhury AK, Das M, Philip P, Bhadury P (2015) An assessment of the implications of seasonal precipitation and anthropogenic influences on a mangrove ecosystem using phytoplankton as proxies. Estuaries Coast 38:854–872
da Silva M, Esposito E, Moody JD, Canhos VP, Cerniglia CE (2004) Metabolism of aromatic hydrocarbons by the filamentous fungus Cyclothyrium sp. Chemosphere 57:943–952
Dadashi M, Ghaffari S, Bakhtiari AR, Tauler R (2018) Multivariate curve resolution of organic pollution patterns in mangrove forest sediment from Qeshm Island and Khamir port-Persian gulf, Iran. Environ Sci Pollut Res 25:723–735. https://doi.org/10.1007/s11356-017-0450-z
Dahdouh-Guebas F, Jayatissa LP, Di Nitto D, Bosire JO, Seen DL, Koedam N (2005) How effective were mangroves as a defence against the recent tsunami? Curr Biol 15:R443–R447
D'Annibale A, Rosetto F, Leonardi V, Federici F, Petruccioli M (2006) Role of autochthonous filamentous fungi in bioremediation of a soil historically contaminated with aromatic hydrocarbons. Appl Environ Microbiol 72:28–36
Donato DC, Kauffman JB, Murdiyarso D, Kurnianto S, Stidham M, Kanninen M (2011) Mangroves among the most carbon-rich forests in the tropics. Nat Geosci 4:293
Duke NC (2016) Oil spill impacts on mangroves: recommendations for operational planning and action based on a global review. Mar Pollut Bull 109(2):700–715
Duke NC et al (2007) A world without mangroves? Science 317:41–42
Ellison JC (2000) How South Pacific mangroves may respond to predicted climate change and sea-level rise. In: Climate change in the South Pacific: impacts and responses in Australia, New Zealand, and small island states, vol 2. Springer, Dordrecht, pp 289–300
Ellison JC (2019) Biogeomorphology of mangroves. In: Coastal wetlands. Elsevier, Amsterdam, pp 687–715
Eslami-Andargoli L, Dale P, Sipe N, Chaseling J (2009) Mangrove expansion and rainfall patterns in Moreton Bay, Southeast Queensland, Australia. Estuar Coast Shelf Sci 85:292–298
Farhadian M, Vachelard C, Duchez D, Larroche C (2008) In situ bioremediation of monoaromatic pollutants in groundwater: a review. Bioresour Technol 99:5296–5308
Feng J, Zhu X, Wu H, Ning C, Lin G (2017) Distribution and ecological risk assessment of heavy metals in surface sediments of a typical restored mangrove–aquaculture wetland in Shenzhen, China. Mar Pollut Bull 124:1033–1039
Field CD (1996) Restoration of mangrove ecosystems. International Society for Mangrove Ecosystems, Okinawa, Japan
Foght J (2008) Anaerobic biodegradation of aromatic hydrocarbons: pathways and prospects. J Mol Microbiol Biotechnol 15:93–120
Fu F, Wang Q (2011) Removal of heavy metal ions from wastewaters: a review. J Environ Manag 92:407–418
Galeano A, Urrego LE, Botero V, Bernal G (2017) Mangrove resilience to climate extreme events in a Colombian Caribbean Island. Wetl Ecol Manag 25:743–760
Gao Y, Sun L, Wu C, Chen Y, Xu H, Chen C, Lin G (2018) Inter-annual and seasonal variations of phytoplankton community and its relation to water pollution in Futian mangrove of Shenzhen, China. Cont Shelf Res 166:138–147
Gao Z, Ruan L, Chen X, Zhang Y, Xu X (2010) A novel salt-tolerant endo-β-1, 4-glucanase Cel5A in Vibrio sp. G21 isolated from mangrove soil. Appl Microbiol Biotechnol 87:1373–1382
Gaur N, Narasimhulu K, PydiSetty Y (2018) Recent advances in the bio-remediation of persistent organic pollutants and its effect on environment. J Clean Prod 198:1602–1631

Ghazali FM, Rahman RNZA, Salleh AB, Basri M (2004) Biodegradation of hydrocarbons in soil by microbial consortium. Int Biodeterior Biodegradation 54:61–67
Ghizelini AM et al (2019) Fungal communities in oil contaminated mangrove sediments–who is in the mud? Mar Pollut Bull 139:181–188
Ghosal D, Ghosh S, Dutta TK, Ahn Y (2016) Current state of knowledge in microbial degradation of polycyclic aromatic hydrocarbons (PAHs): a review. Front Microbiol 7:1369
Gilman EL, Ellison J, Duke NC, Field C (2008) Threats to mangroves from climate change and adaptation options: a review. Aquat Bot 89:237–250
Giri C et al (2011) Status and distribution of mangrove forests of the world using earth observation satellite data. Glob Ecol Biogeogr 20:154–159
Grativol AD, Marchetti AA, Wetler-Tonini RM, Venancio TM, Gatts CE, Thompson FL, Rezende CE (2017) Bacterial interactions and implications for oil biodegradation process in mangrove sediments. Mar Pollut Bull 118:221–228
Hamdan O, Khali Aziz H, Shamsudin I, Raja Barizan R (2012) Status of mangroves in Peninsular Malaysia. Forest Research Institute Malaysia, Malaysia, Kepong
Harayama S, Kasai Y, Hara A (2004) Microbial communities in oil-contaminated seawater. Curr Opin Biotechnol 15:205–214
Hawkes SJ (1997) What is a "heavy metal"? J Chem Educ 74:1374
Herrero M, Stuckey D (2015) Bioaugmentation and its application in wastewater treatment: a review. Chemosphere 140:119–128
Hill NA, Simpson SL, Johnston EL (2013) Beyond the bed: effects of metal contamination on recruitment to bedded sediments and overlying substrata. Environ Pollut 173:182–191
Hogarth PJ (1999) The biology of mangroves. Oxford University Press (OUP), New York
Holguin G, Vazquez P, Bashan Y (2001) The role of sediment microorganisms in the productivity, conservation, and rehabilitation of mangrove ecosystems: an overview. Biol Fertil Soils 33:265–278
Hormisch D et al (2004) Mycobacterium fluoranthenivorans sp. nov., a fluoranthene and aflatoxin B1 degrading bacterium from contaminated soil of a former coal gas plant. Syst Appl Microbiol 27:653–660
Ingole B, Sivadas S, Nanajkar M, Sautya S, Nag A (2009) A comparative study of macrobenthic community from harbours along the central west coast of India. J Environ Monit 154:135
Isaac P, Martínez FL, Bourguignon N, Sánchez LA, Ferrero MA (2015) Improved PAHs removal performance by a defined bacterial consortium of indigenous Pseudomonas and actinobacteria from Patagonia, Argentina. Int Biodeterior Biodegradation 101:23–31
Ishtiaque A, Myint SW, Wang C (2016) Examining the ecosystem health and sustainability of the world's largest mangrove forest using multi-temporal MODIS products. Sci Total Environ 569:1241–1254
Jaekel U, Musat N, Adam B, Kuypers M, Grundmann O, Musat F (2013) Anaerobic degradation of propane and butane by sulfate-reducing bacteria enriched from marine hydrocarbon cold seeps. ISME J 7:885
Jafarabadi AR, Bakhtiari AR, Aliabadian M, Laetitia H, Toosi AS, Yap CK (2018a) First report of bioaccumulation and bioconcentration of aliphatic hydrocarbons (AHs) and persistent organic pollutants (PAHs, PCBs and PCNs) and their effects on alcyonacea and scleractinian corals and their endosymbiotic algae from the Persian Gulf, Iran: inter and intra-species differences. Sci Total Environ 627:141–157
Jafarabadi AR, Bakhtiari AR, Aliabadian M, Toosi AS (2017a) Spatial distribution and composition of aliphatic hydrocarbons, polycyclic aromatic hydrocarbons and hopanes in superficial sediments of the coral reefs of the Persian Gulf, Iran. Environ Pollut 224:195–223
Jafarabadi AR, Bakhtiari AR, Hedouin L, Toosi AS, Cappello T (2018b) Spatio-temporal variability, distribution and sources of n-alkanes and polycyclic aromatic hydrocarbons in reef surface sediments of Kharg and lark coral reefs, Persian gulf, Iran. Ecotoxicol Environ Saf 163:307–322

Jafarabadi AR, Bakhtiari AR, Mitra S, Maisano M, Cappello T, Jadot C (2019a) First polychlorinated biphenyls (PCBs) monitoring in seawater, surface sediments and marine fish communities of the Persian Gulf: distribution, levels, congener profile and health risk assessment. Environ Pollut 253:78–88

Jafarabadi AR, Bakhtiari AR, Toosi AS (2017b) Comprehensive and comparative ecotoxicological and human risk assessment of polycyclic aromatic hydrocarbons (PAHs) in reef surface sediments and coastal seawaters of Iranian Coral Islands, Persian gulf. Ecotoxicol Environ Saf 145:640–652

Jafarabadi AR, Bakhtiari AR, Yaghoobi Z, Yap CK, Maisano M, Cappello T (2019b) Distributions and compositional patterns of polycyclic aromatic hydrocarbons (PAHs) and their derivatives in three edible fishes from Kharg coral island, Persian gulf, Iran. Chemosphere 215:835–845

Jafarabadi AR, Bakhtiyari AR, Toosi AS, Jadot C (2017c) Spatial distribution, ecological and health risk assessment of heavy metals in marine surface sediments and coastal seawaters of fringing coral reefs of the Persian Gulf, Iran. Chemosphere 185:1090–1111

Jafarabadi AR, Dashtbozorg M, Bakhtiari AR, Maisano M, Cappello T (2019c) Geochemical imprints of occurrence, vertical distribution and sources of aliphatic hydrocarbons, aliphatic ketones, hopanes and steranes in sediment cores from ten Iranian Coral Islands, Persian gulf. Mar Pollut Bull 144:287–298

Janbandhu A, Fulekar MH (2011) Biodegradation of phenanthrene using adapted microbial consortium isolated from petrochemical contaminated environment. J Hazard Mater 187:333–340

Jayanthi M, Thirumurthy S, Nagaraj G, Muralidhar M, Ravichandran P (2018) Spatial and temporal changes in mangrove cover across the protected and unprotected forests of India. Estuar Coast Shelf Sci 213:81–91

Jiang H, Ma Y, Chi Z, Liu G-L, Chi Z-M (2016) Production, purification, and gene cloning of a β-fructofuranosidase with a high inulin-hydrolyzing activity produced by a novel yeast Aureobasidium sp. P6 isolated from a mangrove ecosystem. Mar Biotechnol 18:500–510

Jiang X-T, Peng X, Deng G-H, Sheng H-F, Wang Y, Zhou H-W, Tam NF-Y (2013) Illumina sequencing of 16S rRNA tag revealed spatial variations of bacterial communities in a mangrove wetland. Microb Ecol 66:96–104

Jones EG (2000) Marine fungi: some factors influencing biodiversity. Fungal Divers 4:53–73

Jusoff K, Taha D (2008) Managing sustainable mangrove forests in peninsular Malaysia. J Sustain Dev 1:88–96

Kannan L, Vasantha K (1992) Microphytoplankton of the Pitchavaram mangals, southeast coast of India: species composition and population density. In: The ecology of mangrove and related ecosystems. Springer, Cham, pp 77–86

Kauffman JB, Cole TG (2010) Micronesian mangrove forest structure and tree responses to a severe typhoon. Wetlands 30:1077–1084

Kavitha V, Mandal AB, Gnanamani A (2014) Microbial biosurfactant mediated removal and/or solubilization of crude oil contamination from soil and aqueous phase: an approach with Bacillus licheniformis MTCC 5514. Int Biodeterior Biodegradation 94:24–30

Kehrig H, Pinto F, Moreira I, Malm O (2003) Heavy metals and methylmercury in a tropical coastal estuary and a mangrove in Brazil. Org Geochem 34:661–669

Kim YM, Ahn CK, Woo SH, Jung GY, Park JM (2009) Synergic degradation of phenanthrene by consortia of newly isolated bacterial strains. J Biotechnol 144:293–298

Kumar V, Kumar M, Prasad R (2018) Microbial action on hydrocarbons. Springer, Singapore

Lamichhane S, Krishna KB, Sarukkalige R (2016) Polycyclic aromatic hydrocarbons (PAHs) removal by sorption: a review. Chemosphere 148:336–353

Larsson J, Folke C, Kautsky N (1994) Ecological limitations and appropriation of ecosystem support by shrimp farming in Colombia. Environ Manag 18(5):663–676

Leahy JG, Colwell RR (1990) Microbial degradation of hydrocarbons in the environment. Microbial Mol Biol Rev 54:305–315

Lee S (2016) From blue to black: anthropogenic forcing of carbon and nitrogen influx to mangrove-lined estuaries in the South China Sea. Mar Pollut Bull 109:682–690

Li R, Li R, Chai M, Shen X, Xu H, Qiu G (2015) Heavy metal contamination and ecological risk in Futian mangrove forest sediment in Shenzhen Bay, South China. Mar Pollut Bull 101:448–456
Li R, Zhang L, Xue B, Wang Y (2019) Abundance and characteristics of microplastics in the mangrove sediment of the semi-enclosed Maowei Sea of the South China Sea: new implications for location, rhizosphere, and sediment compositions. Environ Pollut 244:685–692
Lima A, Costa M, Barletta M (2014) Distribution patterns of microplastics within the plankton of a tropical estuary. Environ Res 132:146–155
Lin S-Y et al (2012) Sphingomonas formosensis sp. nov., a polycyclic aromatic hydrocarbon-degrading bacterium isolated from agricultural soil. Int J Syst Evol Microbiol 62:1581–1586
Little DI, Holtzmann K, Gundlach ER, Galperin Y (2018) Sediment hydrocarbons in former mangrove areas, southern Ogoniland, Eastern Niger Delta, Nigeria. In: Threats to mangrove forests. Springer, Cham, pp 323–342
Liu S-H et al (2017) Bioremediation mechanisms of combined pollution of PAHs and heavy metals by bacteria and fungi: a mini review. Bioresour Technol 224:25–33
Lotfinasabasl S, Gunale V, Khosroshahi M (2018) Applying geographic information systems and remote sensing for water quality assessment of mangrove forest. Acta Ecol Sin 38:135–143
Lourenço PM, Serra-Gonçalves C, Ferreira JL, Catry T, Granadeiro JP (2017) Plastic and other microfibers in sediments, macroinvertebrates and shorebirds from three intertidal wetlands of southern Europe and West Africa. Environ Pollut 231:123–133
Lovelock CE, Ruess RW, Feller IC (2011) CO_2 efflux from cleared mangrove peat. PLoS One 6: e21279
MacFarlane G, Pulkownik A, Burchett M (2003) Accumulation and distribution of heavy metals in the grey mangrove, Avicennia marina (Forsk.) Vierh.: biological indication potential. Environ Pollut 123:139–151
Maciel-Souza MC, Macrae A, Volpon AGT, Ferreira PS, Mendonça-Hagler LC (2006) Chemical and microbiological characterization of mangrove sediments after a large oil-spill in Guanabara Bay-RJ-Brazil. Braz J Microbiol 37:262–266
Mallick I, Bhattacharyya C, Mukherji S, Dey D, Sarkar SC, Mukhopadhyay UK, Ghosh A (2018) Effective rhizoinoculation and biofilm formation by arsenic immobilizing halophilic plant growth promoting bacteria (PGPB) isolated from mangrove rhizosphere: a step towards arsenic rhizoremediation. Sci Total Environ 610:1239–1250
Manna S, Chaudhuri K, Sarma KS, Naskar P, Bhattacharyya S, Bhattacharyya M (2012) Interplay of physical, chemical and biological components in estuarine ecosystem with special reference to Sundarbans, India. In: Voudouris K (ed) Ecological water quality - water treatment and reuse. InTech Open, New York, pp 205–238. https://doi.org/10.5772/32110
Marchand C, Lallier-Vergès E, Baltzer F, Albéric P, Cossa D, Baillif P (2006) Heavy metals distribution in mangrove sediments along the mobile coastline of French Guiana. Mar Chem 98:1–17
Marcial Gomes NC, Borges LR, Paranhos R, Pinto FN, Mendonça-Hagler LC, Smalla K (2008) Exploring the diversity of bacterial communities in sediments of urban mangrove forests. FEMS Microbiol Ecol 66:96–109
Martin C, Almahasheer H, Duarte CM (2019) Mangrove forests as traps for marine litter. Environ Pollut 247:499–508
McDonald IR, Miguez CB, Rogge G, Bourque D, Wendlandt KD, Groleau D, Murrell JC (2006) Diversity of soluble methane monooxygenase-containing methanotrophs isolated from polluted environments. FEMS Microbiol Lett 255:225–232
Meckenstock RU et al (2016) Anaerobic degradation of benzene and polycyclic aromatic hydrocarbons. J Mol Microbiol Biotechnol 26:92–118
Mitsch WJ, Bernal B, Hernandez ME (2015) Ecosystem services of wetlands. Taylor & Francis, London
Mittal A, Singh P (2009) Isolation of hydrocarbon degrading bacteria from soils contaminated with crude oil spills. CSIR, New Delhi

Moreira IT et al (2013) Phytoremediation in mangrove sediments impacted by persistent total petroleum hydrocarbons (TPH's) using Avicennia schaueriana. Mar Pollut Bull 67:130–136
Mukherjee N, Sutherland WJ, Dicks L, Huge J, Koedam N, Dahdouh-Guebas F (2014) Ecosystem service valuations of mangrove ecosystems to inform decision making and future valuation exercises. PLoS One 9:e107706
Mwashote B, Ohowa B, Wawiye P (2005) Spatial and temporal distribution of dissolved inorganic nutrients and phytoplankton in Mida Creek, Kenya. Wetl Ecol Manag 13:599–614
Nagelkerken I, Cv R, Van Der Velde G, Dorenbosch M, Van Riel M, de la Moriniere EC, Nienhuis P (2002) How important are mangroves and seagrass beds for coral-reef fish? The nursery hypothesis tested on an island scale. Mar Ecol Prog Ser 244:299–305
Naji A, Esmaili Z, Khan FR (2017) Plastic debris and microplastics along the beaches of the strait of Hormuz, Persian gulf. Mar Pollut Bull 114:1057–1062
Nath B, Birch G, Chaudhuri P (2013) Trace metal biogeochemistry in mangrove ecosystems: a comparative assessment of acidified (by acid sulfate soils) and non-acidified sites. Sci Total Environ 463:667–674
Nitto DD, Neukermans G, Koedam N, Defever H, Pattyn F, Kairo JG, Dahdouh-Guebas F (2014) Mangroves facing climate change: landward migration potential in response to projected scenarios of sea level rise. Biogeosciences 11:857–871
Nor NHM, Obbard JP (2014) Microplastics in Singapore's coastal mangrove ecosystems. Mar Pollut Bull 79:278–283
Onyena AP, Sam K (2020) A review of the threat of oil exploitation to mangrove ecosystem: Insights from Niger Delta, Nigeria. Glob Ecol Conserv 22:e00961
Ortega-González DK, Cristiani-Urbina E, Flores-Ortíz CM, Cruz-Maya JA, Cancino-Díaz JC, Jan-Roblero J (2015) Evaluation of the removal of pyrene and fluoranthene by Ochrobactrum anthropi, Fusarium sp. and their coculture. Appl Biochem Biotechnol 175:1123–1138
Ouyang X, Guo F (2016) Paradigms of mangroves in treatment of anthropogenic wastewater pollution. Sci Total Environ 544:971–979
Owens J, Sykes R (2005) The international petroleum industry environmental conservation association social responsibility working group and human rights. Int Soc Sci J 57:131–141
Passarini MR, Rodrigues MV, da Silva M, Sette LD (2011) Marine-derived filamentous fungi and their potential application for polycyclic aromatic hydrocarbon bioremediation. Mar Pollut Bull 62:364–370
Paz-Alberto AM, Celestino AB, Sigua GC (2014) Phytoremediation of Pb in the sediment of a mangrove ecosystem. J Soils Sediments 14:251–258
Pinto AB, Pagnocca FC, Pinheiro MAA, Fontes RFC, de Oliveira AJFC (2015) Heavy metals and TPH effects on microbial abundance and diversity in two estuarine areas of the southern-central coast of São Paulo state, Brazil. Mar Pollut Bull 96:410–417
Polidoro BA, Carpenter KE, Dahdouh-Guebas F, Ellison JC, Koedam NE, Yong JW (2014) Global patterns of mangrove extinction risk: implications for ecosystem services and biodiversity loss. J Coast Conserv 19:15
Qiu Y-W, Yu K-F, Zhang G, Wang W-X (2011) Accumulation and partitioning of seven trace metals in mangroves and sediment cores from three estuarine wetlands of Hainan Island, China. J Hazard Mater 190:631–638
Ramanathan A et al (2008) A study of microbial diversity and its interaction with nutrients in the sediments of Sundarban mangroves. Indian J Mar Sci 37(2):159–165
Ramirez N, Cutright T, Ju L-K (2001) Pyrene biodegradatin in aqueous solutions and soil slurries by Mycobacterium PYR-1 and enriched consortium. Chemosphere 44:1079–1086
Reddy CA (1995) The potential for white-rot fungi in the treatment of pollutants. Curr Opin Biotechnol 6:320–328
Reyes-César A, Absalón ÁE, Fernández FJ, González JM, Cortés-Espinosa DV (2014) Biodegradation of a mixture of PAHs by non-ligninolytic fungal strains isolated from crude oil-contaminated soil. World J Microbiol Biotechnol 30:999–1009

Rigonato J, Alvarenga DO, Andreote FD, Dias ACF, Melo IS, Kent A, Fiore MF (2012) Cyanobacterial diversity in the phyllosphere of a mangrove forest. FEMS Microbiol Ecol 80:312–322

Rocha CA, Pedregosa AM, Laborda F (2011) Biosurfactant-mediated biodegradation of straight and methyl-branched alkanes by Pseudomonas aeruginosa ATCC 55925. AMB Express 1:9

Rojas A, Holguin G, Glick BR, Bashan Y (2001) Synergism between Phyllobacterium sp.(N2-fixer) and Bacillus licheniformis (P-solubilizer), both from a semiarid mangrove rhizosphere. FEMS Microbiol Ecol 35:181–187

Romero M, Cazau M, Giorgieri S, Arambarri A (1998) Phenanthrene degradation by microorganisms isolated from a contaminated stream. Environ Pollut 101:355–359

Romero MC, Urrutia MI, Reinoso HE, Kiernan MM (2010) Benzo [a] pyrene degradation by soil filamentous fungi. J Yeast Fungal Res 1:025–029

Rönnbäck P (1999) The ecological basis for economic value of seafood production supported by mangrove ecosystems. Ecol Econ 29:235–252

Rosales E, Pérez-Paz A, Vázquez X, Pazos M, Sanromán M (2012) Isolation of novel benzo [a] anthracene-degrading microorganisms and continuous bioremediation in an expanded-bed bioreactor bioprocess. Biosyst Eng 35:851–855

Roy S, Hens D, Biswas D, Biswas D, Kumar R (2002) Survey of petroleum-degrading bacteria in coastal waters of Sunderban biosphere reserve. World J Microbiol Biotechnol 18:575–581

Saenger P (2013) Mangrove ecology, silviculture and conservation. Springer, Cham

Sajna KV, Sukumaran RK, Gottumukkala LD, Pandey A (2015) Crude oil biodegradation aided by biosurfactants from Pseudozyma sp. NII 08165 or its culture broth. Bioresour Technol 191:133–139

Salem ME, Mercer DE (2012) The economic value of mangroves: a meta-analysis. Sustainability 4:359–383

Salleh AB, Ghazali FM, Rahman RNZA, Basri M (2003) Bioremediation of petroleum hydrocarbon pollution. Indian J Biotechnol 2:411–425

Sam K, Zabbey N (2018) Contaminated land and wetland remediation in Nigeria: opportunities for sustainable livelihood creation. Sci Total Environ 639:1560–1573

Sandilyan S, Kathiresan K (2012) Mangrove conservation: a global perspective. Biodivers Conserv 21:3523–3542

Santos HF, Carmo FL, Paes JE, Rosado AS, Peixoto RS (2011) Bioremediation of mangroves impacted by petroleum. Water Air Soil Pollut 216:329–350

Sarika P, Chandramohanakumar N (2008) Geochemistry of heavy metals in the surficial sediments of mangroves of the south west coast of India. Chem Ecol 24:437–447

Sathicq MB, Gómez N, Bauer DE, Donadelli J (2017) Use of phytoplankton assemblages to assess the quality of coastal waters of a transitional ecosystem: Río de la Plata estuary. Cont Shelf Res 150:10–17

Scow KM, Hicks KA (2005) Natural attenuation and enhanced bioremediation of organic contaminants in groundwater. Curr Opin Biotechnol 16:246–253

Seo J-S, Keum Y-S, Hu Y, Lee S-E, Li QX (2006) Phenanthrene degradation in Arthrobacter sp. P1-1: initial 1, 2-, 3, 4-and 9, 10-dioxygenation, and meta-and ortho-cleavages of naphthalene-1, 2-diol after its formation from naphthalene-1, 2-dicarboxylic acid and hydroxyl naphthoic acids. Chemosphere 65:2388–2394

Snedaker SC, Saenger P (1993) Pantropical trends in mangrove above-ground biomass and annual litterfall. Oecologia 96:293–299

Souza MR, Santos E, Suzarte JS, Carmo LO, Frena M, Damasceno FC, Alexandre MR (2018) Concentration, distribution and source apportionment of polycyclic aromatic hydrocarbons (PAH) in Poxim River sediments, Brazil. Mar Pollut Bull 127:478–483

Spalding M, Kainuma M, Collins L (2010) World atlas of mangroves. Earthscan, London, p 319

Sruthi P, Shackira AM, Puthur JT (2017) Heavy metal detoxification mechanisms in halophytes: an overview. Wetl Ecol Manag 25:129–148

Tam N, Li S, Lan C, Chen G, Li M, Wong Y (1995) Nutrients and heavy metal contamination of plants and sediments in Futian mangrove forest. Hydrobiologia 295:149–158
Tam N, Wong Y (2000) Spatial variation of heavy metals in surface sediments of Hong Kong mangrove swamps. Environ Pollut 110:195–205
Tamin NM, Zakaria R, Hashim R, Yin Y (2011) Establishment of Avicennia marina mangroves on accreting coastline at Sungai haji Dorani, Selangor, Malaysia. Estuar Coast Shelf Sci 94:334–342
Tanner MK, Moity N, Costa MT, Jarrin JRM, Aburto-Oropeza O, Salinas-de-León P (2019) Mangroves in the Galapagos: ecosystem services and their valuation. Ecol Econ 160:12–24
Thanh-Nho N, Marchand C, Strady E, Huu-Phat N, Nhu-Trang TT (2019) Bioaccumulation of some trace elements in tropical mangrove plants and snails (can Gio, Vietnam). Environ Pollut 248:635–645. https://doi.org/10.1016/j.envpol.2019.02.041
Tomei MC, Daugulis AJ (2013) Ex situ bioremediation of contaminated soils: an overview of conventional and innovative technologies. Crit Rev Env Sci Tec 43:2107–2139
Truong TD, Do LH (2018) Mangrove forests and aquaculture in the Mekong river delta. Land Use Policy 73:20–28
Tsui K-M, Fryar SC, Hodgkiss IJ, Hyde KD, Poonyth AD, Taylor JE (1998) The effect of human disturbance on fungal diversity in the tropics. Fungal Divers
Uad I, Silva-Castro G, Pozo C, González-López J, Calvo C (2010) Biodegradative potential and characterization of bioemulsifiers of marine bacteria isolated from samples of seawater, sediment and fuel extracted at 4000 m of depth (prestige wreck). Int Biodeterior Biodegradation 64:511–518
Urrego LE, Correa-Metrio A, González C, Castaño AR, Yokoyama Y (2013) Contrasting responses of two Caribbean mangroves to sea-level rise in the Guajira peninsula (Colombian Caribbean). Palaeogeogr Palaeoclimatol 370:92–102
Varjani SJ (2017) Microbial degradation of petroleum hydrocarbons. Bioresour Technol 223:277–286
Varjani SJ, Gnansounou E, Pandey A (2017) Comprehensive review on toxicity of persistent organic pollutants from petroleum refinery waste and their degradation by microorganisms. Chemosphere 188:280–291
Varjani SJ, Rana DP, Jain AK, Bateja S, Upasani VN (2015) Synergistic ex-situ biodegradation of crude oil by halotolerant bacterial consortium of indigenous strains isolated from on shore sites of Gujarat, India. Int Biodeterior Biodegradation 103:116–124
Viswanathan P (2016) Multifunctional benefits of community-based mangrove restoration in Gujarat: an analysis. In: Nature, economy and society. Springer, Cham, pp 243–265
Wang J-W, Li Y, Zhang Y-X, Chai T-Y (2013) Molecular cloning and characterization of a Brassica juncea yellow stripe-like gene, BjYSL7, whose overexpression increases heavy metal tolerance of tobacco. Plant Cell Rep 32:651–662
Wang M, Cao W, Jiang C, Yan Y, Guan Q (2018) Potential ecosystem service values of mangrove forests in southeastern China using high-resolution satellite data. Estuar Coast Shelf Sci 209:30–40
Wang Y, Qiu Q, Yang Z, Hu Z, Tam NF-Y, Xin G (2010) Arbuscular mycorrhizal fungi in two mangroves in South China. Plant Soil 331:181–191
Widdel F, Rabus R (2001) Anaerobic biodegradation of saturated and aromatic hydrocarbons. Curr Opin Biotechnol 12:259–276
Wilkes H, Buckel W, Golding BT, Rabus R (2016) Metabolism of hydrocarbons in n-alkane-utilizing anaerobic bacteria. J Mol Microbiol Biotechnol 26:138–151
Wilson SC, Jones KC (1993) Bioremediation of soil contaminated with polynuclear aromatic hydrocarbons (PAHs): a review. Environ Pollut 81:229–249
Xu S et al (2015) Tungsten-and cobalt-dominated heavy metal contamination of mangrove sediments in Shenzhen, China. Mar Pollut Bull 100:562–566
Yakimov MM, Timmis KN, Golyshin PN (2007) Obligate oil-degrading marine bacteria. Curr Opin Biotechnol 18:257–266

Zafra G, Moreno-Montaño A, Absalón ÁE, Cortés-Espinosa DV (2015) Degradation of polycyclic aromatic hydrocarbons in soil by a tolerant strain of Trichoderma asperellum. Environ Sci Pollut Res 22:1034–1042

Zhao F, Zhou J-D, Ma F, Shi R-J, Han S-Q, Zhang J, Zhang Y (2016) Simultaneous inhibition of sulfate-reducing bacteria, removal of H2S and production of rhamnolipid by recombinant Pseudomonas stutzeri Rhl: applications for microbial enhanced oil recovery. Bioresour Technol 207:24–30

Zhu J, Zhang J, Li Q, Han T, Xie J, Hu Y, Chai L (2013) Phylogenetic analysis of bacterial community composition in sediment contaminated with multiple heavy metals from the Xiangjiang River in China. Mar Pollut Bull 70:134–139

Biotherapeutic Approaches: Bioremediation of Industrial Heavy Metals from Ecosphere

23

Reyed M Reyed

Abstract

Sustainable probiotics are cost-effective, active, friendly biosphere, and viable biotherapeutic mediators that increase positive biome inhabitants in the gut micro-bio ecosystem of living organisms. The critical benefit of the potential treatment effectively utilizing such biological agents as a biotherapy approach is the notable absence of their adverse effects. In recent years, extraordinary interest in the possible use of these therapeutic agents has significantly improved to refer to courteously and typically prevent a significant number of complex disorders in our Macro-bio ecosystem. Probiotics biofilms first and foremost restrain gut microbiota directly or indirectly to scale down using biotransformation of complex chemical compounds. Because of the unique structures on its extracellular matrix "MBBM," so many other probiotic microbial communities could already entangle to organic waste product. All strategies merely enable constructive biofilm development and metal-binding of organic compounds. Probiotics biofilm-mediated bioremediation implemented strategically for contaminants. Prebiotics remain naturally, universally potent ingredients with beneficial phytonutrients, fundamental nutritional sources. They are naturally insoluble fiber with complex carbohydrates. Prebiotics has much more to contribute powerfully than purely and simply the systemic application of autochthonous microorganisms in host micro-bio-environments as well as complex environments of plants and animals. Prebiotic indigenous ingredients naturally have to be metabolized by targeted microbiota and microbial processes in a

R. M Reyed (✉)
Bioprocess Development Department, Genetic Engineering and Biotechnology Research Institute (GEBRI), City for Scientific Research and Technological Applications "SRTA-CITY" New Burg El-Arab City, Universities and Research Institutes Zone, Alexandria, Egypt

© The Author(s), under exclusive licence to Springer Nature Singapore Pte Ltd. 2021

V. Kumar et al. (eds.), *Rhizobiont in Bioremediation of Hazardous Waste*,
https://doi.org/10.1007/978-981-16-0602-1_23

specific order to biosynthesize and extensively develop capsular and extracellular biopolymers Membrane-Bound -Biopolymer Matrix MBBM. MBBM released into the unique environment closed capsules or loosely interrelated biofilm blankets. In summary, comprehensive techniques demonstrated to have been an appropriate therapeutic option that explicitly mentioned in this perusal. However, there is a need for more data analysis to focus on the process challenge the interrogator environments in situ. The author hopes that this chapter will create a good literature review that makes substantial contributions to current and promising environmentally therapeutic initiatives in the long term.

Keywords

Bioremediation · Ecosystem · Heavy metals · Microbes · Probiotics · Membrane Bound-Biopolymer Martix "MBBM" · Micronanoremedation · Prebiotics

23.1 Introduction

Bioremediation is strongly involved in trapping "biosorption" (Giese et al. 2020; Contreras-Cortés et al. 2020) bioprocessing "biostimulation" (Zhang et al. 2020); manipulating "bioaugmentation" (Roy et al. 2018); downgrading "biodegradation" (Lee et al. 2019) and clean-up organic, inorganic compounds (Jaiswal and Shukla 2020) and noxious waste (Igiri et al. 2018) from the contiguous Biospheres through the cooperation of microbiome, mycobiome, and plants. This microbiota assimilates organic compounds by biosynthesis certain metabolites, macromolecules, or biomolecules known by enzymes, which brings alterations the nutrient composition and therefore their ecological accessibility. This coordination has been largely employed in agro-ecosystem.

23.2 Probiotics Microbial Strains for Biosphere Cleaning Up

Probiotics pay attention to the particular instances "pro" and "biotic" from the Greek Term "for growth and development." The ability microbe cells to live, called probiotics (even though a heat-inactivated pattern seems to have become useful for livestock) (Amenyogbe et al. 2020; FAO 2002, 2001; Gibson and Roberfroid 1995; Hill et al. 2014; Reyed 2020; Parker 1974)." Additionally, they addressed under "straightforwardly administered microbial, oral consumption of probiotics or probiotics dietary supplements (Vesty et al. 2020)."

Probiotics appropriately represent beneficial microorganisms that would adequately provide therapeutic benefits for the prominent guest just before handled fittingly. Although since it has been the world's most officially known and widely recognized form (Hill et al. 2014; Reyed 2020; Reyed 2007a, 2007b). Promising Probiotics are significant producer for biosurfactants (Ebrahimi et al. 2019), nanomaterial (Nile et al. 2020), metallic nanoparticles (Mohd Yusof et al. 2020), biopolymer (De Prisco and Mauriello 2016; Reyed 2007c), antimicrobial agent

(Karimi et al. 2018), bacteriocin (Maldonado Galdeano et al. 2019); natural biocides (Soliman et al. 2019), and bioactive compound (Binda et al. 2020). Probiotics are categorized as functional and protected microorganisms that progressively improves the host which may be gut microbiome, Biospheres, plant-soil ecobiome, and aquaculture, with necessary prebiotic metabolites and functional ingredient that positively modulates the host's biosphere, thus improving maintaining a stable internal environment association homeostasis (Brodmann et al. 2017). Secondary metabolites obtained directly from plant flora (Jurić et al. 2020), microbiome (Agamennone et al. 2019), mycobiome (Chin et al. 2020), lichens (Olivier-Jimenez et al. 2019), and seaweed "blue-green algae" (Singh et al. 2017a)—are premium of nature, because of their applications in various fields. Recent advances in modern biotechnology have contributed to innovative feasibilities in the dressing, processed foods, pharmaceutical and medicinal sectors of biological resources.

The differentiation of clear and unambiguous engagement arrays among symbiotic organisms permitted use of potential of microbiota to fix biological remediation issues. This resulted in probiotics being regarded as an approach of symbiotic associations. Probiotics could build a number of specific connections which make a range of mutual bionetworks based on different nano-scales platforms, in order to operate properly. These probiotics encounters frequently in the improvement of disease severity or cause therapeutic effect on living organism, including humans. They could also create accomplishments to substance modification and bioprocessing development. Throughout almost all of the biological and ecological issues, farming, conservational research, food manufacturing as well as healthcare consequently play an increasingly important role in the communication among probiotics microbiota. Probiotics are green "nontoxic for the proposed practice" potential long term, and sustainable valuable biofilms could very well precipitously as expected biospheres affirmative (Chung et al. 2016). Probiotics microorganisms are friendly biospheres (Cutcliffe 2017), viable, and sustainable biotherapeutic promoters that naturally strengthen the functional genomics beneficial biomass. The prevalent of treatment using biotherapy represents a reduction of harmful symptoms, such as antagonistic microbes. In earlier years, intellectual curiosity in the usage of such bioactive agents to suppress and mitigate an enormous number of syndromes in our Biospheres has massively increased in the metabolic pathways of biologically active compounds. These probiotics are ubiquitous in the food sector and generally considered safe. In the biospheres, probiotics can sometimes be isolated and characterized sources (Khangwal and Shukla 2019). This microbiota has numerous desirable characteristics that can promote both humans and the Biospheres. Probiotics could very well counteract health effects triggered by toxic chemicals. And therefore, it provides the necessary effective and reliable protection mechanisms in the long term to reduce effects of oxidative stress and cross-link themselves to confiscate and eliminate out from cell wall ecosystem (Roškar et al. 2017).

The recent research for probiotics can also be encompassed in so many other raw materials traditionally based on the intended utilization and bio-formulation (Mastan et al. 2019). It commercialized as dairy products, nutraceuticals, or nutritional

support (Jackson et al. 2019). Even so, while the term probiotics generally marketed as functional ingredients, for instance, capsules/powder (Fu et al. 2018), or as functional foods (Roy et al. 2018), natural yogurt (Scariot et al. 2018), kombucha (Kozyrovska et al. 2012), crop production, biofertilizers (Afzal et al. 2019; Jiménez-Gómez et al. 2017) always improve plant nutrient situation (with positive reinforcement growth and profit harvest) and Feed additive for animal's livestock (Markowiak et al. 2019). Thus, utmost of the present probiotic culture likes all kinds of beneficial microbiota that support their host immune system. Bio-manufacturing probiotic was "universally recognized for all living organisms," necessarily mean that stimulated motivated products are friendly biosphere products, processed foods, and agricultural commodities (Fenster et al. 2019). Many organizations and technologists have officially started using probiotic bacteria on small ruminants, even though they have identified and generally acknowledged agroindustry besides health outcomes and socioeconomic welfare benefit of probiotics in public health and environment safety.

23.3 Potential Prebiotics for Effective Biosphere Biotherapy

Prebiotics are carbohydrates "oligo-fructose or oligo-fructan", that can't be metabolized by living organisms. They are a potential source of nutrition for probiotic microorganisms-beneficial mycobiome and microbiome in the gut of living organisms. That interconnected to endorsing the development of cooperative ecobiome including endophytic fungal, rhizobacterial communities of sustainable autochthonous microbial populations, and as well as in the human microecosystem. Prebiotics are therefore quickly emerging as essential mechanisms of biotechnology as therapeutics, as environmental decontamination agents, and as components for a wide range of developmental handles (Amenyogbe et al. 2020; Davani-Davari et al. 2019; Reyed 2007c). Dietary foodstuffs characterized as a prebiotic or Bifidus Agent (Sasaki et al. 2020; Reyed 2007d, e) on many concepts, such as fermentation tolerance in the upper region of the small intestinal tract and the selective encouragement of the growth of probiotic microbiota. Prebiotic metabolism with appropriate techniques and biological activities is needed if capsular or extracellular polysaccharides generated. Among several others, a membrane-bound biopolymer matrix was established and is well-known as "Membranes-Bonded Biopolymer Matrix" (MBBM) biopolymers. In this specific case, synbiotic (Jost et al. 2015) "living and viable potent microbiota with their metabolites" is used once again to focus on improving their habitat, then will also endorse the macro and microeconomic-bio-ecosystem ex-situ biosorption and biomonitoring process (Goyal et al. 2019).

Beneficial microbes used in bioremediation to neutralize, detoxify, efficiently absorb, purify, break up or break down waste, and other harmful materials into the less volatile or toxic compounds. In organic farming, the beneficial microorganism profitably grows throughout powerfully establishing a relationship with aquaculture and naturally provides straight forward accessibility to the local fish gastrointestinal

systems, with gills and nourishment available. In this chapter, I put forward to profitably use the expression "Membrane-Bound Biopolymer Matrix "MBBM" for Extracellular polymeric substance "EPS" (Gupta and Diwan 2017), but did not drift down into review articles. Meanwhile, at that possible moment, the debate nearby the standard abbreviation has been virtually completed with "Membrane-Bound Biopolymer Matrix MBBM" as the practical implication of Extracellular polymeric substances. "MBBM" same as "EPS". MBBM biofilm organizations well-defined as "Microbial biodynamic biopolymer which has been arising as a consequence in direct relation for both the joining or affix (coherence and collective efficacy) together through cells (bond strength for biofilm formation) and some other particulate material "pollutant materials, heavy metals." Biopolymers in common are macromolecules in the exterior membrane (Biopolymer Matrix Membrane Bound). They secreted in microbial organisms as tightly enclosed capsules or loosely connected biofilm sheets. In industrial bioprocessing MBBM is useful for regulation of biotherapeutic agents and functional nanoscale particles.

An excellent selection of extensive uses would carefully cover novelty items, professionally clean-up, home healthcare goods, macro-ecosystem sustainability, nutrition, and rehabilitation. Microbes are responsible for us with an overwhelming and various biotherapeutic essentials of the macro-ecosystem. Such cautiously approaching adverse possessions are identified and improved by the cutting-edge indigenous materials required to counter the situation of chemical combinations, nitrogenous compounds (risky materials), and thus the microorganism of the Biospheres. Nevertheless comprehensive work in progress, only a few microbial origins has been until now to be identified with specific numerous products. Microbial resources can merely contribute to a more advanced production of microbial syntheses by generating a new golden age of environmental bioprocessing, which has sufficiently developed into one important branch of nano-biotechnology. It is a constructive chapter on contemporary bioremediation by probiotics for treasured microbial biomass bio-based materials to merely enhance the biosphere cleanup development of polluted macro-bio ecosystem applications, to promote renewable bio-resources for bionanoformulation.

23.4 Severely Spoilt Biosphere by Heavy Metals

An element of an unexpectedly extensive urban, newly fifth, and fourth-generation industrializing and population growth has been contaminated with various hazardous xenobiotic substances on the planet (Chang et al. 2019). The biosphere polluted with possibly unsafe carbon-based impurities, and the manufacturing sector in current history. Pigments, dyestuffs have become alarming in our biotic systems (azo dyes, commercially available dyestuffs) (Benkhaya et al. 2020). Our biosphere, including humans, animals, and plants, are threatened by pollutants through disruption of the cell wall, DNA derived, altered enzyme activities, and caused death to the birth, liver and kidneys, neurological problems, and premature heart and brain (Giavasis et al. 2020). Conservation pollution by heavy metal caused considerable

damage to aquatic systems owing to biotic, abiotic, and industrial overflows. Applications usually involve coal and iron extraction and industrial processes, rechargeable batteries and pharmaceutical discharges, manures, insecticides, and much other heavy industry and inappropriately commonly utilized substrates.

The worst most widely recognized toxic heavy metals found in the biosphere are synthetic polymers, and rare earth metals. The toxic metal seeps into the soil, metastasizes, accumulations, and generally speaking, accumulates in surface and groundwater (Jaishankar et al. 2014); (Hossain and Rao 2014). Contaminants are harmful at less dose that cause serious biosphere oncogenic, xenobiotics, and bioaccumulative threats. They lead to the bioaccumulation of toxic elements by food processing interconnection into animals and floras. These xenobiotic contaminants are created commercially and discharged of extensively in the biosphere. Disclosure to poisonous substances results in the implementation of different food chain concentrations (Bharagava et al. 2018). They look as if to have an antagonistic consequence on "biotic diversity" and not recyclable then poisonous to humans. Innovative technologies are now essential to improve treatments. Numerous physicochemical and biological processes are applied because organic compounds released into the biosphere from industrial effluents. Eco-friendly and efficient remediation process deem necessary to improve this situation. Since several methods for pollutants exclusion and dyestuffs are appropriate, biological treatments are robust today, and cleaner because they are sustainable, globalization economic, not begin producing toxic by-products (Allam 2017). In vitro and in vivo as well as on the field microbial clean-up can be implemented through integrating a variety of harmful organic pollutants into high-end chemical products while using organic, biologically healthy, cost-efficient, and composites reinforced across much of the application of microbiota biotransformation for decontaminating and biodegrading a dangerous macro ecosystem (Dick and Stucki 2020).

Microscopic multicellular entities biofilm sustained biomonitoring, pollutant removal, and photocatalysis procedures are more promising nanostrategies than others currently offered by microbial biodegradation combined with the increasing microbial biomass viscosities and the significantly sophisticated natural cell immobilization capability for surveillance and mechanical resistance of bacteria (Yadav and Singh 2019). The monitoring approaches to the harmful effects of such noxious are most important for sustainable economic growth. Using beneficial biofilms "probiotics" as a tool for bioremediation of potentially toxins allow new technologies to remain biosphere sustainable if integrated methods correctly developed and applied. Such a technique using microorganisms and their products to degrade and cleanup various effluents is beneficial in the long run, so they must incorporate into detecting and preventing the harsh chemical from release into the biosphere. Many studies have completed in the way of how biofilms interconnected to infection, but less focus has given to the probiotics beneficial biofilms related to the biosphere. One striking example, however, relates to the current cleaning of the major oil spill by Exxon Oil on the shorelines of Prince William Sound, Alaska, back in 1989 (Prince and Atlas 2016; Beth Lebwoh 2011).

23.5 Microbial Consortia and Pollutants

Consortia of genetically modified microbes have deployed to detoxify pollutants. Such positive biofilm research in the natural biosphere of soil, sand, and sediments has revealed the potential biofilms to treat pollution. The exosome communication system within microbiomes biofilm taxon, together along with microbial community's chemotaxis, could promptly lead to biocompatibility and bioavailability of harmful pollutants, which is extremely important directly positively linked to the gradual degradation of toxic and organic contamination by biofilm creating microbiome. (Edwards and Kjellerup 2013). For synthetic dyes, textile wastewater pigmentation promptly became one of the most imperative biosphere impacts. It is a root cause of stimulated ecosystem pollution. The oxygenation or continuous renewal of oxygenation possessions of natural water sources and trimmed-off exposure to dying sunlight are also affected by massive quantities of staining and finishing colorings in water boards (Yaseen and Scholz 2019). Textile wastewater that is untreated has negative biosphere and social impacts. Near to the ground dose (< 1 ppm) of dyestuff can efficiently generate sensitive Macro-ecosystems colors, impair compositional quality, inhibit photorespiration, and destruction water and land network. (Sghaier et al. 2019). Biological approach as probiotics biofilms-intermediated bioremediation "PBIB" forming membrane-bound biopolymer matrix (MBBM), are necessarily towards the detoxification of toxic chemicals.

23.6 Probiotics Mediated Bioremediation of Biofilms "PIBB": An Innovative Comprehension of Environmental Complications

Microscopic organisms are directly relevant to indisposition and ephemerality. It could be something threatening as well as horrible. Even so, together with digital technologies, the microbiota twenty-first century is not always an invader, and therefore might be best friends. Probiotics intermediate bioremediation biofilms soundly supposed to overcome procedures to affect the control side:

1. Competition and participate cautiously in the gradual progression of potentially treacherous microbial communities "pathogenic biofilm-producing and opportunistic microorganisms".
2. As well as, the nutrient can adhere to the composite surface substrate of mutant cells, through fluid secretion of prebiotic membrane-bound biopolymer matrix (MBBM).
3. Monitoring, controlling, ecobiome eubiosis, and homeostasis augmentations through accelerating hydrogen peroxide emission (Mazzoli et al. 2019), catalases enzymes release (Yu et al. 2019), antioxidant biosynthesis (Chooruk et al. 2017), various prebiotics nanoparticles exudations (Mohd Yusof et al. 2020), and biosurfactant oozing out (Ebrahimi et al. 2019).

Innumerable technological respects of probiotics biofilms-intermediated bioremediation lifecycle, for remarkable instance, water ground remediation by subterranean root system where Phyto-hydraulics biosorption and microbial biotransformation of heavy metals and specific toxins into their gaseous practices. Microorganisms and crops are deteriorating contaminants into several components and carefully withdrawn, modified, changed, and processed for reducing harmful environments. Microorganisms and plants are degrading pollutants into many ingredients and safely removed, modified, adapted, and processed for minimizing hazardous environments. Hopefully, soon, it has been used for all the polluted towns, lines, sediments, reservoirs, and surface water bioconversion systems widely used for extensive irrigation. (Kapahi and Sachdeva 2019). Bioremediation process is used to neutralize, reduce, and remove environmental pollutants by application of probiotics biofilm or metabolite profiling "prebiotics metabolomics" as biological agent for bioremediation or even if plants are used for this purpose, to eradicate, relocation, adsorption, and/or lay off waste product called phytoremediation (Yan et al. 2020). In certain circumstances, Microbial bioremediation, microbiota produced enzymes change the composition and configuration of heavy metals to transform toxic pollutants. The phenomenon is classified as bioconversion or enzyme hydrolysis or microbial degradation. In many deteriorated, the composition of toxic chemicals has been degraded, the structure becomes easier and simple and essentially harmless, ineffective, not harmful, and eventually, metabolites called biomineralization (Zhao et al. 2019).

23.7 Bioremediation Through the Application of Intrinsic or Extrinsic Probiotics Biotherapy

Host protection like plants, aquacultures, animals, and humans, the cognitive processing of these directly linked living organisms, has been understood. The eubiosis and dysbacteriosis (Reyed 2020; Bajinka et al. 2020) protected function of these microbial populations is significant but is very far from putting into corrective action. The probiotic hypothesis being one of the most widely recognized assumptions. It sufficiently indicates a dynamic relation between symbiotic living organisms and environmental conditions that leads to the unique composition of the most valuable meta-organisms. As another advantage, the extensive modification of inhibitory microbiota, including purported soil microbes for the biosphere, may typically have probiotic constructive powers for distinctive florae and faunas. Throughout this approach, it is promising to cooperate with intermediate, bioremediation, and the aggregation of a healthy microbe. This ambitious scheme will naturally inspire the nutrient depletion of emerging contaminants that toxic to ecobiome and other meta-organism. The condition of polybiomics correctly is the impressive array of active viruses, phages, eubacteria, archaea, beneficial fungi, protozoa, and Arthropods stimulating special protection of a host secretion, and many other metabolic abnormalities. Because of higher biomass crosslinking and adsorption capacity with sophisticated defensive and adhesive properties, probiotics

biofilms-intermediated bioremediation "PBIB" would correctly be a much more promising approach.

PBIB attribute to the successful genetic modification between ecobiome/phytobiome and other beneficial organisms induced biocompatibility and biotransformation of toxic chemicals by microbial communities certain chemotaxis. Phytobiome, microbiome, mycobiome, and arthropods composition typically play an integral role absolutely in distinct nutrient absorption and therefore colonized with a massive, dynamic group of biota that merely makes a significant contribution in nutrient decomposition forms sustainable harvest. A large variety of unique microbiota in the intestines, from archaea to eukaryotes, just like many of the mycorrhizal phyllosphere and endophytes, generally occupy the plump tissue of the affected plant. Similarly, rhizosphere microbiota factors also include soil type patterns, moisture levels, evolutionary indicators for agricultural production, roots xenografts, etc. (Dong et al. 2019). A hybridization and cross-pollination with both cultivated plants and beneficial microorganism facultative mode of private life or obligate mutualistic interdependence relationship and legumes developing conditions sometimes including Adzuki beans. Anasazi beans, Black beans, Black-eyed peas, Fava beans, Garbanzo beans (chickpeas), organic Kidney beans, and Lentils represent absolutely just another substantial economic agro-processing, and valuable agricultural dynamic relationship. To thoughtfully provide complimentary access, such profoundly grateful bryophytes offer additional keep providing CO_2 resources, mostly as organic compounds, including one that adequately maintains beneficial microorganisms stable and enthusiastic (Harris et al. 2020).

As seen with the residents' densities of lichen and rhizopus-Azolla, demanding and many-sided chemical compounds enable beneficial bacteria to regulate their biochemical processes with that of the necessary requirements of other representatives of their active populations (Sehar and Naz 2016). Throughout the whole scenario, the single-celled microbiome, mycobiome, their residences inside the vesicles of the rhizobia "nodules" where every day they tighten and help hold nitrogen from the atmosphere to the plants, microbiome "bacterial inhabit" or mycobiome "fungal occupies" that living inside plant soft tissue, dispossessed producing infection. This phenomenon well famous by phytobiomic probiotics microbiomic or mycobiome endophyte and invertebrates "creepy-crawlies, arachnids, myriad pods, and prawns" relationship, this remarkable statement abbreviated by triple genuine compacted network "probiotics biofilm phytobiome" (Kumari et al. 2020).

Probiotic biofilm phytobiome "PBP" Triple interactions amongst Plants, Microbes, and bugs relationship are multifarious, and more than a few complex dynamics possibly will touch its specific configuration, like phytobiome-microbiome and microbiome–microbiome interfaces and macroecolgical distinctions. (Maria 2020). Biospheres potential application of probiotics biofilm phytobiome as green fermentation bioprocess miscellaneous fertilizers, the commonly bio-based product on valuable plant beneficial biofilm connection from probiotic biofilm phytobiome. Additionally, the unique capability to biosynthesize hormones and iron-chelating complexes efficiently are two of the utmost communal

Phyto-improvement stimulating mechanisms discovered by probiotics biofilm phytobiome. Besides, PBP also has bioregulator characterization, performing as phyto-shielding potential mediators alongside pathogens living things of a deferent environment. The successful production of siderophores and cell wall-hydrolytic elevated enzymes like "chitinase, glucanase, protease, and cellulose" are competent to progressively destroy the mycobiome and microbiome cell wall and sufficient possible reasons the cell dissolution of microbiological septicity. As well as release and ecological development of chemotherapeutic polymers via volatile compounds (VC) efficiently is between those biocontrol of phytopathogens.

The appropriate use of probiotics phytobiome not only increases harvest production, then again as well as valuable products typically resulting from these yields. There are specific additional probiotics biofilms-intermediated bioremediation such as *Ralstonia eutropha "Alcaligenes eutrophus"* (Xu et al. 2019) The function of *Ralstonia eutropha* is efficient because all organic carbon, vitamins, and minerals are typically restricted, it is sometimes intracellular biogenerate and continue eagerly to bio produce a massive amount of polyhydroxybutyrate biocomposite (PHB), which is environmental friendly biodegradable and nanocomposites to manufacture hydrocarbons plastics in abundant amounts. Nevertheless, *Ralstonia eutropha* improves for somewhat other than PHB yields, like distilled alcohol, methyl ketone bodies, unsaturated fats, and alkyl and *Deinococcus radiodurans* "*polyextremophile*" (Ott et al. 2017) struggle to particle emission, oxidants, and desiccation and resistance to UV. It is capable of withstanding acute irradiation doses and growth under chronic radiation that could accept high levels of heavy metals and radiation. *Deinococcus radiodurans* (Manobala 2019) would be used in iron, copper, silver, and uranium mines to start cleaning up harmful emissions.

Encouraging microscopic organisms as well as other pathogenic microorganisms, small biotechnology specialists, could perhaps help accelerate huge numbers of biochemical processes that are already unaware of "better" species involved in regulating. Tiny microbes mediated procedures have always been constructive in the long run for each other, but they are still worthwhile for everyone else in the biogeochemical cycles, which would include humans in general. Supposedly, those life structures may not even have originated, notwithstanding these ongoing planet inhabitants, and omnipresence would not function habitually. We recognize and comprehend. Microbial communities consequently frustrate our earth's ordinary production processes wobbling. Through most of the physical and biologically-created bioaccumulation technologies, numerous microorganisms have already used. There are excessively voluminous *Bacilli pseudomonads*, and methane bacteria are listed. These minuscule organisms, for instance, facilitate now over trillion cubic meters of industrial wastewater to be manufactured and cleaned occur annually worldwide. Through several stage systems, including autotrophic and heterotrophic digestion, microorganisms such as bacteria promote the elimination of biomass, organic and inorganic derivatives, while materials remove unwanted poisonous, aromatic hydrocarbons, herbicides, insecticides, and environmental pollutants (Yang et al. 2019). Species of *Candidatus Accumulibacter phosphatis* was a potential probiotics biofilms-intermediated bioremediation that is becoming the

predominant phosphorus cleaner coordinator (Nurmiyanto et al. 2017). Of significant relevance, these and many other forms of life sometimes monitor the microbial ecological balance even though no individual in the population may circumnavigate another.

As a direct result, "recycling" wastewater is a precious environmental resource through reasonable standards of microbial. It should have been blatantly coherent, and even so are additionally, that microbes are the strongest bio-indicators harvesters, grinders, and compost piles on the globe! Across the whole of fact, humans and other types of life choose their potential to improve them, both physiological and biochemical. For example, in the case, in arthropod earthworm and bed bug specific microbiota involved, therefore, allow each one to utilize it for consumption lignocellulosic materials as well as other plant materials. Probiotics microbiota from time to time even produce insect-specific compounds, which overwhelmingly support their host and promote biodiversity (Zoghlami and Paes 2019). Beneficial bacteria produce natural chemicals and pesticides designed to fight infectious pathogens, and agrochemicals technology implemented throughout cultivation. Sometimes even antibiotics put an end to many bacteria used to remedy pathogens. They also definitely covet them to discourage infectious agents. The significant development of contemporary beneficial microbial communities in agricultural production regularly tends to avoid like using hazardous and potentially dangerous disinfectant and chemical substances without distinction. The microbial biofilms concept of this innovative model for chemical agents and danger to the public confirms that somehow the biosphere isn't even the first synthetic bioweapons to utilize (ASBMB 2018).

The microbial enzyme that efficiently breaks down and decomposes dying forests and deceased human organisms, which used to historically create biomolecules and will successfully lead to the healthy production of each other as well as other organizations. Naturally, almost any type of healthy food in the biosphere today and at the glorious beginning. Nearly anything else in the global economy could produce future profits from these microbial populations effectively (Leonhardt et al. 2019). Scientists wish to give responsibility to something about microorganisms. There could be another probiotics biofilms-intermediated bioremediation "PBIB" species, and bionetwork has several desirable properties that used to benefit both humans and the environment (Maftei 2019). Mitigating or preventing xenobiotic compound toxic effects. Lichen is a microorganism's life form, which could also thrive on a peculiar stone's exposed surface area. Lichen consists of fungal species which split rock to extract minerals, cyanobacteria that mostly absorb light fuel to produce carbohydrates as well as carbon compounds, and cyanobacteria which absorb nitrogen to generate organic nitrogen compounds. They go forward as on its own bases of nutrition, with ragged stone and used oxygen (Dal Grande et al. 2018). Cyanophyta aquatic fern *Scenedesmus*, and *Anabaena, Azolla*, blossoms, and flourishes together in flowering meadow and wetland in all planet. *Anabaena* blue-green photorespiration series, Cells are translucent or monochrome, distinguished, sprinkled with Units defined as organic process vacuoles focus on providing and act appropriately a resource nitrogen synthesis by the aquatic rhododendrons (Pereira 2017).

Integrating sustainability health-conscious bacterial organisms must have undoubtedly had some attractive features which economically exploited for the maximum potential of both human beings and the natural environment. Strategies to mitigate or attempt to prevent xenobiotic compound with their adverse health effects. Subterranean rhizosphere rhizome, and from the other hand, Underground plant roots, as well, synergistic modalities of biofilms known as "Phytobiotics" or plant probiotics) may also work in superior conjunction much more coherently) Ferdous et al. 2019; Menendez and Garcia-Fraile 2017). For example, Endophytic-type bacteria restore atmospheric nitrogen via transforming Nitrogen gas into ammonia. It may simultaneously involve action potentials between some of these exotic plants and in broad-spectrum and particularly the microbiota subsidizing to the considerable expansion of "nodes" impenetrable and exterior the rhizome, where dissolved used oxygen routinely occurs. Then again, the direct connection between the rhizobia and the rhizospheric organisms and adapted plant would adequately represent the most dynamic contractual relationship (Singh et al. 2017b).

The probiotics biofilm intermediated bioremediation efficiently produces, along with several other items, a probiotics biofilm mostly on the sensitive surface of the rhizobia, and therefore also continues to sufficiently develop a responsible multi-stakeholder synergistic relationship that precisely requires there symbiotic organisms to construct biofilms. Then again, Endophytes precious are acutely powerful positive probiotics biofilms biosphere system (Ancheeva et al. 2020). The endosymbiotic community "Biotic components of microbial endophytes Inhabitants" of probiotics biofilms association with synergistic effect with other rhizospheric organisms—root microbiome, mycobiome, and invertebrate which are unique ecological zones of depleted soil that near to root system—are developmental tool drugs for the acute treatment of various complex illnesses with potential applications in sustainable agriculture, pharmaceuticals, used food, and personal hygiene products (Mashiane et al. 2018). Maybe that is why they need organic farming probiotic microorganisms to focus not only through guidelines recommended benefits but its direct impact on the farming community as well. A twofold availability of probiotics for publics approaches, one through direct feed (blended into a meal) and the other through dilute water with organic matter). Utilization as the direct feed approach improves efficiency and effectiveness nutrient by incorporating probiotic ingredients and dissolution throughout the diet. This way impacts feed quality by integrating them into metabolites that assimilated inside the gut. Consequently, probiotics increasing biomass production enhance mineral bio-availability, escalating fatty acid metabolism, and rising growth performance, towards the nutrient (Wanka et al. 2018). One main reason to progress enhanced productivity of the Soil mantle "Pedo-sphere" must efficiently be through the used implementation of organic matter by probiotics as green organic biofertilizers, and biomass dependent products. In the diverse types of natural bio-based products of agricultural and domestic operations, it is essential to naturally stimulate meaningful amounts of organic or biofertilizer, manufacturing sector, and waste management (Teng and Chen 2019).

Potential biofertilizers or probiotics biofilms intermediated bioremediation intermittently used to undoubtedly constitute biomass technological innovations, boosting the biodegradation of the organic components, that most positively impact plants biomass on contaminated soil a deliberate process as well-known by biodegradation and in agricultures fields by the potential application of Integrated bio-enhanced coffee stirrer organic fertilizer with bio-stimulants coalitions naturally appears to willingly offer a dual opportunity: aiming accurately to improve tremendously the microstructure of soils microorganisms, rheological properties, physiochemical characterization and continuing eagerly to progressively increase the specific content of microbial biomass, upturn organic matter in the exposed soil and personal recovery for soil fertility (Menénadez and Paço 2020). Rhizoremediation is a mechanism where living organisms eliminate rhizospheric topsoil harmful emissions and xenobiotic. Rhizosphere ecobiome that mostly propagate plant growth and development have recovered the infertility complications land for enhancing crop productivity. Rhizoremediation using the root system with sustainable synergism to build up microbiome associations with organisms like Nematodes and earthworm. These invertebrate and plant interconnected with microbial biodiversity to boost hypertrophic degeneration of potential pollutants (Vergani et al. 2019). This property indicates a direct interface between probiotic and bioremediation.

Probiotics provide their host with great benefits. When probiotics handed in sufficient quantity and quality (humans, animals), microbial remediation results in biostimulation of microbial diversity through enough concentration and responsible for diverse range with health benefits, for example, protective effect, ecological benefit, competent size, nutritional value, and rehabilitation of contaminated living beings. The solutions indicated are indeed reasonably cost-effective, straightforward to use, and extremely adaptable for all numerous types of aqueous solution functional groups are convenient (Villela et al. 2019). Chromium is a natural element in the earth's crust and emitted by changing weather patterns into the ecosystem. Bio-eradication of contaminated soil by bioaccumulation and detoxification of hexavalent atomic number 24 "chromium (Cr(VI))," two *Bacillus cereus* species endure extremely resistant strains with reduction potential. Both strains are naturally hyper-entrapment in sodium alginate with diatomite function as more than just a micro-protective agent to mitigate emotional complexities and merely enable bio-absorption, and biotransformation toxic hexavalent chromium to chromium (III) endurance beneath 8 mM 99.9%, that being the case these used species typically displayed high pH and temperature adaptability. *Bacillus* was cautiously removed from Hexavalent chromium in culture in 24 h. It is the most outrageous efficient removal in the historiography that has been seeing until just now (Li et al. 2020).

The highest possible bioaccumulation of 3.562 mg Cdg-1 of cells from the water phase in *Lactobacillus Plantarum* strain HD 48 had shown. The Cd bioavailability through in vitro gastric model diminishes by such culture between 24.71 and 41.62%. In this understanding, probiotics strain *lactobacillus* has the potential to manage and sizeable experience to process Cadmium from water solution that would otherwise, therefore, evaluated to mitigate the morbidity and mortality of the body

for a degree of multidimensional economic benefit (Kumar et al. 2017). Contamination of heavy metals in food products directly impacts public health and safety. Food supplemented with probiotic lactic acid bacteria could indeed shield and immunize livestock and humans from toxic metals, but the pathway about biotransformation adequately resolved. Mice were administered here with *Pediococcus spp*, strain BT36. BT36 suppressed biosynthesis of chromate but after 480 h overnight of non-chromate degradation. Oxidative disruption and reduced histochemical disruption of hepatocyte modified mice. Pro-inflammatory cytokine biosynthesized via (Cr VI), BT36 can attenuate the intestinal permeability and carefully preserve potential Cr toxicity (Feng et al. 2020). Higher plasma concentrations from trimethylamine oxide risk for undesirable cardiovascular factors. Trimethylamine oxide enthusiastically encourages the successful establishment of macrophages and thus motivates coronary artery disease to develop. Dropping iso-antibody of trimethylamine oxide "IATMAO" is auspicious methodology in the social inhibition of the vascular syndromes, at an inspired guess of independent investigators. Then again, typically decreasing the dietary supplement originators of "IATMAO" is both improbable and risky. Nonetheless, modulation of the gut by biotransformation to breakdown and preventing trimethylamine synthesized. Unconventional bioremediate of trimethylamine in situ the human gut into an inert compound. Archaeal microbiota has been found suitable to eliminate methylated compounds.

However, some archaea lawfully residing in the human gut may realistically achieve this conversion by efficiently producing methane as a metabolic by-product. We enthusiastic endorse economic theory that specific distinctive archaeal microbiota for forthcoming bioremediation. Glorious blossom unsurprisingly in the gut is succeeding brilliantly generation prospective bioremediation probiotics (Brugère et al. 2018). Just in the similar approach for bioremediation, where new studies are illuminating the ways in which environmental contaminants are affecting, and are affected by microbes. Le and Yang (2019). Showed an exploration on the assessment of two Strains of *Pediococcus pentosaceus* obtained from the fermented aquatic fish as well as then taken into practical consideration extremely significant resistance to Cd. Virtually all species documented resistant to the human intestinal tract. These varieties claimed to have become innovative, effective chelation to prevent and manage cadmium cytotoxic effects in the bodily organism. Cd′s adhesion to bacterial cells characterized by continuous presence on the cell surface of various binding sites includes carbonyl, amine groups, and phosphate. For appropriate responding in situ digestion model, Cd bioavailability dramatically reduced by 44.7–46.8%.

23.8 Micronano-Remediation: For Safe, Protected and Hygienic Macro-ecosystem

A short time ago, Biotechnology of bioaugmentation and biostimulation are essential tools for applications of bioremediation (Titah et al. 2019). For undoubtedly enhancing microbial population at an active site to progressively improve contamination

cleanup and sufficiently reduce local time, for the biodeterioration and eradication of dangerous chemical contaminants were increasingly desirable because of their rising resistance to adverse environmental stress. Environmental bioprocess is the most suitable strategy in which positive impacts of the microbial population are widely used as a therapeutic agent, up to the current date. Amicrobial probiotics attack" novel approach naturally create eco-friendly bio-Nano composite components (Durazzo et al. 2020). Sustainable power for enhancing complex bioremediation process of contaminated waters, soils, and poisonous gases. The potential application of functionalized bio preparation constituents. Biodiversity of microbiota provides inherent prospective capacity in bioprocessing development and bio-manufacturing for nanoparticles. Microbial green synthesis of nanoparticles (Ezzeldin 2020) ordinarily has, however, emerged nano-biotechnology multidisciplinary field business (Baptista et al. 2018).

To understand molecular switches, in addition to critical factors genuinely needed to adequately control the specific dimension, complex nature, crystal arrangement of nanomolecules, and molecular tool that intermediate microbial bio-production of nanoparticles progressively improve the unique situation. In actuality, biological processes continue being relatively unexplored. Nanotechnologists use beneficial living organisms for the synthesis of prospect nanomaterials. A sophisticated and engrossing methodology for manufacturing "more eco-friendly" agricultural products and novel materials is the fermentation of metallic nanoparticles through biomass feedstock microbial communities to the ultimate bio-based invention. Depth insight into biogenesis pathway and upcoming opportunities afford by recombinant DNA technology. Naturally tend to encourage manual labor into paradigm change and commercial application in micro-biotechnology downstream processing in nano-biosynthesis for possible economic development and effective implementation. Probiotics technology is the cutting-edge, environmentally safe, and cost-effective nano-manufacture material for biosphere bioremediation by nanoparticles. The biosynthetic pathway of ZnO metallic nanoparticles produces by probiotics. Numerous probiotic bacteria seem to be a component to anything other than the prevention of Zn^{2+} human risk of injury. The highest probiotic value obtained for highly resistant Lactobacillus zinc isolates. Zinc oxide nanoparticles formed by particles at the molecular stage (Mohd Yusof et al. 2020).

23.9 Prebiotics Exobioploymer "Membrane - Bound Biopolymer Matrix" (MBBM).

The prebiotics membrane-bound biopolymer matrix biosecreted and released by probiotics microbiota differ by monosaccharide configuration, charge, connection, the prevalence of recurrent side-chains, and replacements. In general, the prebiotics Membrane-bound biopolymer matrix classified into homopolysaccharides (HoPs) and heteropolysaccharides (HePs), prebiotics Membrane-bound biopolymer matrix (MBBM), with vast functional properties and impacts in the field of medicine, pharmaceuticals, bioremediation, treatment of water, and operations. Microbial

polysaccharides are versatile, ubiquitous, eco-friendly, robust, parsimoniously low-cost, and pigeonholed into exopolysaccharides formed and retained in the cell, functional or structural polysaccharides and prebiotics Membrane-bound biopolymer matrix (MBBM). The polysaccharide is multi-efficient, Extracellular biopolymer substances industrialized by prokaryotic organisms, archaea & eukaryotes, fungi, and algae. New algorithms have developed nowadays to substitute their microbial models for the conventional usage of vegetable adhesives. Microbial exo-biopolymers mostly used emulsifying agents and biodegradable polymers, and enormous bioremediation application scenarios for reduction of bioaccumulation, biodynamic environmental responsibility, and natural resources used in adverse weather conditions. Membrane-Bound Biopolymer Matrix (MBBM) is positively outer membrane macromolecules and excreted in microbial species as enclosed capsules or densely interconnected biofilm mats. They naturally make a significant contribution to fighting drying, oxidative metabolism, cell identification, phage invasion, antimicrobials, or harmful substances, and osmotic tension. Alive thanks to their functional efficiency, nanoparticles have enthusiastically received considerable interest from modern scientists and academic researchers in the completed last several eons. The MBBM sustainably harvested from probiotic strains regarding multiple different macronutrient compositions in general addition to especially incorporate a comprehensive range of environmental agents. Membrane-Bound Biopolymer Matrix "MBBM" defined as Microbial biodynamic polymeric materials that almost always attach used cells and some other composites around each other (practical sense of active community) to polymer (mechanical strength) in biofilm architectures (cooperation).

23.10 How Ruinous Exobioploymer Are Created in Real World?

Even if you do not recognize the word biofilm, you have frequently seen biofilms. One type of bacterial biofilm, for example, is the plaque that forms on your teeth and causes tooth decay. A biofilm is also the "sludge," which blockages the kitchen drainage. If you have ever passed across any lake or river, you can even walk on stones colonized with slim association from different biomes known by biofilm. Dangerous potential biofilm a chronic tight spot infection from a sports injury, so it is biological animations, where you want to be.

MBBM microbiomic polysaccharides are a concrete "cement" significant class of biological polymers in living organisms, could therefore generally speaking be reclassified as a sizable amount of intracellular processing highly hydrated biopolymers polysaccharides, functional polysaccharides" glycogen-capsular polysaccharides closely linked to the cell surface and extracellular bacterial polysaccharides are complex heterogeneous macromolecules biopolymers made up of sugar residual and discharged also, called exopolysaccharides (Xu et al. 2020), or extracellular polymeric substance (Orhan-Yanıkan et al. 2020). For example, Xanthan gum is a common food additive sphingan "associates of the genus Sphingomonas". It uses in numerous food products, additives, and other agricultural

sectors. Alginate found in brown algae as carboxylic acids, natural, and foldable nanoparticles that express with nutritional value in the cell walls of the algae (Pereira and Cotas 2020). MBBM is a natural linear, homopolymer, essential for biofilm creation. It is extracellular heterogeneous, long-chain substances, with high molecular weight, and biosynthesized by microbiota. It becomes a critical component to quantify the physicochemical characteristics, functional and structural integrities of biofilms (Pereira and Cotas 2020). It supposed to be medium from polysaccharides and proteins, although macro components, such as DNA, lipids, and humic material. Membrane-bound biopolymer matrix is the building material of bacterial colonies, and bound to the outer surface of the cell or isolated from its medium of development. These nanoscale molecules are vital for the improvement of exobioploymer and the attachment of cells to surfaces. Membrane-bound biopolymer matrix make up 50% to 90% of the general carbon-based content in an exobioploymer (Staudt et al. 2004; Donlan 2002). Owing to the range of membrane-bound biopolymer matrix structures has been used in different nutritional and medicinal industries. Furthermore, enormous procedures have taken towards the identification and manufacture of new, microbial MBBM for medical and industrial applications (Mody 2009).

23.11 Membrane-Bound Biopolymer Matrixomic Biofilm Hypothesis

Microbiota "Commensal, mutually beneficial relationship and infectious agent environmental ecosystems" are categorized in the mainstream of olden times of microbiology as plankton, freely suspended cells, and have been identified nutritional rich media based on their growth characteristics (Sharma et al. 2019). Regeneration of microbial hypothesis that microbe adheres to something and expand spontaneously on open surfaces. Polymicrobial biofilms formation has nanostrategies for everything from the preliminary commitment of materials, densely inhabited network, biodiversity, and differentiation (Catherine and Matthew 2018). Membrane-Bound Biopolymer matrixomic Biofilm is biotic agglomeration that ultimately hooked up with a substrate (not omitted by delicate cleaning). It incorporates in a framework of mainly polysaccharide product. Non-cells, including mineral stones, decay pieces, limestone, sawdust, and fluid resources, identified in the biofilm matrix depend on more than just the environment under which biofilms have accumulated. (Jamal et al. 2018).

Also, organisms that are associated with Membrane-Bound Biopolymer Matrix Biofilm differ in terms of the genes transcribed from their phytoplankton counterparts. Membrane-Bound Biopolymer Matrix Biofilm on a variety of surfaces, including living tissues, medical instruments, piping of industrial or drinking water systems, or natural aquatic systems, can develop. The modifying composition of Membrane-Bound Biopolymer Matrix Biofilm highlight by the evaluation of electronic micrographs from the biofilm industry and healthcare. The harsh restraining effect of biocides and antibiotics on the development of systematized populations of

microbiomic cells identified as biofilms can be lethal thru course operation and in the urinary tract contagions (Jamal et al. 2018). There are thousands of victims in US health facilities alone due to disease in the biofilm surgery of the site and urinary bladder (APA 2018; Lo Giudice and Poli 2020).

Membrane-Bound Biopolymer Matrix MBBM immobilized particles of food and clay and other minerals. The substance stuck in the bodily fluid modes nanometric microclimate, every one possessing a distinctly different extracellular matrix, countenancing microbiota that dissimilar prerequisites to instigate together to run through microbiota association (Sapare 2018). The origin MBBM confined microbes involved in the creation of biofilms to make a positive contribution to gene expression. As well they have water networks for nourishment and microbial activity (Pathak and Navneet 2017). Also, the MBBM encompasses secondary metabolites, termed biosurfactants, which might also penetrate water-insoluble surfactant or other xenobiotic mediums quite effectively eco-compatible and the bio-based way during the reclamation and bioremediation progressions (Selvi et al. 2019). The growth and development of Membrane-Bound Biopolymer Matrix Biofilm usually occur via the five successions of biofilm formation: (1) early adherence, (2) unpreventable, and persistent fitting together, (3) growth and development I, (4). borrowings II, and (5) aggregating and redistributing. The biofilms then regularly interact and to metabolize the resulting Membrane-Bound Biopolymer Matrix MBBM and messages for biofilm development. When the signal increased, nutrients decrease, and cells begin to scatter signals. Biofilm formation considerable effort has been eager to pathogenic microorganisms and their toxic effects (Wang et al. 2020).

Inhabitants of biofilms possess interdependent biological and physiological interplay for micronutrients and gene expression interactions between the enrolled bioecosystem and empower against various biotic and abiotic stresses through intense food insecurity, pH, temperature, biocides stress, and/or opportunistic zooplankton (Karygianni et al. 2020). According to its metabolic capabilities to eradicate toxins, adaptive responses and great promise for survival continued to be enhanced especially in the environmental influence, because they had been produced naturally throughout the matrixomic cell, substantial chemical contaminant resistance, and many biological functions. Microbial communities live together in biofilm formation, which acts as naturally produced and environmental mechanisms that are much more powerful and productive than free-bacterial swimming in heavy metals bioremediation (de Carvalho 2018).

23.12 Role of Membrane Bound Biopolymer Matrix "MBBM"

Membrane-bound biopolymer matrix binding impermeable membranes cover and against desiccation (Ghosh and Maiti 2016). MBBM planktonic microbial population used as an affirmative defense against possible violence (Harimawan and Peng Ting 2016). The physicochemical characteristics of microbial cells should be encouraged by the formulations of a membrane-bound biopolymer matrix which can sometimes have a direct or indirect effect on variables that include the cellular

recognition, agglomeration, and resistance of the global environment. (Harimawan and Peng Ting 2016). Many bacterial strains that produce lactic acid have a membrane-bound biocomposite network, such as *Lactococcus lactis* subsp. It makes a significant step towards the enzyme hydrolysis of foodstuffs already bioavailable by polysaccharides (Welman 2009). The usage of panettones and others shows the development of a more membrane-binding biopolymer matrix multiplication in textile industries (Ullrich 2009). MBBM Bionetwork: the membrane-binding biopolymer matrix actually encourages nitrogen-fixing microbes anchor to host tissues and groundwater as a mutually dependent mediator (Ghosh and Maiti 2016).

As a result, it tends to be extremely important for endophytic for the supply of nutrients and an important part of terrestrial ecosystems. As a natural product, it appears to be highly advantageous for rhizobia for nutrients availability and essential element for terrestrial ecosystems and established positive penetration of bioactive material through the aisle (Ghosh and Maiti 2016). Bioremediation of noxious metals aided and abetted by bacterial membrane-bonding biopolymer matrix. This is effective in treating wastewater systems, and just biofilm formation entangles and starts to remove metal ions like cope, plumb, nickel, and cadmium (Pal and Paul 2008). The integrating innate predisposition and predictability of membrane-bound biopolymer matrix depending on a polymeric matrix and maybe even some variables such as compositions as well as on capabilities to adsorption capacity metal cation among other substances dissolved (Pal and Paul 2008). Intrinsic rigidity and binding potency of MBBM show a significant effect on the destruction of natural resources from both biological and environmental perspectives. The interrelationship between MBBM anthropogenic and natural environments allow MBBM to have a direct effect on the operation of the environment (Tourney and Ngwenya 2014).

23.13 Engineering Rebellion Proposal

As an environmentally friendly and infrastructural possible solution to mainstream wastewater management become more extremely important. The sectors of the economy give attention to something like the mechanism of microorganisms and their membrane-binding biopolymer matrix in the removal of heavy metals (Biswas et al. 2020). Scientists have discovered that attempting to apply microalgae to industrial wastewater with such a membrane-bound biopolymer matrix helps to remove cadmium. Membrane biopolymer structure can bind and capture of toxic compounds. Hazardous waste infrastructure may enhance by diverse oxidizing agents when applying it to sewage by effectively managing the Membrane Binder Biopolymer matrix (Duque et al. 2019). The MBBM secrete enzymes include oxidoreductase and hydrolase that are capable of dissolving gas, oil, and lubricant (Goel et al. 2020). The capacity of polycyclic sweet-scented hydrocarbon degradation controlled by the consistency of the membrane-bound biopolymer network of the complementary and unclean habitats. The unhygienic habitat contains polynuclear sweet-smelling hydrocarbons from partial burning of carbon-based products such as lubricating oil, manure, industrial debris, and tobacco. *Aspergillus niger* is

naturally involved in the potential removal of such toxic compounds polycyclic aromatic hydrocarbons (PAHs) (Balaji et al. 2014).

This effective technique sufficiently demonstrates the comparative comfort of potential application, very successful, and very environmentally friendly (Zhou and Gao 2019; Storey et al. 2018). Over the last few years, biopolymer matrixes of marine bacteria discovered to progressive accelerate the level of remediation of waste oil materials. MBBM produces beneficial bacteria, developed, designed, and implemented, were able to scale up and propagate rapidly during the British Petroleum deep-water horizon explosion. It was investigated and found to dissolve the oil and form oil aggregates in their membrane-binding biopolymers on the surface of the ocean, thus enhancing the performance of cleaning. (Alejandra 2020; White et al. 2020). Many such petroleum products admixtures have offered numerous different aquacultures with a potentially useful source of bioactive compounds. It encourages analysts to identify and facilitate better being used in this environment to evaluate and accelerate the use of the membrane biopolymer matrix for eutrophication, oil slicks, and marine pollution (Alejandra 2020; White et al. 2020).

23.14 Conclusion

Many microorganisms that exist in an unfavorable polluted biosphere may encompass probiotics biofilms-intermediated bioremediation "PBIB" for strengthening sustainability. Many pathogens throughout the infected biosphere can require the intermediate "PBIB," biofilm probiotics, for ecology enhancement. Now become a potential outlet for the solution of numerous biological toxins that they have shown due to dynamic architecture. Suppose it depends mostly on observational data of numerous researches, in situ, and ex situ biological treatment successfully applied to simple or combination microorganisms in specific biosphere. This critique has encouraged development, improvement of different types of microbial probiotic attack in contaminated biosphere by innovating and improving throughout microbial populations' scientific knowledge all over the biosphere. The ecological modernization of sustainable and environmentally friendly technologies in the potential field of environmental parameters developed even further. The macro-ecosystem epigenetic alteration is adequately investigated for the preparation of bio-engineered probiotic attacks and helping better study aquatic habitats and land-residential plans. The role and function of the "Membrane-Bound -Biopolymer Matrix" MBBM in the bionetworks should not be overlooked or over-reported. Their constructiveness and their cognitive ability enabled them to pursue an unconventional and impactful approach. The role of microbial polysaccharides is very important in ecology. While possible problem in microbiology shown. They have not applied omnipresent. In a short period, microbial polysaccharides proved that they make such a dynamic process competitive. In reality, waste management systems are expensive and effective methods worldwide. MBBM has shown the excellent technique to counter biosphere contamination by dyes and heavy metals, one of the most complicated and challenging pollutants to manage, as a consequence rather than the possible effects

of successful application of both dyestuff and heavy metals. Based on our historiography evaluated, methodologies with development strategies identified to continue serving as an alternative for the removal of hazardous and material recovery from highly contaminated industrial sites. Therefore, we conclude that probiotics processes and phytoremediation showed astonishing results of a significant reduction in metal levels and toxicity, with minimal disturbance to the biosphere. We almost always suspect that these integration services can be through in situ processes in both industrialized and developing economies where rapid population growth, agricultural development, and industrial development are leaving a legacy of biodiversity loss.

References

Afzal I, Shinwari ZK, Sikandar S, Shahzad S (2019) Plant beneficial endophytic bacteria: mechanisms, diversity, host range and genetic determinants. Microbiol Res 221:36–49. https://doi.org/10.1016/j.micres.2019.02.001

Agamennone V, Le NG, van Straalen NM, Brouwer A, Roelofs D (2019) Antimicrobial activity and carbohydrate metabolism in the bacterial metagenome of the soil living invertebrate *Folsomia candida*. Sci Rep 9(1):7308. https://doi.org/10.1038/s41598-019-43828-w

Alejandra B (2020). https://www.nationalgeographic.com/science/2020/04/bp-oil-spill-still-dot-know-effects-decade-later/APRIL20

Allam NG (2017) Bioremediation efficiency of heavy metals and Azo dyes by individual or consortium bacterial species either as free or immobilized cells: a comparative study. Egypt J Bot 57(3):555–564

Amenyogbe E, Chen G, Wang Z et al (2020) The exploitation of probiotics, prebiotics and synbiotics in aquaculture: present study, limitations and future directions.: a review. Aquac Int 28:1017–1041. https://doi.org/10.1007/s10499-020-00509-0

American Society for Biochemistry and Molecular Biology (ASBMB) 2018 Molecular weapons of the plant microbiome. Science daily, www.sciencedaily.com/releases/2018/02/180205154151.htm

Ancheeva E, Daletos G, Proksch P (2020) Bioactive secondary metabolites from endophytic fungi. Curr Med Chem 27(11):1836–1854. https://doi.org/10.2174/0929867326666190916144709

APA citation (2018) Researchers discover how fatal biofilms form. https://phys.org/news/2018-10-fatal-biofilms.html

Bajinka O, Tan Y, Abdelhalim KA, Özdemir G, Qiu X (2020) Extrinsic factors influencing gut microbes, the immediate consequences and restoring eubiosis. AMB Expr 10:130–136. https://doi.org/10.1186/s13568-020-01066-8

Balaji V, Arulazhagan P, Ebenezer P (2014) Enzymatic bioremediation of polyaromatic hydrocarbons by fungal consortia enriched from petroleum contaminated soil and oil seeds. J Environ Biol 35:521–529

Baptista PV, McCusker MP, Carvalho A, Ferreira DA, Mohan NM, Martins M, Fernandes AR (2018) Nano-strategies to fight multidrug resistant bacteria-a Battle of the titan. Front Microbiol 9:1441. https://doi.org/10.3389/fmicb.2018.01441

Benkhaya S, M'rabet S, El Harfi A (2020) Classifications, properties, recent synthesis and applications of azo dyes. Heliyon 6(1):e03271. https://doi.org/10.1016/j.heliyon.2020.e03271

Beth Lebwoh (2011) Need to clean an oil spill? Microbes are key, study says in Earth. https://earthsky.org/earth/need-to-clean-an-oil-spill-microbes-are-key-study-says

Bharagava RN, Saxena G, Mulla SI, Patel DK (2018) Characterization and identification of recalcitrant organic pollutants (ROPs) in tannery wastewater and its phytotoxicity evaluation

for environmental safety. Arch Environ Contam Toxicol 75:259–272. https://doi.org/10.1007/s00244-017-0490-x

Binda S, Hill C, Johansen E, Obis D, Pot B, Sanders ME, Tremblay A, Ouwehand AC (2020) Criteria to qualify microorganisms as "probiotic" in foods and dietary supplements. Front Microbiol 11:1662. https://doi.org/10.3389/fmicb.2020.01662

Biswas JK, Banerjee A, Sarkar B, Sarkar D, Sarkar SK, Rai M, Vithanage M (2020) Exploration of an extracellular polymeric substance from earthworm gut bacterium (*Bacillus licheniformis*) for bioflocculation and heavy metal removal potential. Appl Sci 10(1):349. https://doi.org/10.3390/app10010349

Brodmann T, Endo A, Gueimonde M, Vinderola G, Kneifel W, de Vos WM, Salminen S, Gómez-Gallego C (2017) Safety of novel microbes for human consumption: practical examples of assessment in the European Union. Front Microbiol 8:1725. https://doi.org/10.3389/fmicb.2017.01725

Brugère JF, Hania WB, Arnal ME, Ribière C, Ballet N, Vandeckerkove P, Ollivier B, O'Toole PW (2018) Archaea: microbial candidates in next-generation probiotics development. J Clin Gastroenterol 52(1):S71–S73. https://doi.org/10.1097/MCG.0000000000001043

Catherine RA, Matthew RP (2018) New insight into the early stages of biofilm formation. Proc Nat Acad Sci 115(17):4317–4319. https://doi.org/10.1073/pnas.1804084115

Chang CJ, Lin TL, Tsai YL, Wu TR, Lai WF, Lu CC, Lai HC (2019) Next generation probiotics in disease amelioration. J Food Drug Anal 27(3):615–622. https://doi.org/10.1016/j.jfda.2018.12.011. Epub 2019 Feb 2. PMID: 31324278

Chin VK, Yong VC, Chong PP, Amin Nordin S, Basir R, Abdullah M (2020) Mycobiome in the gut: a multiperspective review. Mediat Inflam 2020:9560684. https://doi.org/10.1155/2020/9560684

Chooruk A, Piwat S, Teanpaisan R (2017) Antoxidant activity of various oral *Lactobacillus* strains. J Appl Microbiol 123:271–279

Chung WSF, Walker AW, Louis P, Parkhill J, Vermeiren J, Bosscher D, Duncan SH, Flint HJ (2016) Modulation of the human gut microbiota by dietary fibres occurs at the species level. BMC Biol 14:3–11

Contreras-Cortés AG, Almendariz-Tapia FJ, Cortez-Rocha MO, Burgos-Hernández A, Rosas-Burgos EC, Rodríguez-Félix F, Gómez-Álvarez A, Quevedo-López MA, Plascencia-Jatomea M (2020) Biosorption of copper by immobilized biomass of *Aspergillus australensis*. Effect of metal on the viability, cellular components, polyhydroxyalkanoates production, and oxidative stress. Environ Sci Pollut Res 27:28545–28560. https://doi.org/10.1007/s11356-020-07747-y

Cutcliffe T (2017) Probiotics offer prospect of cheap, eco-friendly nanoparticles. https://www.nutraingredients.com/Article/2017/07/28/Probiotics-offer-prospect-of-cheap-eco-friendly-nanoparticles

Dal Grande F, Rolshausen G, Divakar PK, Crespo A, Otte J, Schleuning M, Schmitt I (2018) Environment and host identity structure communities of green algal symbionts in lichens. New Phytol 217:277–289

Davani-Davari D, Negahdaripour M, Karimzadeh I, Seifan M, Mohkam M, Masoumi SJ, Berenjian A, Ghasemi Y (2019) Prebiotics: definition, types, sources, mechanisms, and clinical applications. Foods 8(3):92–103. https://doi.org/10.3390/foods8030092

de Carvalho CCCR (2018) Marine biofilms: a successful microbial strategy with economic implications. Front Mar Sci 5:126. https://doi.org/10.3389/fmars.00126

De Prisco A, Mauriello G (2016) Probiotication of foods: a focus on microencapsulation tool. Trends Food Sci Technol 48:27–39

Dick BJ, Stucki G (2020) Perspectives of genetically engineered microbes for groundwater bioremediation. Environ Sci: Processes Impacts 22:487–499

Dong CJ, Wang LL, Li Q, Shang QM (2019) Bacterial communities in the rhizosphere, phyllosphere and endosphere of tomato plants. PLoS One 14(11):e0223847. https://doi.org/10.1371/journal.pone.0223847

Donlan RM (2002) Biofilms: microbial life on surfaces. Emerg Infect Dis 8(9):881–890. https://doi.org/10.3201/eid0809.020063

Duque D, Montoya C, Botero LR (2019) Cadmium (cd) tolerance evaluation of three strains of microalgae of the genus *Ankistrodesmus*, *Chlorella* and *Scenedesmus*. Rev Facult Ingen Univers Antioq 92:88–95. https://doi.org/10.17533/udea.redin.20190523

Durazzo A, Nazhand A, Lucarini M, Atanasov AG, Souto EB, Novellino E, Capasso R, Santini A (2020) An updated overview on nanonutraceuticals: focus on nanoprebiotics and nanoprobiotics. Int J Mol Sci 21:2285. https://doi.org/10.3390/ijms21072285

Ebrahimi S, Jalili H, Khajeh K, Akbari Noghabi K, Tajabadi Ebrahimi M, Amrane A (2019) Production and characterization of biosurfactants using bacteria isolated from acidic hot springs. Appl Food Biotechnol 6(2):127–138. https://doi.org/10.22037/afb.v6i2.23663

Edwards SJ, Kjellerup BV (2013) Applications of biofilms in bioremediation and biotransformation of persistent organic pollutants, pharmaceuticals/personal care products, and heavy metals. Appl Microbiol Biotechnol 97:9909–9921. https://doi.org/10.1007/s00253-013-5216-z

FAO/WHO (2001) Expert consultation on evaluation of health and nutritional properties of probiotics in food including powder milk with live lactic acid bacteria, 1–4 October

FAO/WHO (2002) Working group report on drafting guidelines for the evaluation of probiotics in food London, Ontario, Canada, 30 April–1 May

Feng P, Ye Z, Han H et al (2020) Tibet plateau probiotic mitigates chromate toxicity in mice by alleviating oxidative stress in gut microbiota. Commun Biol 3(1):242–247. https://doi.org/10.1038/s42003-020-0968-3

Fenster K, Freeburg B, Hollard C, Wong C, Rønhave Laursen R, Ouwehand AC (2019) The production and delivery of probiotics: a review of a practical approach. Microorganisms 7(3):83. https://doi.org/10.3390/microorganisms7030083

Ferdous MF, Arefin MS, Rahman MM, Ripon MMR, Rashid MH, Sultana MR, Hossain MT, Ahammad MU, Rafiq K (2019) Beneficial effects of probiotic and phytobiotic as growth promoter alternative to antibiotic for safe broiler production. J Adv Vet Anim Res 6 (3):409–415. https://doi.org/10.5455/javar.2019.f361

Fu N, Huang S, Xiao J, Chen XD (2018) Producing powders containing active dry probiotics with the aid of spray drying. Adv Food Nutr Res 85:211–262. https://doi.org/10.1016/bs.afnr.2018.02.003

Ghosh PK, Maiti TK (2016) Structure of extracellular polysaccharides (MBBM) produced by rhizobia and their functions in legume–bacteria symbiosis: a review. Achieve Life Sci 10 (2):136–143. https://doi.org/10.1016/j.als.2016.11.003

Giavasis I, Seviour RJ, Hudman P, McNeil B (2020) Fungal bioproducts for use in food: polysaccharides, organic acids, and mycoprotein

Gibson GR, Roberfroid MB (1995) Dietary modulation of the colonic microbiota: introducing the concept of prebiotics. J Nutr 125:1401–1412

Giese EC, Silva DDV, Costa AFM, Almeida SGC, Dussán KJ (2020) Immobilized microbial nanoparticles for biosorption. Crit Rev Biotechnol 40(5):653–666. https://doi.org/10.1080/07388551.2020.1751583

Goel A, Halami PM, Tamang JP (2020) Genome analysis of *Lactobacillus plantarum* isolated from some Indian fermented foods for bacteriocin production and probiotic marker genes. Front Microbiol 11:40. https://doi.org/10.3389/fmicb.2020.00040

Goyal P, Belapurkar P, Kar A (2019) A review on in vitro and in vivo bioremediation potential of environmental and probiotic species of *Bacillus* and other probiotic microorganisms for two heavy metals, cadmium and nickel. Biosci Biotech Res Asia 6(1):65–71. https://bit.ly/2VK8qNN

Gupta P, Diwan B (2017) Bacterial exopolysaccharide mediated heavy metal removal: a review on biosynthesis, mechanism and remediation strategies. Biotechnol Rep (Amst) 13:58–71

Harimawan A, PengTing Y (2016) Investigation of extracellular polymeric substances (EPS) properties of *P. aeruginosa* and *B. subtilis* and their role in bacterial adhesion. Colloid Sur B 146:459–467

Harris PBJ, Harrison CJ, Hetherington AM, Williams TA (2020) Phylogenomic evidence for the monophyly of bryophytes and the reductive evolution of stomata. Curr Biol 30(11):2001–2012. e2

Hill C, Guarner F, Reid G, Gibson GR, Merenstein DJ, Pot B, Morelli L, Canani RB, Flint HJ, Salminen S, Calder PC, Sanders ME (2014) The international scientific association for probiotics and prebiotics consensus statement on the scope and appropriate use of the term probiotic. Nat Rev Gastroenterol Hepatol 11:506–514. https://doi.org/10.1038/nrgastro.2014.66

Hossain K, Rao AR (2014) Environmental change and it's affect. Eur J Sustain Dev 3(2):89–96

Ibrahim E, Zhang M, Yang Z, Hossain A, Qiu W, Chen Y, Wang Y, Wu W, Sun G, Li B (2020) Green-synthesization of silver nanoparticles using endophytic bacteria isolated from garlic and its antifungal activity against wheat fusarium head blight pathogen fusarium graminearum. Nanomaterials 2020(10):219. https://doi.org/10.3390/nano10020219

Igiri BE, Okoduwa SI, Idoko GO, Akabuogu EP, Adeyi AO, Ejiogu IK (2018) Toxicity and bioremediation of heavy metals contaminated ecosystem from tannery wastewater: a review. J Toxicol 2018:2568038. https://doi.org/10.1155/2018/2568038

Jackson SA, Schoeni JL, Vegge C, Pane M, Stahl B, Bradley M, Goldman VS, Burguière P, Atwater JB, Sanders ME (2019) Improving end user trust in the quality of commercial probiotic products. Front Microbiol 10:739. https://doi.org/10.3389/fmicb.2019.00739

Jaishankar M, Tseten T, Anbalagan N, Mathew BB, Beeregowda KN (2014) Toxicity, mechanism and health effects of some heavy metals. Interdiscip Toxicol 7(2):60–72

Jaiswal S, Shukla P (2020) Alternative strategies for microbial remediation of pollutants via synthetic biology. Front Microbiol 11:808. https://doi.org/10.3389/fmicb.2020.00808

Jamal M, Ahmad W, Andleeb S, Jalil F, Imran M, Nawaz MA, Hussain T, Ali M, Rafiq M, Kamil MA (2018) Bacterial biofilm and associated infections. J Chin Med Assoc 81(1):7–11. https://doi.org/10.1016/j.jcma.2017.07.012

Jiménez-Gómez A, Celador-Lera L, Fradejas-Bayón M, Rivas R (2017) Plant probiotic bacteria enhance the quality of fruit and horticultural crops. AIMS Microbiol 3:483–501

Jost T, Lacroix C, Braegger C, Chassard C (2015) Impact of human milk bacteria and oligosaccharides on neonatal gut microbiota establishment and gut health. Nutr Rev 73:426–437

Jurić S, Stracenski KS, Król-Kilińska Ż, Žutić I, Uher SF, Đermić E, Topolovec-Pintarić S, Vinceković M (2020) The enhancement of plant secondary metabolites content in *Lactuca sativa* L by encapsulated bioactive agents. Sci Rep 10:3737. https://doi.org/10.1038/s41598-020-60690-3

Kapahi M, Sachdeva S (2019) Bioremediation options for heavy metal pollution. J Health Pollu 9 (24):191203–119209

Karimi S, Azizi F, Nayeb-Aghaee M, Mahmoodnia L (2018) The antimicrobial activity of probiotic bacteria Escherichia coli isolated from different natural sources against hemorrhagic *E. coli* O157:H7. Electron Phys 10(3):6548–6553. https://doi.org/10.19082/6548

Karygianni L, Ren Z, Koo H, Thurnheer T (2020) Biofilm matrixome: extracellular components in structured microbial communities. Trends Microbiol 28(8):668–681. https://doi.org/10.1016/j.tim.2020.03.016

Khangwal I, Shukla P (2019) Potential prebiotics and their transmission mechanisms: recent approaches. J Food Drug Anal 27:649–656

Kozyrovska NO, Reva OM, Goginyan VB, Devera JP (2012) Kombucha microbiome as a probiotic: a view from the perspective of post-genomics and synthetic ecology. Biopolym Cell 28 (2):103–113

Kumar N, Kumar V, Panwar R, Ram C (2017) Efficacy of indigenous probiotic *Lactobacillus* strains to reduce cadmium bioaccessibility-an in vitro digestion model. Environ Sci Pollut Res Int 24(2):1241–1250. https://doi.org/10.1007/s11356-016-7779-6

Kumari B, Mani M, Solanki AC, Solanki MK, Hora A, Mallick MA (2020) Phytobiome engineering and its impact on next-generation agriculture. In: Solanki M, Kashyap P, Kumari B (eds) Phytobiomes: current insights and future vistas. Springer, Singapore. https://doi.org/10.1007/978-981-15-3151-4_15

Le B, Yang SH (2019) Biosorption of cadmium by potential probiotic *Pediococcus pentosaceus* using in vitro digestion model. Biotechnol Appl Biochem 66(4):673–680. https://doi.org/10.1002/bab.1783

Lee Y, Lee Y, Jeon CO (2019) Biodegradation of naphthalene, BTEX, and aliphatic hydrocarbons by *Paraburkholderia aromaticivorans* BN5 isolated from petroleum-contaminated soil. Sci Rep 9:860. https://doi.org/10.1038/s41598-018-36165-x

Leonhardt S, Hoppe B, Stengel E, Noll L, Moll J, Bässler C, Dahl A, Buscot F, Hofrichter M, Kellner H (2019) Molecular fungal community and its decomposition activity in sapwood and heartwood of 13 temperate European tree species. PLoS One 14(2):e0212120. https://doi.org/10.1371/journal.pone.0212120

Li M-h, Gao X-y, Li C, Yang C-l, Chang-ai F, Liu J, Wang R, Chen L-x, Lin J-q, Liu X-m, Lin J-q, Pang X (2020) Isolation and identification of chromium reducing Bacillus Cereus species from chromium-contaminated soil for the biological detoxification of chromium. Int J Environ Res Public Health 17:2118. https://doi.org/10.3390/ijerph17062118

Lo Giudice A, Poli A, Finore I, Rizzo A (2020) Peculiarities of exopolysaccharides (EPS) produced by Antarctic bacteria and their possible applications. Appl Microbiol Biotechnol 104:2923–2934. https://doi.org/10.1007/s00253-020-10448-8

Maftei NM (2019) Probiotic, prebiotic and synbiotic products in human health. In: Solís-Oviedo RL, de la Cruz Pech-Canul Á (eds) Frontiers and new trends in the science of fermented food and beverages. IntechOpen, New York. https://doi.org/10.5772/intechopen.81553

Maldonado Galdeano C, Cazorla SI, Lemme Dumit JM, Vélez E, Perdigón G (2019) Beneficial effects of probiotic consumption on the immune system. Ann Nutr Metab 74:115–124. https://doi.org/10.1159/000496426

Manobala T, Shukla SK, Rao TS, Kumar MD (2019) A new uranium bioremediation approach using radio-tolerant *Deinococcus radiodurans* biofilm. J Biosci 44(5):122–128

Markowiak P, Slizewska K, Nowak A, Chlebicz A, Zbikowski A, Pawłowski K, Szeleszczuk P (2019) Probiotic microorganisms detoxify ochratoxin a in both a chicken liver cell line and chickens. J Sci Food Agric 99:4309–4318

Mashiane AR, Adeleke RA, Bezuidenhout CC, Chirima GJ (2018) Community composition and functions of endophytic bacteria of Bt maize. S Afr J Sci 114(7/8):0018. https://doi.org/10.17159/sajs.2018/20170018

Mastan A, Rane D, Dastager SG, Vivek Babu CS (2019) Development of low-cost plant probiotic formulations of functional endophytes for sustainable cultivation of *Coleus forskohlii*. Microbiol Res 227:126310. https://doi.org/10.1016/j.micres.2019.126310

Mazzoli A, Donadio G, Lanzilli M, Saggese A, Guarino AM, Rivetti M, Crescenzo R, Ricca E, Ferrandino I, Iossa S, Pollice A, Isticato R (2019) *Bacillus megaterium* SF185 spores exert protective effects against oxidative stress in vivo and in vitro. Sci Rep 9:12082. https://doi.org/10.1038/s41598-019-48531-4

Menéndez E, Paço A (2020) Is the application of plant probiotic bacterial consortia always beneficial for plants? Exploring synergies between rhizobial and non-rhizobial bacteria and their effects on agro-economically valuable crops. Life 10(3):24. https://doi.org/10.3390/life10030024

Mody S (2009) Microbial exopolysaccharides: variety and potential applications. In: Microbial production of biopolymers and polymer precursors. Caister Academic Press, Poole, UK

Mohd Yusof H, Mohamad R, Zaidan UH, Rahman NA (2020) Sustainable microbial cell nanofactory for zinc oxide nanoparticles production by zinc-tolerant probiotic Lactobacillus plantarum strain TA4. Microb Cell Fact 19(1):10. https://doi.org/10.1186/s12934-020-1279-6

Nile SH, Baskar V, Selvaraj D, Nile A, Xiao J, Kai G (2020) Nanotechnologies in food science: applications, recent trends, and future perspectives. Nano-Micro Lett 12:45–51. https://doi.org/10.1007/s40820-020-0383-9

Nurmiyanto A, Kodera H, Kindaichi T, Ozaki N, Aoi Y, Ohashi A (2017) Dominant *Candidatus accumulibacter* phosphatis enriched in response to phosphate concentrations in EBPR process. Microbes Environ 32(3):260–267. https://doi.org/10.1264/jsme2.ME17020

Olivier-Jimenez D, Chollet-Krugler M, Rondeau D, Beniddir MA, Ferron S, Delhaye T, Allard PM, Wolfender JL, Sipman HJM, Lücking R, Boustie J, Le Pogam P (2019) A database of high-resolution MS/MS spectra for lichen metabolites. Sci Data 286(1):294. https://doi.org/10.1038/s41597-019-0305-1

Orhan-Yanıkan E, Gülseren G, Ayhana K (2020) Protein profile of bacterial extracellular polymeric substance by Fourier transform infrared spectroscopy. Microchem J 156:104831–104839

Ott E, Kawaguchi Y, Kölbl D, Chaturvedi P, Nakagawa K, Yamagishi A, Weckwerth W, Milojevic T (2017) Proteometabolomic response of *Deinococcus radiodurans* exposed to UVC and vacuum conditions: initial studies prior to the Tanpopo space mission. PLoS One 12(12): e0189381. https://doi.org/10.1371/journal.pone.0189381

Pal A, Paul AK (2008) Microbial extracellular polymeric substances: central elements in heavy metal bioremediation. Indian J Microbiol 48(1):49–64. https://doi.org/10.1007/s12088-008-0006-5

Parker RB (1974) Probiotics the other half of the antibiotic story. Anim Nutr Health 29:4–8

Pathak VM, Navneet (2017) Review on the current status of polymer degradation: a microbial approach. Bioresour Bioprocess 4:15–22. https://doi.org/10.1186/s40643-017-0145-9

Pereira AL (2017) The unique symbiotic system between a Fern and a Cyanobacterium, Azolla-Anabaena azollae: their potential as biofertilizer, feed, and remediation, symbiosis, Everlon Cid Rigobelo. Intech Open, New York. https://doi.org/10.5772/intechopen.7046

Pereira L, Cotas J (2020) Introductory chapter: alginates – a general overview, alginates – recent uses of this natural polymer. Leonel Pereira, IntechOpen. https://doi.org/10.5772/intechopen.88381. https://www.intechopen.com/books/alginates-recent-uses-of-this-natural-polymer/introductory-chapter-alginates-a-general-overview

Pozo MJ, Albrectsen BR, Bejarano ER, de la Peña E, Herrero S, Martinez-Medina A, Pastor V, Ravnsko S, Williams M, Biere A (2020) New teaching tool, "three-way interactions between plants, microbes, and arthropods (PMA): impacts, mechanisms, and prospects for sustainable plant protection. https://community.plantae.org/article/5540149710167213661/ttpb43

Prince RC, Atlas RM (2016) Bioremediation of marine oil spills. In: Steffan R (ed) Consequences of microbial interactions with hydrocarbons, oils, and lipids: biodegradation and bioremediation. Handbook of hydrocarbon and lipid microbiology. Springer, Cham, pp 1–25. https://doi.org/10.1007/978-3-319-44535-9_13-1

Reyed MR (2007a) Review probiotics: a new strategies for prevention and therapy of diarrhea disease. J Appl Sci Res 3(4):291–299

Reyed MR (2007b) Novel hybrid entrapment approach for probiotic cultures and its application during lyophilization. Internet J Biol Anthropol 3(2):36–41

Reyed MR (2007c) Biosynthesis and properties of extracellular amylase by bioencapsulation *Bifidobatrium bifidum* in batch culture. Australian J Basic Appl Sci 1(1):7–14

Reyed MR (2007d) The role of *Bifidobacteria* in health. Res J Med Medical Sci 2(1):14–24

Reyed MR (2020) Investigation of the antimicrobial resistance wastewater based on public health: is prospective an integrated methodology for coronavirus (Covid-19) outbreak tracking schemes and reoccurrence real-time detection. J Infect Dis Case Rep 1(2):3–5

Roškar I, Švigelj K, Štempelj M, Volfand J, Štabuc B, Malovrh Š, Rogelj I (2017) Effects of a probiotic product containing *Bifidobacterium animalis* subsp. animalis IM386 and *Lactobacillus plantarum* MP2026 in lactose intolerant individuals: randomized, placebo-controlled clinical trial. J Funct Foods 35:1–8

Roy A, Dutta A, Pal S, Gupta A, Sarkar J, Chatterjee A, Saha A, Sarkar P, Sar P, Kazy SK (2018) Biostimulation and bioaugmentation of native microbial community accelerated bioremediation of oil refinery sludge. Bioresour Technol 253:22–32

Suresh Sapare (2018) Development of blended polymeric fibers to alter the release of peptide targeting Porphyromonas gingivalis. Electronic Theses and Dissertations. Paper 2927. https://doi.org/10.18297/etd/292

Sasaki H, Lyu Y, Nakayama Y, Nakamura F, Watanabe A, Miyakawa H, Nakao Y, Shibata S (2020) Combinatorial effects of soluble, insoluble, and organic extracts from Jerusalem

artichokes on gut microbiota in mice. Microorganisms 8(6):954. https://doi.org/10.3390/microorganisms8060954

Scariot MC, Venturelli GL, Prudencio ES, Arisi ACM (2018) Quantification of *Lactobacillus paracasei* viable cells in probiotic yoghurt by *Propidium monoazide* combined with quantitative PCR. Int J Food Microbiol 264:1–7. https://doi.org/10.1016/j.ijfoodmicro.2017.10.021

Sehar S, Naz I (2016) In: Dhanasekaran D, Thajuddin N (eds) Role of the biofilms in wastewater treatment, in: microbial biofilms-importance and applications. IntechOpen, New York. https://doi.org/10.5772/63499

Selvi A, Rajasekar A, Theerthagiri J, Ananthaselvam A, Sathishkumar K, Madhavan J, Rahman PKSM (2019) Integrated remediation processes toward heavy metal removal/recovery from various environments-a review. Front Environ Sci 7:66. https://doi.org/10.3389/fenvs.2019.00066

Sghaier I, Guembri M, Chouchane H, Mosbah A, Ouzari HI, Jaouani A, Cherif A, Neifar M (2019) Recent advances in textile wastewater treatment using microbial consortia. J Textile Eng Fashion Technol 5(3):134–146. https://doi.org/10.15406/jteft.2019.05.00194

Sharma D, Misba L, Khan AU (2019) Antibiotics versus biofilm: an emerging battleground in microbial communities. Antimicrob Resist Infect Control 8:76–82. https://doi.org/10.1186/s13756-019-0533-3

Singh M, Kumar A, Singh R, Pandey KD (2017a) Endophytic bacteria: a new source of bioactive compounds. 3 Biotech 7(5):315–321. https://doi.org/10.1007/s13205-017-0942-z

Singh R, Parihar P, Singh M, Bajguz A, Kumar J, Singh S, Singh VP, Prasad SM (2017b) Uncovering potential applications of cyanobacteria and algal metabolites in biology, agriculture and medicine: current status and future prospects. Front Microbiol 8:515. https://doi.org/10.3389/fmicb.2017.00515

Soliman WS, Shaapan RM, Mohamed LA, Gayed SSR (2019) Recent biocontrol measures for fish bacterial diseases, in particular to probiotics, bio-encapsulated vaccines, and phage therapy. Open Vet J 9(3):190–195. https://doi.org/10.4314/ovj.v9i3.2

Staudt C, Horn H, Hempel DC, Neu TR (2004) Volumetric measurements of bacterial cells and extracellular polymeric substance glycoconjugates in biofilms. Biotechnol Bioeng 88(5):585–592. https://doi.org/10.1002/bit.20241

Storey S, Ashaari MM, Clipson N, Doyle E, de Menezes AB (2018) Opportunistic bacteria dominate the soil microbiome response to phenanthrene in a microcosm-based study. Front Microbiol 9:2815. https://doi.org/10.3389/fmicb.2018.02815

Teng Y, Chen W (2019) Soil microbiomes-a promising strategy for contaminated soil remediation: a review. Pedosphere 29(3):283–297

Titah HS, Pratikno H, Moesriati A (2019) Removal of Iron using isolated bacteria (Vibrio alginolyticus) in seawater at Ship Dismantling Area, E3S Web of Conferences, vol 125, p 03005

Tourney J, Ngwenya BT (2014) The role of bacterial extracellular polymeric substances in geomicrobiology. Cheml Geol 386:115–132. https://doi.org/10.1016/j.chemgeo.2014.08.011

Ullrich M (2009) Bacterial polysaccharides: current innovations and future trends. Caister Academic Press, Poole, UK

Vergani L, Mapelli F, Suman J, Cajthaml T, Uhlik O, Borin S (2019) Novel PCB degrading *Rhodococcus* strains able to promote plant growth for assisted rhizoremediation of historically polluted soils. PLoS One 14(8):e0221253. https://doi.org/10.1371/journal.pone.0221253

Vesty A, Gear K, Boutell S, Taylor MW, Douglas RG, Biswas K (2020) Randomised, double-blind, placebo-controlled trial of oral probiotic *Streptococcus salivarius* M18 on head and neck cancer patients post-radiotherapy: a pilot study. Sci Rep 10:13201. https://doi.org/10.1038/s41598-020-70024-y

Villela HDM, Vilela CLS, Assis JM, Varona N, Burke C, Coil DA, Eisen JA, Peixoto RS (2019) Prospecting microbial strains for bioremediation and probiotics development for metaorganism research and preservation. J Vis Exp 152:e60238. https://doi.org/10.3791/60238

Wang H, Christiansen DE, Mehraeena S, Winning GC (2020) The fight against biofilms: the first six-month study showing no biofilm formation on zwitterionic polyurethanes. Chem Sci 11:4709–4721

Wanka KM, Damerau T, Costas B et al (2018) Isolation and characterization of native probiotics for fish farming. BMC Microbiol 18:119. https://doi.org/10.1186/s12866-018-1260-2

Welman AD (2009) Exploitation of membrane bound biopolymer matrix from lactic acid bacteria bacterial polysaccharides: current innovations and future trends. Caister Academic Press, Poole, UK

White AR, Jalali M, Boufadel MC, Sheng J (2020) Bacteria forming drag-increasing streamers on a drop implicates complementary fates of rising deep-sea oil droplets. Sci Rep 10(1):4305. https://doi.org/10.1038/s41598-020-61214-9

Xu M, Tremblay PL, Jiang L, Zhang T (2019) Stimulating bioplastic production with light energy by coupling *Ralstonia eutropha* with the photocatalyst graphitic carbon nitride. Green Chem 21:2392–2400

Xu X, Peng Q, Zhang Y, Tian D, Zhang P, Huang Y, Ma L, Qiao Y, Shi B (2020) A novel exopolysaccharide produced by *Lactobacillus coryniformis* NA-3 exhibits antioxidant and biofilm-inhibiting properties in vitro. Food Nutr Res 2020:64. https://doi.org/10.29219/fnr.v64.3744

Yadav MK, Singh BP (2019) Current research and future trends in microbial biofilms. In: New and future developments in microbial biotechnology and bioengineering: microbial biofilms. Elsevier, Amsterdam

Yan A, Wang Y, Tan SN, Mohd Yusof ML, Ghosh S, Chen Z (2020) Phytoremediation: a promising approach for revegetation of heavy metal-polluted land. Front Plant Sci 11:359. https://doi.org/10.3389/fpls.2020.00359

Yang X, Liang Q, Chen Y, Wang B (2019) Alteration of methanogenic archaeon by ethanol contribute to the enhancement of biogenic methane production of lignite. Front Microbiol 10:2323. https://doi.org/10.3389/fmicb.2019.02323

Yaseen DA, Scholz M (2019) Textile dye wastewater characteristics and constituents of synthetic effluents: a critical review. Int J Environ Sci Technol 16:1193–1226. https://doi.org/10.1007/s13762-018-2130-z

Yu T, Kong J, Zhang L, Gu X, Wang M, Guo T (2019) New crosstalk between probiotics *Lactobacillus plantarum* and *Bacillus subtilis*. Sci Rep 9:13151. https://doi.org/10.1038/s41598-019-49688-8

Zhang C, Wu D, Ren H (2020) Bioremediation of oil contaminated soil using agricultural wastes via microbial consortium. Sci Rep 10:9188. https://doi.org/10.1038/s41598-020-66169-5

Zhao X, Wang M, Wang H, Tang D, Huang J, Sun Y (2019) Study on the remediation of cd pollution by the biomineralization of urease-producing Bacteria. Int J Environ Res Public Health 16(2):268. https://doi.org/10.3390/ijerph16020268

Zhou Y, Gao X (2019) Characterization of biofilm formed by Phenanthrene-degrading bacteria on rice root surfaces for reduction of PAH contamination in rice. Int J Environ Res Public Health 16 (11):2002. https://doi.org/10.3390/ijerph16112002

Zoghlami A, Paës G (2019) Lignocellulosic biomass: understanding recalcitrance and predicting hydrolysis. Front Chem 7:874. https://doi.org/10.3389/fchem.2019.00874

ISBN - 978-81-951551-5-6

भारताच्या जडणघडणीत महिलांचे योगदान

Peer-Reviewed Book Chapter

संपादक डॉ. अनिल एन. ठाकरे





ISBN-978-81-951551-5-6

भारताच्या जडणघडणीत महिलांचे योगदान

Peer-Reviewed
Book Chapter

संपादक

डॉ. अनिल एन. ठाकरे

सहयोगी प्राध्यापक
श्री गाडगे महाराज महाविद्यालय
मूर्तिजापुर जिल्हा अकोला

आधार पब्लिकेशन, अमरावती

OPPO A9 2020

ISBN-978-81-951551-5-6

१२) भारताच्या जडणघडणीत महीलांचे सामाजिक योगदान /७०
डॉ. महेश प्रल्हादराव गोमासे

१३) महीला सक्षमीकरणातील अडथळे व उपाय /७९
डॉ. विलास आबा गायकवाड

१४) सामाजिक कार्य करणाऱ्या स्त्रियांच्या आत्मचरित्रांचे मराठी साहित्यातील योगदान /८५
प्रा. डॉ. संतोष विष्णू चतुर

१५) भारताच्या जडणघडणीत आधुनिक महिलांचे योगदान /९६
प्रा.दिलीप एम. मोरे

१६) भारताच्या शैक्षणिक जडणघडणीत महिलांचे योगदान: एक शोध. /११०
डॉ.हरिदास देविदास आखरे

१७) वर्धा येथील मावशी केळकर यांचे स्वातंत्रपूर्व काळातील सामाजिक, शैक्षणिक कार्य /११९
प्रा. डॉ. किशोर एच. बारापात्रे

१८) अमरावती जिल्हयातील महिलांचे सामाजिक प्रबोधनाचे कार्य /१२४
डॉ.अमोल रमेशराव बोरकर

१९) वैदर्भिय स्त्री शिक्षणाच्या क्षेत्रात कमलाताई हॉस्पेट व शांताबाई रानीवाला यांचे योगदान /१३०
डॉ. अभिलाषा राऊत,

२०) भारताच्या जडणघडणीत महीलांचे सामाजिक योगदान /१४५
डॉ.कोकीळा अ. गावंडे

२१) स्वराज्याच्या जडणघडणीत महाराणी येसूबाईचे योगदान /१५५
डॉ. विष्णू नामदेव लांडे

OPPO A9 2020

अनुक्रमणिका

१) सावित्रीबाई फुले यांचे शैक्षणिक व सामाजिक क्षेत्रातील योगदान /१
डॉ संजय गोपाळराव ठवळे

२) भारतीय राजकारणात महिलाचे योगदान /८
प्रा. डॉ. विकास चांदजकर

3) एकोणीसाव्या शतकात शैक्षणिक क्षेत्रात स्त्रियांनी केलेल्या संघर्षाचा अभ्यास /११
प्रा. डॉ. भाऊराव रामेश्वर तनपुरे

४) राष्ट्र उन्नतीमध्ये सावित्रीबाई फुलेंचे योगदान / २१
प्रा. डॉ. गजानन लिंबाराव सोडनर

५) वर्धा जिल्ह्यातील उत्कृष्ट व्यक्तिमत्व, शांतीबाई रानीवाला / २९
प्रा. डॉ. रफिक शेख

६) भारताच्या इतिहासातील महिलांचे योगदान / ३७
प्रा. डॉ. एस. व्ही. भुरले

७) भारतीय संगीतात स्त्रियांना स्थान मिळवून देणारी अजरामर गायिका हिराबाई बडोदेकर / ४२
प्रा. डॉ. संचिन सुरेशराव बंडगर

८) राजमाता जिजाबाई यांचे राजकिय योगदान / ४६
प्रा.डॉ.गणेश हरिभाऊ घुगे

९) भारताच्या विकासात महीलांचे योगदान /५०
प्रा. आर.आर.पाटील

१०) बहिणाबाईच्या कवितेतील कृषी जीवनाचे संदर्भ / ५६
प्रा. पुरुषोत्तम एस. निर्मळ

११) भारतीय जडणघडणीच्या इतिहासात स्वातंत्र्यलढ्यातील क्रांतीकारी महिलांचे योगदान / ६४
प्रा.डॉ.निलय देशमुख

OPPO A9 2020

ISBN-978-81-951551-5-6

वर्धा येथील मावशी केळकर यांचे स्वातंत्रपूर्व काळातील सामाजिक, शैक्षणिक कार्य

प्रा. डॉ. किशोर एच. बारापात्रे
आदर्श महाविद्यालय धामणगाव—रेल्वे.
जिल्हा—अमरावती.

भारताच्या राजकीय, सामाजिक, आर्थिक, धार्मिक, शैक्षणिक, साहित्यिक व कलेच्या क्षेत्रातिल जडणघडणीमध्ये ज्या प्रमाणे पुरूषांचे मोठे योगदान आहे. त्याप्रमाणे महिला वर्गाचेही योगदान फार मोठे आहे. महिला वर्गाचीही कामगिरी अनन्यसाधारण आहे. वर्धा जिल्ह्यात महात्मा गांधीच्या प्रेरणेने ई. स. १८८६ मध्ये स्थापन झालेली माहिलाश्रम संस्था म्हणजे स्त्री—कर्तुत्वाचे प्रतिकच होते. राष्ट्रीय आंदोलनात संपूर्ण भारतातून सर्वप्रथम येथीलच स्त्रियांनी सहभाग घेतला होता हे विशेष उल्लेखनीय आहे. वर्धा जिल्ह्यातील स्त्रियांनी राजकीय, सामाजिक, आर्थिक, धार्मिक व ईतर क्षेत्रात जी उल्लेखनीय कामगिरी केली त्या मागील महात्मा गांधी व महिलाश्रम संस्थेची प्रेरणा होती.

वर्धा येथील रहिवाशी असलेल्या मावशी केळकरांचे स्त्री उद्धाराचे व सामाजिक, शैक्षणिक कार्य प्रशंसनीय आहे. त्यांचे पती हरिभाऊ केळकर वर्ध्याचे सुप्रसिद्ध वकील होते. ई. स. १९१९ मध्ये कमल दाते नागपूर यांनी (सौ. मावशी

OPPO A9 2020

ISBN-978-81-951551-5-6

केळकर) हरिभाऊ केळकर यांचेशी विवाह केला. याच दरम्यान डिसेंबर १९२० मध्ये नागपूरला काँग्रेससचे अधिवेशन होते लोकमान्यांच्या मृत्यूनंतर हे पहिलेच अधिवेशन असल्यामुळे साऱ्या देशाचे लक्ष्य अधिवेशनाकडे लागलेले होते. श्री. जमनालाल बजाज व त्यांच्या पत्नी जानकीदेवी बजाज हे दोघेही आले होते. जमनालालजी भाऊसाहेबांचे मित्र असल्यामुळे जानकिबाईचाही मावशी केळकरांशी परिचय होता. जानकीदेवी बजाज आणि मावशी केळकर यांचे संबंध दिवसेंदिवस घनिष्टत्वाचे होत जावून पुढे त्याही स्त्री व समाज उद्धारक आणि राष्ट्रकार्यासाठी समर्पक वृत्तीच्या त्या बनत गेल्या.

वर्धा येथील लक्ष्मीनारायण चौकात १९२१ मध्ये महात्मा गांधीचे भाषण आयोजित केल्या गेले. भाषणाला स्त्री–पुरुषांची अलोट गर्दी होती. मावशी केळकर सुद्धा भाषणाला आवर्जून उपस्थित होत्या. राष्ट्राच्या स्वास्थावरच व्यक्तीचे स्वास्थ्य अवलंबून आहे हा महात्मा गांधीचा संदेश मावशीच्या मनात घर करून गेला. महात्मा गांधींचे भाषण फारच प्रभावी झाले. यावेळी महात्मा गांधीनी आवाहन केले कि, राष्ट्रकार्यासाठी उभारण्यात आलेल्या टिळक फंडासाठी प्रत्येकाने मदत करणे आवश्यक आहे व त्यासाठी प्रत्येकाने हातभार लावावा. स्त्री–पुरुषांच्या जनसमूहात झोळी फिरविण्यात आली. त्या झोळीत जनतेने भराभर पैसे टाकले मावशी केळकर यांनी आपली एकदाणी कशाचाही विचार न करता झोळीत अर्पण

OPPO A9 2020

ISBN-978-81-951551-5-6

केली आणि मावशीनी येथूनच राष्ट्र व समाजकार्याला प्रारंभ केला.

जानकीदेवी बजाज यांच्याशी झालेली मैत्री आणि महात्मा गांधीच्या प्रभावाने मावशीला समाजकार्याची तळमळ निर्माण झालेली होती. अनुसयाबाई काळेच्या महिला उन्नतीच्या कार्याचा प्रभाव संपूर्ण विदर्भावर होता यावेळी मावशीलाही आपण काहीतरी समाजकार्य करावे अशी तळमळ निर्माण झाली. तेव्हा मावशी केळकर यांनी वर्धा येथे काही मैत्रीणीच्या सहकार्याने १९२६ मध्ये भगिनी मंडळाची स्थापना केली. या मंडळात पुस्तकांचे वाचन सुरू झाले. भगिनी एकत्र येवून शिक्षित होऊ लागल्या. वर्धा येथे महाविद्यालय सुरू झालेले असले तरी मुलींच्या शिक्षणाची फारशी काहीच व्यवस्था नव्हती. वर्धा जिल्ह्यात मुलींची एकही माध्यमिक शाळा नव्हती. वर्धा येथे महाविद्यालय स्थापन करण्यात श्री. बाबूराव खरे व मावशीचे दीर यशवंतराव केळकर यांनी पुढाकार घेतला होता मावशी केळकर यांनी पुढाकार घेवून यशवंतराव केळकर यांच्या सहकार्याने १९३६ मध्ये पहिली मुलींची माध्यमिक शाळा स्थापन केली. त्या बरेच वर्ष या संस्थेच्या उपाध्यक्ष राहिल्या.

समाजकार्याचा ध्यास लागलेल्या मावशी केळकरला एखाद्या स्त्री संघटनेची गरज भासू लागली. स्त्री संघटनेसाठी स्त्रीयांनीच पुढाकार घेतला पाहिजे हा विचार त्यांच्या मनात पक्का झाला. नागपूरला राष्ट्रीय स्वयंसेवक संघाची स्थापना १९२५ मध्ये झालेलीच होती. स्त्री उन्नतीची प्रेरणा त्यांना राष्ट्रीय स्वयंसेवक संघापासूनच मिळाली होती. महिला संघटनेची

OPPO A9 2020

ISBN-978-81-

आवश्यकता त्यांनी डॉ. हेडगेवाराना बोलून दाखविली. शेवटी डॉ. हेडगेवाराच्या मार्गदर्शनाने २५ ऑक्टोबर १९३६ रोजी बुलढाण्याचे इतिहास संशोधक डॉ. यादव माधव काळे यांचे हस्ते उद्घाटन होऊन राष्ट्र सेविका समितीची वर्धा येथे मावशी केळकरांच्या पुढाकाराने स्थापना झाली. या संघटनेच्या माध्यमातून स्त्री उन्नतीचे व समाजकार्याचे काम सुरू झाले. तसेच स्त्रीयांना आत्मनिर्भर व स्वयंनिर्भरतेचे धडे देण्यात येऊ लागले. स्त्री वर्ग संघटित झाल्याशिवाय विविध समस्याना वाचा फुटणार नाही याची जाणीव जिल्ह्यातील स्त्री वर्गाला झाली होती याच अनूषंगाणे मावशी केळकर यांनी वर्धा शहरात "महिला समाजाची" ई. स. १९३६ मध्ये स्थापना केली.

१९३६ मध्ये पतीच्या मृत्यूनंतर मावशीनी रूढी, प्रथा. परंपरेचा त्याग केला. त्या काळात महार, मांग, चांभार व इतर तत्सम जातीना अस्पृश्य समजले जात असे. त्या ब्राह्मण असूनही त्यांनी आपल्या घरी घरकामाकरिता महार बाई ठेवली होती त्या बद्दल आजूबाजुला शेजारी चर्चा सुद्धा झाली. पण मावशीनी त्याकडे अजिबात लक्ष्य दीले नाही. मावशीच्या मते, नोकर कोणत्या जातीचा आहे त्यापेक्षा त्याला स्वच्छतेची किती जान आहे हे महत्वाचे आहे. त्या महार बाईला मावशीनी सर्व शिक्षण दिले. सोवळया—ओवळयाच्या भ्रामक कल्पनाना तिलांजलि दिली. मानवजात ही एकच जात आहे असे त्या मानीत असत. त्यांनी जातिभेद न पाळता सर्वच जाती—जमातीच्या स्त्रीयांना संघटीत करण्याचे महत्वपूर्ण कार्य करून शिक्षणाची जाणीव त्यांच्यात निर्माण करून दिली.

OPPO A9 2020

ISBN-978-81-951551-5-6

संदर्भ साधने :

१) महाजन सुशिला, 'वं मावशी केळकर यांचे चरित्र'— मंजरी ताम्हणकर, शिल्पा प्रकाशन पुणे, तृतीय आवृत्ती फेब्रुवारी २००४ पृ. ३५ — ३६

२) बजाज जानकीदेवी, 'माझी जीवनयात्रा' पॉप्युलर बुक डेपो ,मुंबई — ०७, १९६०पृ. १५५

३) वक्काणी, डॉ. नि. भा. 'आधुनिक विदर्भ का इतिहास' — श्री मंगेश प्रकाशन नागपूर — १० पृ २३०

४) पाठक, डॉ. दमयंती, वैदर्भिय महिलांचे स्वातंत्र्य संग्रामातील सहकार्य' श्री मंगेश प्रकाशन नागपूर, आवृत्ती १ ली २००३ पृ. १३७

५) स्वर्णजयंती स्मरणिका, महिला सेवा मंडळ, महिला आश्रम, वर्धा.

2020 - 2021

LangLit

An International Peer Reviewed Open Access Journal

ISSN 2349-5189 / Indexed Journal/ Impact Factor 5.61/ www.langlit.org

Special Issue August 2020

One Day National Level E-Conference

on

Re-reading of English Language & Literature in Current Pandemic Situation

27 August 2020

Chief Editor
Dr. B. S. Kavhar
Head, Dept. of English
Appaswami
Mahavidyalaya,
shendurjana Adhao.

Associate Editors
Prof. A. M. Shekh
Dept. of English
Shri. V N Art's & A N Comm.
College,
Mangrulpir.

: Organised by :

Department of English & IQAC
Appaswami Mahavidyalaya, Shendurjana Adhao

I: Indexed :I
ICI, Google Scholar, Research Gate, Academia.edu.,
181, IIFC, ORJI, The Cite Factor

Scanned with CamScanner

IMPACT FACTOR – 5.61

LangLit

ISSN 2349-5189

An International Peer-Reviewed Open Access Journal

Langlit Latur (MS) India AIPROAJ

SR. NO	NAME OF THE TOPIC	AUTHOR
*.	*CONTENT*	*WWW.LANGLIT.ORG*
#.	*COVER PAGE*	*WWW.LANGLIT.ORG*
1.	RE-READING OF THE ELEMENT OF LOVE AND EVIL IN EMILY BRONTE'S *WUTHERING HEIGHTS*	DR. DEEPAK. T. R.
2.	DEBILITATING CIVILISATION, APOCALYPTIC WORLD, PANDEMIC AND DYSTOPIAN SOCIETY IN ALBERT CAMUS' *THE PLAGUE*	DR. RABIA KHANAM
3.	RE-READING "PALE HORSE, PALERIDER", AS A BIBLICAL METAPHOR FOR PATHETIC PANDEMICS	DR JAGRUTIS.VYAS
4.	A CRITICAL SURVEY OF ANITA DESAI'S SELECTED NOVELS	DR. GHEGADE SHANTILAL INDRABHAN
5.	"THE ROLE OF POETRY AND FICTION IN PANDEMIC"	PROF. RAJENDRA N. KALE
6.	REREADING OF VICTORIAN POETRY	DR. PRACHI SHARAD PATHARKAR
7.	RE–READING OF "QUEST FOR DIASPORIC IDENTITY" IN AMITAV GHOSH' S "THE CIRCLE OF REASON"	DR FURQUAN AHEMAD KHAN CHANDKHAN PATHAN
8.	RE-READING OF FEMALE FOETICIDE AND WOMEN EMPOWERMENT IN THE CURRENT PANDEMIC SITUATION	MRS. SAVITA A P DR. C BASAVARAJU
9.	RE-READING LITERATURE RESEMBLING TO RECENT PANDEMIC WITH REFERENCE TO QUAMEN'S SPILLOVER	MR. D. B. WANKHADE
10.	SEARCH FOR IDENTITY AND THE SPIRIT OF REVOLT: RE-READING OF THE FICTIONAL WORLD OF INDIAN WOMEN NOVELISTS	DR. RAJESH G. MASKE
11.	RE-READING OF POST-COLONIAL DISCOURSE IN THE POETRY OF KAMALA DAS	DR. SANJAY. S. TAMGADGE
12.	RE-READING WHITE RACISM, NEGROPHOBIA AND THE PLIGHT OF AFRICAN-AMERICANS	DR. SHYAM M. GEDAM

Scanned with CamScanner

IMPACT FACTOR – 5.61

LangLit

ISSN 2349-5189

An International Peer-Reviewed Open Access Journal

Langlit Latur (MS) India AIPROAJ

RE–READING OF "QUEST FOR DIASPORIC IDENTITY" IN AMITAV GHOSH' S "THE CIRCLE OF REASON"

DR. FURQUAN AHEMAD KHAN CHANDKHAN PATHAN
ASSISTANT PROFESSOR
DEPARTMENT OF ENGLISH
ADARSHA SCIENCE, J. B. ARTS & BIRLA COMMERCE COLLEGE
DHAMANGAON RLY, DIST-AMRAVATI (MS) INDIA
EMAIL- PATHANFURQUAN@GMAIL.COM
CONTACT NO. +917875383639

ABSTRACT

This paper aims to re-read the Amitav Ghosh's The Circle of Reason and to show the quest for diasporic identity reflected in the given novel. Amitav Ghosh, an author of Indian origin who at present separates his time between New York, Calcutta and Goa, focuses on the Indian Diaspora of the 19th century. As he travelled in many countries along with lived in different places; his imagination becomes purely diasporic. He remains an Indian even though he lived in foreign.

KEYWORDS: Diaspora, Identity, the Circle of Reason.

INTRODUCTION

Amitav Ghosh explains in his essay "The Diaspora in Indian Culture" that diasporic Indians takes with them not so much things but they carry processes: "India exported with her population….not a language, as other civilizations have done, but a linguistic process…..the process of adaptation to heteroglossia." R. S. Pathak rightly remarks: "Though a gifted craftsman, the novelist never ceases to be an Indian even in his superb flights of fantasy, which impart to his novels the folktale charm of the Arabian Nights and make him a Don Quixote of another era."

Amitav Ghosh finds importance in the diaspora as it catches the attention towards the edges of culture and which is nothing but an eminent mark of Indian culture. He involves the idea

Scanned with CamScanner

of a perfect cultural identity which heteroglossia rejects. His life possesses different colours of movements not only across geographic but also cultural boundaries where diaspora gives a precious transnational viewpoint in order to undermine harmonized commencements of national identity. He got a unique insight for the processes of cultural presentation from his rigorous travelling in different countries; he also understands the culture of many countries such as Middle East.

His first novel, "The Circle of Reason" (1986) gets a prominent place in the galaxy of postcolonial diasporic existence by showing the condition of people who lost their home and become migrant in search of their livelihood. The novel reflects the transcultural nature of human experience. Actually there are three stories in the novel which move around the three important characters-the first part of the novel tells the story of Balaram Bose who is highly inspired by the book 'Life of Pasteur' and the devoted follower of Louis Pasteur. Balaram Bose, the village school master, works with his target to eradicate germs from public life which makes him self-destructive as he gets engaged with his revise ego, Bhudeb Roy, a crooked landlord and a congress man, who establishes his control over the school management. Balaram gets dismiss from his job of teacher from the school as he stands against the Bhudeb Roy and the conflict between Bhudeb Roy and Balaram Bose ends at the point when Balaram's house was burnt in which Balaram and his wife were killed excluding Alu, the orphan boy whose parents had died in a car accident and due to this he left Calcutta and lived with his childless uncle, Balaram Bose and aunty, Torudebi at Lalpukar, a small village. Bhudeb Roy denounces Alu as a terrorist. And Alu's diasporic journey starts; he runs away from Lalpukur in order to escape from Jyoti Das, the policeman who is in search of Alu, and takes refuge in Gopal's house (his uncle's friend) at Calcutta. And from Calcutta he flees to Kerala; then he begins his journey to al-Ghazira in the company of the Calcutta whores Zindi, Kulfi and Karthamma.

The second part of the novel moves around Zindi-at-Tiffaha who handles to collect a community of Indians in the Middle East. Alu sets sail for al-Ghazira with Zindi. All the passengers on the steamer, Mariamma, have been dislocated from their inhabitant place; most of them not having valid passport or other legal document which is required to get entry in

Scanned with CamScanner

any country and they all are labourers. They migrate to other countries in order to secure better life because in most of the overpopulated countries in Asia, the labour is very cheap. Zindi-at-Tiffaha leads this group and she works for trafficking women to al-Ghazira. Karthamma, a tall back lady, finds herself in difficult situation on the steamer as she is on her last stage of her pregnancy. She is deceived by someone who made her pregnant. She is not in favour to give birth to her baby who is in her womb but is convinced that if she may get to al-Ghazira her child will get, "houses and cars and multi-storeyed buildings" (CR-177). She also does not have the visa or passport and she is totally unaware about difficulties and problems regarding her migration as well as her migrant life in other country along with she does not know the procedure which is required for migration. She herself requested to Zindi to take her away from India. This shows that she herself chooses to migrate. Most of the passengers take the journey to al-Ghazira in order to flee from police or court of law in India. Kulfi, another passenger on the board of the ship, is willingly migrating to al-Ghazira as her marriage life was not sound. Kulfi's husband's insufficient income created terrible situation for her as her husband enforced her to whoring. In order to get honest work she came to Zindi in Bangalore and like Karthamma, Kulfi too requested to Zindi to take her away from India. On arrival they find accommodation in Zindi's house that affords shelter for a group of migrants from the Indian subcontinent as well as from Egypt along with North Africa. Amitav Ghosh skillfully represents the diasporic life of the migrants in the apartment of Zindi. Here all the migrants try their luck in different fields such as business, weaving and tailoring by facing various problems like rootlessness and alienation. They all get refuge under the roof of Zindi's apartment.

The third part of the novel revolves around Mrs. Verma, the microbiologist who develops an oasis in the desert for Indian community life. The refugees come across the Dr. Uma Verma, an Indian lady doctor, who becomes hospitable on seeing Indian travellers. Amitav Ghosh rightly remarks:

"It is impossible to be imperfectly Indian…..If there is any one pattern in Indian culture in the broadest sense it is simply this: that the culture seems to be constructed around the proliferation of differences (albeit within certain parameters). To be different in a world of

Scanned with CamScanner

differences is irrevocably to belong. Thus, anybody anywhere who has even the most tenuous links with India; potentially a player within the culture. The mother country simply does not have the cultural means to cut them off." [3]

As this new place required a new identity, Kulfi on the suggestion of Zindi acts as a wife of Alu and the mother of Boss along with she tells Dr. Verma that she is here with her family as a tourists whereas Zindi plays the role of Ayah of Boss.

The novel begins with the incidental annotations on Indian migrations. For instance, the birth of Balaram in the year 1924 recalls the narrator of critical moments in the history of Indian emigration to the West. In this section Amitav Ghosh supplies many examples of Diaspora. As the people of Lalpukur threw up from their native place in the bloodshed attached with the partition of India and again they faced the same due to the civil war which gave birth to Bangladesh. The focal point of the novel perfectly reflects the Amitav Ghosh's diasporic awareness when Alu wanders throughout the India as well as Middle East. Alu starts his journey to Calcutta at first then moves to the South in order to escape from the clutches police and at last he arrives to Kerala, with Jyoti Das in pursuit. But he never stops his journey; he migrates to al-Ghazira in the Persian Gulf port, he continues his diasporic move on a boat to al-Ghazira.

Through the diasporic journey of Alu, Amitav Ghosh very competently represents the menaces which are faced by the thousands of Indian who abscond their native place in order to secure a peaceful life. But these unlawful expatriates create a danger for them which totally disturb their lives. Kavita Daiya rightly writes:

"Focusing on a motley group of illegal migrants drawn from various parts of India who travel to the imaginary Gulf state al- Ghazira and then Algeria, the novel depicts the struggle for survival of those displaced by dispossession in globalization: people whose very bodies bear the violent marks of this historical passage."

Amitav Ghosh shows the variety of passengers on a mechanized boat on which Alu is crossing the Indian Ocean such as there is a travelling salesman, a professor, etc. "The illegal

Scanned with CamScanner

migrant laborers heading for al-Ghazira, an imaginary seaport of trade, include the child-protagonist Alu who is evading Indian police who are after him because of an absurd charge made by the corrupt village landlord Bhudeb Roy and the Egyptian Zindi, who runs a lodging and boarding house for illegal migrant workers in al-Ghazira after she was banished from her matrimonial home." Amitav Ghosh also depicts the reasons for their emigration, for instance a woman who is pregnant migrates to al-Ghazira as she has been promised by someone that he will provide everything to her future's child in al-Ghazira. This al-Ghazira's part of the novel represents the Amitav Ghosh's enthrallment with a diasporic awareness as well as the unstable existences of the migrant workers. This section depicts the trap and burial of Alu in "The Star", the multi-storeyed building which collapses due to false workmanship. Fortunately Alu is saved by an old solid sewing machine on which the falling slab takes to rest.

CONCLUSION

Amitav Ghosh here in this novel shows the terrible suffering of the displaced people. He actually wants to focus on the problems which are faced by the immigrants such as language problem, food along with social problem including economic also. The novel very perfectly represents: "If there is a home then it is to be found in the way we perceive and relate to our world."

REFERENCES

1. Pathak, R. S. Recent Indian Fiction, Prestige Books: New Delhi, 1994.P.18
2. Ghosh, Amitav, 'The Diaspora in Indian Culture', Public Culture, 2.1,1989. P. 75
3. Ghosh, Amitav, 'The Diaspora in Indian Culture' in The Imam and the Indian. Ravi Dayal Publishers, Delhi, 2002.P.250
4. Daiya, Kavita. "Home and the nation: Women, citizenship and transnational migration in postcolonial literature." Journal of Postcolonial Writing, 44.4, Dec. 2008. P.392-393
5. Ibid. P.393
6. Dutta, Pradip. "A Voice Among Bullet Holes" Novel of Amitav Ghosh, Ed. R. K. Dhawan, Prestige, New Delhi, 1999. P.42

Scanned with CamScanner

Framework of Language, Literature and Communication

Tracing Harmony and Culture through English

EDITORS

DR. G. SUNEETHA BAI
DR. HEMAMALINI N.
MS. V. KANCHANA

Scanned with CamScanner

Framework of Language, Literature and Communication

Tracing Harmony and Culture through English

EDITORS

DR. G. SUNEETHA BAI

DR. HEMAMALINI N.

MS. V. KANCHANA



AUTHORS PRESS

Scanned with CamScanner

Contents

Preface
Prof. Dr. G. Suneetha Bai 5

Preface
Dr. Hemamalini N. 7

Preface
Kanchana V. 9

Foreword
Dr. Angel Ruth 11

Foreword
Hemant Gahlot 15

Introduction 23

1. Teaching Oral Communication Skills of French as a Foreign Language through Podcasts 31
Dr. Walter Hugh Parker and **Pritha Basu**

2. Analysis and Uses of Second Language Learning: A Research 40
Dr. Susheela B.

3. Strategies in Teaching English Language in Undergraduate Level: An Evaluation 48
Dr. Lt Indrani M.R.

4. Learning Polite Turns in Group Discussion: Perspective of Indian Engineering Students in ESL Context 55
Dr. D. Ravi and **Dr. K. Venkat Reddy**

5. Cyber World and the Language of Media are Constructive or Destructive in Making Women Image in India 80
Dr. Abha Singh

6. Exploring the Role of Language and Communication at Workplace 89
Shruti Mishra

Scanned with CamScanner

7. Malayalam Kinship Terms as Terms of Address and Reference: A Sociolinguistic Study 99
Rosmin B. Joseph

8. The Linguistics in the Vedas 108
Dr. Vedprakash Borkar

9. Evolution of English Language as a Global Language 115
Dr. Alekya Chalumuri

10. Trajectories of Language and Identity Politics among Tribals in India 122
Dr. Saheli Guha Neogi Ghatak

11. Innovative Teaching of English Literature in Virtual Classroom 128
Dr. Pinky Sagolsem

12. English as a Global Language: A Historical Survey 134
Mamta

13. Subtle Complexities in Language Education and Teaching 141
Dr. Pratik O. Khaire

14. Reinforcing Human Values through Poetry to Ensure Harmony 151
Dr. Shalini Yadav

15. Importance of Pronunciation for Effective Oral Communication in English 158
Dr. Alka Bansal

16. Empowering Rural Students with Communicative English 169
Barulkar Jeetendrasingh

17. Building World Harmony through Language and Communication 178
Vanita Nagabhushan and **Nalini Purushothama**

18. Harmony, The Nation and the World-Welfare 187
Dr. Vedprakash Borkar

19. English Language and Employability in India: The Chinese Case Referred 197
Dr. Anupama Rawat and **Dr. Tanima Dutta**

20. Competence in Intercultural Communication: A Study in the Perspectives of Indo-Russian Ventures 206
Dr. Sharda Acharya and **Dr. K. P. Singh**

Scanned with CamScanner

CHAPTER 16

Empowering Rural Students with Communicative English

Barulkar Jeetendrasingh

Communication in English and related soft skills is a major differentiator in the career opportunities of today's youth. The students from traditional courses and particularly from colleges in rural areas are facing a disadvantage while entering work life. The placement of urban area college students is distinctly high compared to rural area. Over the years it has been noticed that skills like – listening, speaking, reading and writing involve more than just grammar and vocabulary. Many of our brilliant students fail to create a good impression simply because they lack required language competence (communicative competence). There is a wide gulf between regional students' speaking skills and the requirements/ expectations of the corporate world or the industry. It's because the importance of speaking skills in English has been overlooked by most of the students and the institutes.

The present paper attempts to fill in this gap. It won't be sufficient to introduce a course in Communication Skills or in English because the problem is more with awareness of our students than with English as a language. We have done a survey of about 200 students in order to get details regarding their language competence. After knowing their difficulties, we exercised some innovative techniques with these students in our institute. We have taken feedback, evolved/ developed some methods to improve speaking skills. The paper will conclude with outcomes and suggestions for empowering students with communicative English and Soft Skills.

Introduction

It has been observed that English Language Proficiency plays a great role in the process of employment. The recruiters expect interview candidates to be confident in English language and overall

Scanned with CamScanner

communication skills. Most of the researchers agree that Employability has become a major factor in English Language Learning. More importantly it has become a point of focus in a candidate or an employee's life. English Language learning has now a days become more of effective communication and soft skills than just grammar and literature. It is observed that the key is going to be Effective Communication in English and Soft Skills for jobs beyond 2025.

In an extensive survey, it has been found that certain groups of students who are fluent in English do well in the interviews and their chances of selection are pretty high. The problem is clearly evident in the rural areas or the students coming from the rural background where there is a great fear of the language. Since, language skills and soft skills have acquired a great weight age in the process of getting a job and the world is changing in terms of global market and competitiveness we can't afford to ignore the role of English language in the process of employment and success in their career. As most of the businesses nowadays are multi-national, the working environments have dramatically changed. Both the employer and the employee are in need to upgrade themselves. With English becoming language of most of the businesses and services, there has been unprecedented growth in the need of English language skill to communicate with the clients, both national and international.

In the globally connected market, English Language for business communication is considered to be a great asset for a candidate. English language proficiency helps the businesses ensure the outcomes of deals and corporate interactions in their favour. It is always a profitable deal for the corporate to have competent employees. This is the reason why employers, during placement drives, look for candidates with such competencies.

As already stated, professional institutes have started to ensure that English as a skill is given due importance in its curriculum. But most of the traditional courses still lack this awareness. These are still focusing on age old practices of learning language through prose, poetry, grammar and composition. We need to prepare our students for successfully cracking their interviews and helping them enter the job market. These students are continuously expected to upgrade their skills to stand themselves in the competitive professional world. A course that is designed to provide the students with ample opportunities in listening and practical speaking in English is helpful

Scanned with CamScanner

in such a scenario. Students who may not have had the opportunity to use English as their language of everyday transaction benefit from such a course while the language proficiency of other students will also improve.

Challenges/ Obstacles

In our study on rural students' English language competence, we observed that they have certain common needs and the challenges faced by teachers were more or less the same. The most common issues are …

Students' Background

The primary focus of the article is to understand the role of English language competence in the employability of the rural background students. The students from these areas were found to be under the impact of their rural environment. The kind of language they use is not suitable for careers in multi-national companies or the service sectors in metropolitan regions. They had a great impact of their rural accent and lack of courage to speak in English. Their basics were not clear, they had very less awareness about voice modulation. Most of the students from have illiterate parents. These things play a great role in shaping of personality and ability to communicate. Since we can't change the situation, we have to find out some methods to overcome this challenge.

Lack of Environment

It is rightly said that man is shaped by his environment. It is the common grudge that reason behind improper communicative competence is the lack of favorable English speaking environment. If we consider the responses of students we come to know that around 85% of the students had no proper environment to practice speaking in English. Even we observe that the environment is not conducive to speaking in English.

Attitudinal Problems

Students do have their views and attitudes towards Speaking in English. These attitudes are formed by social and academic environment around them. Teachers are one of the most important factors that shape the attitudes of students. The attitude towards teacher, the subject being studied, course content, methodology *etc.*

Scanned with CamScanner

varies according to students. The problem is both with rural and urban background students. Some of them have negative attitudes, while some others are over-confident about their language.

Impact of E-Texting

Language, these days, is under great influence of the Internet and other e-media, such as SMS, Messengers, Online Teaching-Learning Platforms, *etc.* The rise and rapid spread of e-communication and lockdown due to COVID pandemic have deeply influenced formal/ Standard English language. The widespread mistakes in writing as well as the absence of grammar in speaking are mostly due to the impact of e-language.

Negligence of English as a Language

Another major challenge in teaching English Speaking is negligence of English language. It has been observed that English as language has always been taken for granted. They (students) think that English is a COMPULSORY SUBJECT to be cleared somehow. The students of rural areas think that being students of science, commerce or humanities, there is very less importance of Speaking in their career, in shaping their professional image. They believe that English language competence is expected only in professional or information and technology courses.

Gap between Needs of Students and Prescribed Syllabus

When a teacher of English language teaches in a traditional class, what he teaches is forced and he fails to satisfy the needs of the students. Difficulties faced by students vary to a great degree. Some of the students have problems with basics, some lack in vocabulary, few are good but get bored with the course, and some are afraid to speak. Most of the courses still prescribe prose and poetry and traditional grammar.

Lack of Advanced Teaching Aids

These days technology is very advanced in the field of education. Highly versatile technology likes 'Digital Language Laboratory', 'Smart-Class, 'Smart-Interactive-Board' *etc.* are available to assist teacher of English Language. Scholars consider these as indispensable tools for language teaching and learning. But in most of the rural colleges, there are no such advanced technical tools

Scanned with CamScanner

available for teaching and learning. Some of the colleges can't even afford to set up such an expensive infrastructure. For this purpose we have to evolve some of the methods which will not put much pressure on the pockets.

Too Busy Schedules

If a student is pursuing his degree, he has to study lot of subjects, which are already very difficult (for most of the students). They have classes from morning to evening and they have very less time and energy and enthusiasm to attend English language classes. Moreover these students, who belong to remote areas, have to travel for longer hours in order to attend the college. Many of the students are also busy in farming activities and some part time jobs for financial assistance to their families.

Activities to Develop English Speaking Skills and their Empowerment

In order to overcome the problems in teaching-learning English speaking skills, we practiced various activities. Taking advantage of some extra-classes and remedial coaching, we were able to design our own activities and course contents. Considering the needs of rural students we designed some the activities to fit our requirements and availability. We used continuous evaluation method to assess the performance of our students and adjusted various activities to fulfill the changing needs of the students. Some of the important activities designed and practiced are as following…

Extempore Video

This activity involves unplanned exposure to a short video recording. A student is asked to speak only for 2-3 minutes about things that he has recently talked about in his mother tongue. For example he may be asked to talk about …

Asking for items at grocery store
Making an inquiry at Railway Station
Taking an appointment by telephone
Talking socially to a variety of people

These kinds of unprepared talks help both the teacher and the student to know the level of language competence. The advantage of video recording is that it helps to understand expression at the time of sudden exposure to speaking in English. If the student is able to

Scanned with CamScanner

watch his own recording, he clearly understands the way he performed and what changes are required.

Story Telling

We are always excited to listen to interesting stories from mythology, history or fables. All of us know a lot of stories. This could prove to be a very useful tool in English language learning. This activity involves a great fun. It could be used in three different ways…

Picture Stories

We used series pictures which communicate a story. Students observed the pictures and were made to tell the story.

Translating Stories

Students read a story in Marathi/ Hindi and immediately tell the tale in English.

Re-telling Stories

Students were provided with short stories in English. Comics, folk tales, historical stories, fables could be provided to them in English. These have to be very short stories. As he finishes reading, he will start retelling it.

There are number of advantages of this activity. It inculcates in them the habit of using the vocabulary in the context. Some of the students struggle to recall the proper word and they switch to their mother-tongue. In this activity we can work for both good speakers and poor speakers. Those who are good will be focusing more on art of narrating the story. They concentrate on their voice modulation, pronunciation, adding dramatic effect in their voice *etc.* These activities could be video or audio-recorded in order to be analysed by students themselves. This activity proved to be more useful with students coming from rural areas. Since it had some material for their help, they were encouraged to speak. Stories familiar to them were chosen by the teachers.

Role Plays

Role plays are known by various names like simulation, role play game, simulation games, role play simulation *etc.* It is an activity in which the students assume the roles of some imaginary characters and enact the story. The objective of role-plays is to help students

Scanned with CamScanner

practice certain language functions and learn speaking skills. In the beginning they are given the situation and time to prepare. After this activity, they are assigned the situation on the spot and they have to perform at the very same time. The teachers listens the performances of the students and comments on the individual performances. We have video recorded all these plays. These are proving to be a great source of encouragement for students to actively participate in language learning process.

Drama

Similar to role plays, this activity can also be very useful in developing speaking skills. Students are divided in various groups; each group consists of 6-7 students. Groups will be assigned themes for performing. In this activity, students write their own dialogues. When they write it, they rehearse it and finally perform. This activity has various benefits like it tests their imagination, language, soft skills, ability to work in groups, performance, voice, pronunciation *etc.* In this activity help of literary works was taken. Students adapted their plays from works of Shakespeare, Sudha Murthy, ChetanBhagat, Sherlock Holmes series, some Hindi/ Marathi movies *etc.* We have got some of the wonderful performances through this activity.

Reading to Speak

Reading as an activity is a good source of self-learning. But what we are concerned with is speaking. How can reading help in speaking? We can use loud reading for developing skills of speaking. The teacher reads aloud the particular passage (most probably an interesting story) paying attention to pronunciation, rhythm *etc.* The same passage is read by students. Students learn by imitation which is the natural way of language acquisition. In loud reading your voice, pronunciation, pauses *etc.* are exercised. It can be used to practice proper pronunciation as well as to improve their confidence level with spoken words. This activity has threefold advantage: reading with proper sounds, listening

Visual Media as Tool in Teaching Speaking Skills

Instead of taking up a travelled path, we can go by *Road Not Taken.* One of the innovative techniques is to use movies, animations, motivational videos, task-based clippings, informative videos, documentaries *etc.* to promote speaking skills. Under this activity,

Scanned with CamScanner

what we do is commutainment or infotainment. Films, animations are enjoyed by all of us. Considering the interests of the groups, we can choose movies/ documentaries. In this activity our focus is going to be on several expressions, phrases, tone, pronunciation, vocabulary and so on. While enjoying the video, students learn lot of things. The teacher has to carefully choose his material. It must be having some message or theme of students' interest so as to encourage involvement and discussion. We have practiced with some of the Charlie Chaplin movies, documentaries about planet earth, few animation films, some motivational videos, and educational videos.

Presentation Series

One of the essential activities in studies as well as in jobs is presentations. All the students are required to give presentation on several topics as part of their education and they will be in need of it as part of their jobs. Besides this, presentations are also important in recruitment processes. But most of the students fail to create good impression with their presentation skills. The fear of stage, formal settings make them panic. They are unable to use proper language. In order to meet this need we practiced this skill extensively with graduation students by assigning them with various non-technical topics to present. They will be presenting at least one topic every month. Students are divided in the batches of 20. Each batch is allotted particular time-slot and teacher observes their performances thereby suggesting improvements.

Soft Skills

It is a well-known and proven fact that soft skills are the need of the hour. Not just effective communication but proper soft skills have a major share in the success of a student in academic and professional life. Considering the importance, we have designed various sessions for our students from first year of their graduation. Topics like Goal Setting, Motivation, Time Management, Group Discussion, Negotiation, Stress Management, Manners and Etiquettes, Interview Skills *etc*... are conducted throughout the year.

After understanding the needs of our students, we practiced above mentioned methods which resulted in considerable progress in students' performance. For the assessment purpose we used continuous evaluation method which has benefits of its own. With this evaluation method we maintained a track of progress which

Scanned with CamScanner

helped, from time to time, to shuffle the participating students and adjust them in various activities. Some students underwent rapid change whereas some of them were in need of more and more encouragement. We spent more time with students with low confidence levels and poor basics. Apart from the activities discussed, we also practiced Group Discussions, Interview Skills, writing competitions, classroom discussion and language lab modules. I must insist, here, that students need more intimate talk with them and encouragement and motivation are must to ensure gradual progress in their speaking skills. The role language teacher plays crucial role not only through the prescribed course-work but throughout their presence at the campus.

References

1. McDonough, JO, Christopher Shaw, HitomiMasuhara. *Materials and Methods in ELT: A Teacher's Guide*.3rd ed. Wiley-Blackwell. New Delhi. 2013.
2. Penny, U R and Marion Williams. *The Techniques of Language Learning and Teaching*. New York. Cambridge University Press, 1991.
3. P'Rayan, Albert and Ramakrishna Shetty, "Developing Engineering Students' Communication Skills by Reducing their Communication Apprehension." *ESP World*, Issue 4(20), Volume 7, 1-24. 2008.
4. Rahman, M. "Teaching Oral Communication Skills: A Task-based Approach." *ESP World*, Issue 1(27), Volume 9, 1-11. 2010.
5. Tickoo, M L, *Teaching and Learning English*, Orient Blackswan, Kolkata. 2010.

Scanned with CamScanner