Lee Newman · Abid Ali Ansari ·
Sarvajeet Singh Gill · M. Naeem ·
Ritu Gill *Editors*

Phytoremediation

Management of Environmental Contaminants, Volume 7

Springer

Phytoremediation

Lee Newman • Abid Ali Ansari
Sarvajeet Singh Gill • M. Naeem • Ritu Gill
Editors

Phytoremediation

Management of Environmental Contaminants, Volume 7

Springer

Editors
Lee Newman
College of Environmental Science
State University of New York
Syracuse, NY, USA

Abid Ali Ansari
Department of Biology
University of Tabuk
Tabuk, Saudi Arabia

Sarvajeet Singh Gill
Centre for Biotechnology
Maharshi Dayanand University
Rohtak, Haryana, India

M. Naeem
Department of Botany
Aligarh Muslim University
Aligarh, Uttar Pradesh, India

Ritu Gill
Centre for Biotechnology
Maharshi Dayanand University
Rohtak, Haryana, India

ISBN 978-3-031-17987-7 ISBN 978-3-031-17988-4 (eBook)
https://doi.org/10.1007/978-3-031-17988-4

© The Editor(s) (if applicable) and The Author(s), under exclusive license to Springer Nature Switzerland AG 2023
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 Switzerland AG
The registered company address is: Gewerbestrasse 11, 6330 Cham, Switzerland

This book is dedicated to
Professor (Retd.) Fareed Ahmad Khan
Department of Botany, Aligarh Muslim
University, Aligarh, India

Foreword

> The soil is the great connector of lives, the source and destination of all. It is the healer and restorer and resurrector, by which disease passes into health, age into youth, and death into life. Without proper care for it we can have no community, because without proper care for it we can have no life. – Wendell Berry, The Unsettling of America: Culture and Agriculture

We are living in an environment which is being seriously challenged by human interventions, and the soil and water are significantly contaminated with chemicals, pesticides, heavy metals and metalloids by anthropogenic activities. The onset of global climate change further aggravated climatic conditions which result in extreme drought conditions, temprature alterations (very high and low), prolonged flooding and submergence conditions, luxurious application of agrochemicals (fertilizers and pesticides), soil salinization and compaction, degraded soil and rhizospheric microbial health, depleting water table, war and war-like situations pose an obvious threat to cultivable land and food security thus human health. To get optimal crop production, the health of agriculturally viable land is one of the very important components. Therefore, it becomes imperative to look for options to remediate the health of soil and water to ensure soil quality, crop growth and productivity in a sustainable manner. Phyto-remediation has vast potential to remediate contaminated lands in an ecofriendly manner.

The editors of the seventh volume ‘Phytoremediation: Management of Environmental Contaminants’ have done admirable job of assembling a wealth of information on some new approaches for remediation of contaminated soil and water bodies. Editors have complied chapters from expert authors from all over the world. The number of chapters included in different sections brought comprehensiveness to the book. Sections starting with overview of the component chapters will definitely attract the reader’s attention. There are excellent chapters on nano-phytoremediation and NPs-mediated remediation of polluted sites. This comprehensive volume with twenty-seven chapters written by experts from countries USA, Italy, Brazil, Argentina, Nigeria, India, Pakistan, Saudi Arabia, Thailand, Turkey, China and Algeria proves useful for basic researchers, plant scientists, teachers and students interested in phytoremediation.

I would like to congratulate the publisher Springer Nature and Editors of the book (Lee Newman, Abid Ali Ansari, Sarvajeet Singh Gill, M. Naeem and Ritu Gill) for their labour for preparing this valuable scientific resource.

Narendra Tuteja
ICGEB ,
New Delhi, India

Preface

> Land is becoming a diminishing resource for agriculture, in spite of a growing understanding that the future of food security will depend upon the sustainable management of land resources as well as the conservation of prime farmland for agriculture. – M. S. Swaminathan

Volume 7 of 'Phytoremediation: Management of Environmental Contaminants' book series adds recent literature concerning modern phytoremediation techniques such as use of bioformulations, application of electroremediation-coupled phytoremediation, microorganisms consortium mediated phytoremediation, phytostabilization of biogeochemical and microbiological processes, plant root exudates and microbial interactions, nano-phytoremediation, nano-bioremediation and nanobiotechnology for the cleanup environmental contaminants from soil and water. The book chapters in Volume 7 comprehensively provide additional examples that illustrate how phytoremediation applications can be strengthened and serve as one of several useful components in the overall management and control of contaminants using relatively low-cost solar-driven physiological/biochemical mechanisms common to most plants. This volume exclusively deals with the use of nano-particles and nano-biotechnology for the removal of pollutants from contaminated sites.

Volume 7 has been subsectioned into six different sections for the ease of readers, which defines as Part I: Overview of current phytotechnology and phytoremediation applications; Part II: Planning and engineering applications to phytoremediation; Part III: Phytoremediation applications for contaminated water and soil; Part IV: Phytoremediation using microbial assemblages in water and soil; Part V: Phytoremediation of organic and inorganic contaminants and organic-inorganic mixtures; and Part VI: Nanotechnology in management of environmental contaminants. Part I contains six chapters namely Phytoremediation and Management of Environmental Contaminants: An Overview; Phytoremediation and Contaminants; Phytoremediation by Wild Weeds: A Natural Asset; Phytoremediation: Sustainable and Organic Technology for the Removal of Heavy Metals Contaminants; Structure and Function of Heavy Metal Transporting ATPases in Brassica species; and Bioformulations for Sustainable Phytoremediation of Heavy Metal Contaminated Soil written by the authors from India, Italy, USA and Pakistan; Part II contains a chapter on Application of Electroremediation Coupled with Phytoremediation

Techniques for the Removal of Trace Metals in Sewage Sludge; Part III contains a chapter on Phytoremediation of Heavy Metals by *Trapa natans* in Hokersar Wetland: A Ramsar Site of Kashmir Himalayas; Part IV contains four chapters namely Spinoffs of Phyoremediation and/or Microorganisms Consortium in Soil, Sediment and Water Treatments and Improvement: Study of Specific Cases and Its Socioeconomic and Environmental Advantages; Applying Amendments for Metal(loid) Phytostabilization: Effects on Biogeochemical and Microbiological Processes in Soils; Rhizodegradation: The Plant Root Exudate and Microbial Interactions, and Role of Microorganisms in the Remediation of Toxic Metals from Contaminated Soil; Part V contains three chapters namely Prospects for the Use of Sorghum Bicolor for Phytoremediation of Soils Contaminated with Heavy Metals in Temperate Climates; Comparative Effect of Cadmium on Germination and Early Growth of Two Halophytes: *Atriplex halimus* L. and *A. nummularia* Lindl. for Phytoremediation Applications, and Phytoremediation of Soils Polluted by Heavy Metals and Metalloids: Recent Case Studies in Latin America provided by the scientists from Russia, Argentina and Algeria; and Part VI encompasses twelve chapters namely Nano-phytoremediation and Its Applications; Potentials and Frontiers of Nanotechnology for Phytoremediation; Nanotechnology in the Management of Environmental Contaminants; Nanotechnologies and Phytoremediation: Pros and Cons; Nanotechnology in Phytoremediation: Applications and Future; Nano-phytoremediation: The Successful Combination of Nanotechnology and Phytoremediation; Nano-bioremediation and Its Application for Sustainable Environment; Nanoparticles Assisted Phytoremediation of Polluted Soils: Potential Application and Challenges; A Systematic Analysis of Nanotechnology Application in Water Contaminations Removal; Nanoparticles-Based Management of Cadmium Toxicity in Crop Plants; Heavy Metal Remediation by Nanotechnology; and Phytoremediation and Management of Environmental Contaminants: Conclusion and Future Perspectives written by the experts from the countries Italy, Brazil, Nigeria and Pakistan. The editors and contributing authors hope that this book will include a practical update on our knowledge for improving phytoremediation potential to de-contaminate environmental contaminants. This book will lead to new discussions and efforts to the use of various tools for the improvement of phyto-remediation techniques.

We are highly thankful to Dr. Narendra Tuteja, International Centre for Genetic Engineering and Biotechnology (ICGEB), New Delhi, for valuable help in incorporating editorial changes in the manuscripts. We would like to thank Springer, particularly Eric Stannard, Senior Editor, Botany, Springer, New York, and Kate Lazaro, Springer for their professional support and efforts in the layout. We are also thankful to Shanthini Kamaraj Project Coordinator (Books), Springer Nature for providing help in the finalization of book. We heartily dedicate this book to Prof. Rajbir Singh, Vice Chancellor, Maharshi Dayanand University, and Rohtak.

Syracuse, NY, USA	Lee Newman
Tabuk, Saudi Arabia	Abid Ali Ansari
Rohtak, India	Sarvajeet Singh Gill
Aligarh, India	M. Naeem
Rohtak, India	Ritu Gill

Contents

Part I Overview of Current Phytotechnology & Phytoremediation Applications

Part II Planning and Engineering Applications to Phytoremediation

Part III Phytoremediation Applications for Contaminated Water and Soil

Part IV Phytoremediation Using Microbial Assemblages in Water and Soil

Part V Phytoremediation of Organic and Inorganic Contaminants and Organic-Inorganic Mixtures

Part VI Nanotechnology in Management of Environmental Contaminants

Contributors

E. F. Adegboye Environmental Botany Unit, Department of Plant Biology, P. M. B. 1515, University of Ilorin, Ilorin, Nigeria

C. O. Adenipekun Plant Physiology Unit, Department of Botany, University of Ibadan, Ibadan, Nigeria

Sajid Rashid Ahmad College of Earth and Environmental Sciences, Quaid-e-Azam Campus, University of the Punjab Lahore, Punjab Lahore, Pakistan

Syed Shakeel Ahmad Department of Botany, University of Kashmir, Srinagar, J & K, India

Qasim Ali Department of Soil Sciences, The Islamia University of Bahalwalpur, Bahalwalpur, Pakistan

Hussein Alserae Institute of Soil and Environmental Sciences, University of Agriculture Faisalabad, Faisalabad, Pakistan

A. A. Ansari Department of Biology, Faculty of Science, University of Tabuk, Tabuk, Saudi Arabia

Roshan Ara Department of Botany, University of Kashmir, Srinagar, J & K, India

Sana Ashraf College of Earth and Environmental Sciences, Quaid-e-Azam Campus, University of the Punjab Lahore, Punjab Lahore, Pakistan

Sobia Ashraf Department of Environmental Sciences & Engineering, Government College University Faisalabad, Faisalabad, Pakistan

Sangeeta Bajpai AMITY School of Applied Sciences, Amity University, Lucknow, UP, India

Anouar Bardi Higher Institute of Management of Gabès, Gabès, Rue Jilani Lahbib, Gabès, Tunisia

Sabreen Bashir School of Bioengineering and Biosciences, Lovely Professional, University, Phagwara, Punjab, India

Gabriel Basílico Museo Argentino de Ciencia Naturales, CONICET, Ciudad Autónoma de Buenos Aires, Argentina

Madhulika Bhati CSIR-National Insitute of Science Communication and Policy Research, Dr. K.S. Krishnan Marg, Pusa, New Delhi, India

Trinath Biswal Department of Chemistry, VSS University of Technology, Burla, India

Sylvain Bourgerie INRAE USC1328, LBLGC EA1207, University of Orléans, Orléans, France

Anindita Chakraborthy UGC DAE, Consortium for Scientific Research, Kolkata Centre, Kolkata, India

Hina Chaudhry Department of Environmental Sciences, Lahore College for Women University, Lahore, Pakistan

Alessia Corami MIUR, Ministry of University and Research, Rome, Italy

I. Daniel Coria Universidad del Centro Educativo Latinoamericano, Rosario, Argentina

Maycon Lucas de Oliveira Department of Chemistry, FFCLRP-USP, University of São Paulo - USP, Ribeirão Preto, SP, Brazil

Maryam Dogar Sustainable Development Study Centre, GC University, Lahore, Pakistan

Ana Faggi Universidad de Flores, Facultad de Ingeniería, Laboratorio de Bioindicadores y Remediación, Ciudad Autónoma de Buenos Aires, Argentina

Zia Ur Rahman Farooqi Institute of Soil and Environmental Sciences, University of Agriculture Faisalabad, Faisalabad, Pakistan

M. V. Frontasyeva Joint Institute for Nuclear Research, Dubna, Moscow, Russia

Ritu Gill Centre for Biotechnology, Maharshi Dayanand University, Rohtak, Haryana, India

Sarvajeet Singh Gill Centre for Biotechnology, Maharshi Dayanand University, Rohtak, Haryana, India

Madhuri Girdhar School of Bioengineering and Biosciences, Lovely Professional, University, Phagwara, Punjab, India

S. V. Gorelova Tula State University, Natural Science Institute, Tula, Russia

Alvina Gu Atta ur Rahman School of Applied Biosciences (ASAB), National University of Sciences and Technology (NUST), Islamabad, Pakistan

Alvina Gul Atta ur Rahman School of Applied Biosciences (ASAB), National University of Sciences and Technology (NUST), Islamabad, Pakistan

Sabrina N. Hernández Guiance Universidad del Centro Educativo Latinoamericano, Rosario, Argentina

Instituto de Física de Rosario, Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Rosario, Argentina

Sameen Ruqia Imadi Commission on Science and Technology for Sustainable Development in the South (COMSATS) Secretariat, Islamabad, Pakistan

Haram Javed Institute of Soil and Environmental Sciences, University of Agriculture Faisalabad, Faisalabad, Pakistan

M. A. Jimoh Department of Plant Biology, Osun State University, Osogbo, Nigeria

A. P. Kolbas Brest State A. Pushkin University, Brest, Belarus

Institute of Nature Management of the National Academy of Sciences of Belarus, Minsk, Belarus

K. Suresh Kumar Department of Environmental Science, School of Science, School of Science, GITAM (Deemed to be University), Visakhapatnam, India

Manhattan Lebrun INRAE USC1328, LBLGC EA1207, University of Orléans, Orléans, France

UMR Ecosys, INRAE, AgroParisTech, Université Paris-Saclay, Thiverval-Grignon, France

Mahnoor Sustainable Development Study Centre, GC University, Lahore, Pakistan

Zahra Majid College of Earth and Environmental Sciences, Quaid-e-Azam Campus, University of the Punjab Lahore, Punjab Lahore, Pakistan

Shafia Maryam Atta ur Rahman School of Applied Biosciences (ASAB), National University of Sciences and Technology (NUST), Islamabad, Pakistan

Abdulrezzak Memon Department of Molecular Biology and Genetics, Arts and Science Faculty, Usak University, Usak, Turkey

Nuriye Meraklı Department of Molecular Biology and Genetics, Arts and Science Faculty, Usak University, Usak, Turkey

Anand Mohan School of Bioengineering and Biosciences, Lovely Professional, University, Phagwara, Punjab, India

Domenico Morabito INRAE USC1328, LBLGC EA1207, University of Orléans, Orléans, France

A. Yu. Muratova Institute of Biochemistry and Physiology of Plants and Microorganisms, Russian Academy of Sciences, Saratov, Russia

M. Naeem Plant Physiology Section, Department of Botany, Aligarh Muslim University, Aligarh, UP, India

Yogesh Nagar CSIR-National Institute of Science Communication and Policy Research, Dr. K.S. Krishnan Marg, Pusa, New Delhi, India

Humaira Nawaz College of Earth and Environmental Sciences, Quaid-e-Azam Campus, University of the Punjab Lahore, Punjab Lahore, Pakistan

Rida Nawaz Institute of Soil and Environmental Sciences, University of Agriculture Faisalabad, Faisalabad, Pakistan

Bouzid Nedjimi Laboratory of Exploration and Valorization of Steppe Ecosystem, Faculty of Science of Nature and Life, Ziane Achour University of Djelfa, Cité Aîn Chih, Djelfa, Algeria

C. O. Ogunkunle Environmental Botany Unit, Department of Plant Biology, P. M. B. 1515, University of Ilorin, Ilorin, Nigeria

Department of Plant Biology, Osun State University, Osogbo, Nigeria

O. I. Okina Geological Institute of the Russian Academy of Sciences, Moscow, Russia

G. O. Okunlola Department of Plant Biology, Osun State University, Osogbo, Nigeria

O. A. Olatunji Department of Plant Biology, Osun State University, Osogbo, Nigeria

Garima Pandey SRM-Institute of Science and Technology, Delhi-NCR Campus, Modinagar, Ghaziabad, UP, India

Bhaskara Nand Pant Department of Chemistry, Atma Ram Sanatan Dharma College, University of Delhi, New Delhi, India

Prayad Pokethitiyook Department of Biology, Faculty of Science, Mahidol University, Bangkok, Thailand

Center of Excellence on Environmental Health and Toxicology (EHT), OPS, MHESI, Thailand

Toemthip Poolpak Department of Biology, Faculty of Science, Mahidol University, Bangkok, Thailand

Center of Excellence on Environmental Health and Toxicology (EHT), OPS, MHESI, Thailand

G. Padma Priya Department of Chemistry, Jain University, Bangalore, Karnataka, India

Ayesha Abdul Qadir Institute of Soil and Environmental Sciences, University of Agriculture Faisalabad, Faisalabad, Pakistan

Muhammad Javid Qamar Soil and Water Testing Laboratory, Bahawalpur, Pakistan

Muhammad Akram Qazi Soil Fertility Research Institute, Lahore, Punjab, Pakistan

Hayfa Rajhi Laboratory of Applied Microbiology, Department of Molecular Biology, Universidad Autonoma de Madrid, Madrid, Spain

Rizwan Rasheed Sustainable Development Study Centre, GC University, Lahore, Pakistan

Irfan Rashid Department of Botany, University of Kashmir, Srinagar, J & K, India

Sehar Razzaq State Key Laboratory of Eco-hydraulics in Northwest Arid Region of China, Xi'an University of Technology, Xi'an, China

Zafar A. Reshi Department of Botany, University of Kashmir, Srinagar, J & K, India

Sobia Riaz Institute of Soil and Environmental Sciences, University of Agriculture Faisalabad, Faisalabad, Pakistan

Shaik Riyazuddin Department of Environmental Science, School of Science, GITAM (Deemed to be University), Visakhapatnam, India

Ali Rizwan Institute of Soil and Environmental Sciences, University of Agriculture, Faisalabad, Pakistan

A. B. Rufai Department of Plant Biology, Osun State University, Osogbo, Nigeria

Ammara Saeed Institute of Soil and Environmental Sciences, University of Agriculture Faisalabad, Faisalabad, Pakistan

A. Ram Sailesh Department of Environmental Science, School of Science, GITAM (Deemed to be University), Visakhapatnam, India

Manzoor A. Shah Department of Botany, University of Kashmir, Srinagar, J & K, India

Muhammad Bilal Shakoor College of Earth and Environmental Sciences, Quaid-e-Azam Campus, University of the Punjab Lahore, Punjab Lahore, Pakistan

Raghav Sharma CSIR-National Institute of Science Communication and Policy Research, Dr. K.S. Krishnan Marg, Pusa, New Delhi, India

Prashant Singh Department of Chemistry, Atma Ram Sanatan Dharma College, University of Delhi, New Delhi, India

Himanshi Singh CSIR-National Insitute of Science Communication and Policy Research, Dr. K.S. Krishnan Marg, Pusa, New Delhi, India

Lilian Rodrigues Rosa Souza Department of Chemistry, FFCLRP-USP, University of São Paulo - USP, Ribeirão Preto, SP, Brazil

Srinivas Namuduri Department of Environmental Science, School of Science, GITAM (Deemed to be University), Visakhapatnam, India

Vikram Srivastava Department of Biomedical Sciences, Iowa State University, Ames, IA, USA

G. Subbulakshmi Department of Chemistry, Jain University, Bangalore, Karnataka, India

Amtul Bari Tabinda Sustainable Development Study Centre, GC University, Lahore, Pakistan

Ajwa Tahir Sustainable Development Study Centre, GC University, Lahore, Pakistan

R. Thiruneelakandan Department of Chemistry University, College of Engineering Bit Campus, Anna University Tiruchirappalli, Tiruchirappalli, Tamil Nadu, India

Lukáš Trakal Department of Environmental Geosciences, Faculty of Environmental Sciences, Czech University of Life Sciences Prague, Praha 6 Suchdol, Czech Republic

Muhammad Umair Institute of Soil and Environmental Sciences, University of Agriculture, Faisalabad, Pakistan

Kwang Mo Yang Department of Biology, Faculty of Science, Mahidol University, Bangkok, Thailand

Center of Excellence on Environmental Health and Toxicology (EHT), OPS, MHESI, Thailand

Abdullah Yasar Sustainable Development Study Centre, GC University, Lahore, Pakistan

Tayyaba Yasmin COMSATS University Islamabad, Islamabad, Pakistan

Melina Borges Teixeira Zanatta Environmental Studies Center (CEA), São Paulo State University, Rio Claro, SP, Brazil

Muhammad Zia-ur-Rehman Institute of Soil and Environmental Sciences, University of Agriculture, Faisalabad, Pakistan

I. Zinicovscaia Joint Institute for Nuclear Research, Dubna, Moscow, Russia

Part I

Overview of Current Phytotechnology & Phytoremediation Applications

Chapter 1
Phytoremediation and Management of Environmental Contaminants: An Overview

Ritu Gill, M. Naeem, A. A. Ansari, and Sarvajeet Singh Gill

Abstract The rapid increase in the global population, urbanization and industrialization, electroplating, nonferrous metal smelting, mine tailing, and intensive use of agrochemicals in agriculture has increased the frequency of addition of metals, metalloids, and pesticides into the soil, water, and environment, and poses a severe threat on crop productivity and human health. Both natural and anthropogenic activities contribute to the degradation of ecosystem. Therefore, it becomes imperative to restore the natural habitats to safeguard food security and human health. Modern and effective remediation/chemical remediation technologies or methods have emerged successfully, but they involve heavy resources, demand high energy, are expensive, and produce huge waste. Therefore, phytoremediation or plant-derived compound-mediated remediation of environment is considered an ecofriendly and sustainable approach for cleaning contaminated sites.

Keywords Contaminated sites · Soil remediation technology · Phytodegradation · Phytoextraction · Phytostabilization or Phytoimmobilization · Phytovolatilization · Rhizodegradation · Rhizofiltration

---

R. Gill · S. S. Gill (✉)
Centre for Biotechnology, Maharshi Dayanand University, Rohtak, Haryana, India
e-mail: ssgill14@mdurohtak.ac.in

M. Naeem
Plant Physiology Section, Department of Botany, Aligarh Muslim University,
Aligarh, UP, India

A. A. Ansari
Department of Biology, Faculty of Science, University of Tabuk, Tabuk, Saudi Arabia

L. Newman et al. (eds.), *Phytoremediation*,
https://doi.org/10.1007/978-3-031-17988-4_1

1.1 Introduction

The rapid increase in the global population, urbanization and industrialization, electroplating, nonferrous metal smelting, mine tailing, and intensive use of agrochemicals in agriculture has increased the frequency of addition of metals, metalloids, and pesticides into the soil, water, and environment, and poses a severe threat on crop productivity and human health (Cherniwchan 2012; Wu et al. 2016; Saleem et al. 2020; Zaheer et al. 2020; Kamran et al. 2021; Corami 2021; Naeem et al. 2022; Kafle et al. 2022). Both natural and anthropogenic activities contribute to the degradation of ecosystem (Mózner et al. 2012). Continuous exposure of environment (soil and water) to metals and metalloids (cadmium, Cd; chromium, Cr; copper, Cu; arsenic, As; lead, Pb; zinc, Zn; nickel, Ni; iron, Fe; and manganese, Mn), radionuclides (naturally occurring radioactive materials (U, Th, Ra, Rn, Pb, and Po) as well as technologically enhanced naturally occurring radioactive materials, volcanic activities, erosion, weathering, nuclear accidents (^{133}Xe, ^{131}I, ^{134}Cs, ^{137}Cs, and ^{90}Sr), nuclear weapon testing, leakage of nuclear wastes, and medical and agricultural testing facilities with isotopes such as ^{131}I and ^{14}C), organic contaminants (aromatic compounds, hydrocarbons, substituted hydrocarbons, phenols, organo-chlorines, and pesticides), agrochemicals (chemical fertilizers, plant-protection agents, and plant growth promoting hormones), and oil spills (complex mixture of hydrocarbon and organic compounds, including benzene and poly-aromatic hydrocarbons) (He et al. 2015; Prakash et al. 2013; Afzal et al. 2014; Liu et al., 2017a, b; Jagetiya et al. 2014; Yana et al. 2021; Malik et al. 2017; Naeem et al. 2022; Ron and Rosenberg 2014; Kafle et al. 2022) is a serious concern to the researchers. Therefore, it becomes imperative to restore natural habitats to safeguard food security and human health. Modern and effective remediation/chemical remediation technologies or methods have emerged successfully, but they involve heavy resources, demand high energy, are expensive, and produce huge waste. Some important remediation methods include bioremediation (e.g., plant-based (phytoremediation) and microbe-based (microbial remediation)) and chemical remediation such as chemical leaching, chemical stabilization, electro-kinetic remediation-permeable reactive barrier, and chemical oxidation/reduction and physical remediation. Among these, phytoremediation or plant-derived compound-mediated remediation is one of the ecofriendly and sustainable approaches for cleaning contaminated sites. Plants with the ability to accumulate contaminants are basically used in the process of phytoremediation, where contaminants are removed, stabilized, or transformed by the accumulating plants and associated rhizospheric microorganisms. It is well documented that plants used in phytoremediation can remediate both kinds of contaminants (organic and inorganic contaminants) in a sustainable manner with low input but take a long time to grow and consume the contaminants (Ansari et al., 2015a, b, 2016a, b, 2017, 2018; Banioko and Eslamian 2015; Corami 2017; Ali et al. 2020; Corami 2021; Kafle et al. 2022).

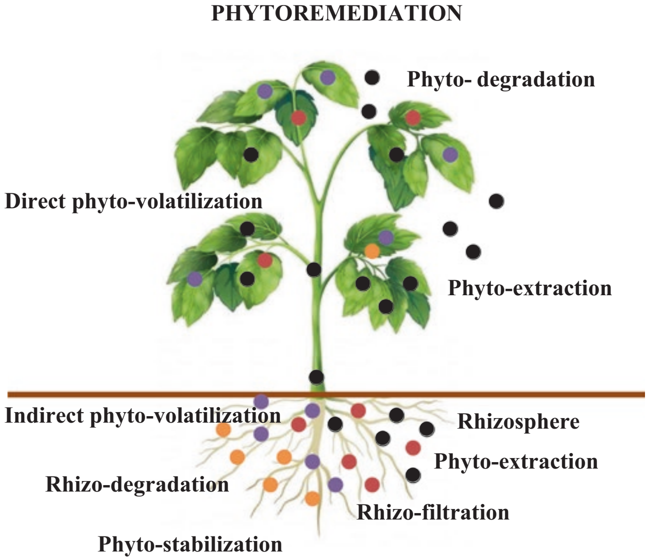


Fig. 1.1 Phytoremediation and management of environmental contaminants

1.2 Phytoremediation Technology

In this technology, plants with a high accumulation capacity of organic and inorganic contaminants are employed to remediate the contaminated sites in an eco-friendly and sustainable manner. Phytoremediation can be further divided into the following categories (Yan et al. 2020) (Fig. 1.1):

- Phytodegradation.
- Phytoextraction.
- Phytostabilization or phytoimmobilization.
- Phytovolatilization.
- Rhizodegradation.
- Rhizofiltration.

1.3 Phytodegradation

Phytodegradation is a process in which plants uptake, mobilize, and degrade the contaminants in the plant tissues itself. It has been well researched and documented that plants can degrade organic contaminants such as aromatic compounds, hydrocarbons, substituted hydrocarbons, phenols, organo-chlorines, and pesticides in the plant tissues by converting them into less toxic compounds and clean the contaminated sites. Plants like *Tegetes patula*, *Mirabilis jalapa*, and *Ipomea balsamina* have the ability to dechlorinate chlorinated hydrocarbons by the process of phytodegradation. Garrison et al. (2000) reported that the aquatic plant *Elodea canadensis* and the terrestrial plant kudzu (*Pueraria thunbergiana*) have the ability to phytodegrade Dichlorodiphenyltrichloroethane (DDT) and suggested that the process phytodegradation can be further complemented or enhanced by an achiral enzyme cofactor or other achiral biomolecule. In another study, Liu et al., (2017a) tested 14 plant species for hydrocarbon de-contamination and observed that *P. nil* removed saturated hydrocarbons significantly; *M. jalapa* removed aromatic hydrocarbons significantly; and *I. balsamina* significantly removed the asphaltenes and polar compounds. Furthermore, it has been recommended that *M. jalapa* and *I. balsamina* are more suitable plants for the degradation of aromatic hydrocarbons, asphaltenes, and polar compounds Liu et al., (2017a).

1.4 Phytoextraction

Plants with the ability to take up the environmental contaminants through their roots and bioaccumulation in the ground through tissues, cell wall, and vacuoles comes under the category of phytoextraction and phytoaccumulation. It has been well documented that plants with high accumulation capacity (hyperaccumulator plants belonging to the family Brassicaceae and others) accumulated high concentration of metals and metalloids in the roots and shoot tissues and detoxify with the help of phytochelatins. A numbers of heavy metals such as cadmium, lead, arsenic, and copper have been found to be accumulated by many plant species. *Sedum alfredii* is a well-known hyperaccumulator of Cd. Lin et al. (2020) isolated and cloned a gene *SaPCR2* (Cd resistant gene) from *S. alfredii* and noted high activity of *SaPCR2* in plant roots as it contains highly conserved cysteine-rich domain which further helps in the detoxification of Cd in the plant. Furthermore, it has been suggested that the overexpression of *SaPCR2* results in the leaking of Cd from the roots which in turn protects the roots from the phytotoxicity of Cd (Lin et al. 2020). Coakley et al. (2019) studied the response of invasive *Impatiens glandulifera* for the phytoaccumulation of Cd focusing on bio-concentration factor, translocation factor, and total removal capacity and noted that 150 mg kg^{-1} Cd did not significantly affect the plant biomass in experimental conditions. Furthermore, it has also been reported that *I. glandulifera* accumulated Cd at 276–1562 mg kg^{-1} in stems, with bio-concentration factor, translocation factor, and total removal capacity of 64.6–236.4, 0.2–1.2, and 3.6–29.2 mg Cd, respectively. The study reflects the potential of Cd hyperaccumulation by the invasive plant *I. glandulifera* for phytoremediation of Cd-contaminated marginal lands (Coakley et al. 2019). It has been reported that over 450 plant species globally hyperaccumulate metalloids to the aboveground plant parts which provide an opportunity for phytoextraction or phytoaccumulation of metalloid-contaminated sites and remediation purpose in sustainable manner (Rascio and Navari-Izzo 2011; Wu et al. 2015; Li et al. 2018; Matzen et al. 2022). It has been noted that fronds and rhizomes of *Pteris vittata* accumulate large amount of As (Kohda et al. 2021). The long-distance transport and accumulation of As in the fronds and rhizomes of *Pteris vittata* were studied using positron-emitting tracer imaging system with positron-emitting ^{74}As-labeled tracer, and the resulted autoradiograph revealed the function of rhizomes in *P. vittata* in As accumulation and regulation of As translocation to the mature fronds for the protection of young fronds from As toxicity (Kohda et al. 2021). In another experiment, Matzen et al. (2022) studied the effect of phosphorus fertilization and mycorrhizal fungi inoculation on *P. vittata* As uptake and leaching using synchrotron-based spectromicroscopy and noted rhizospheric As accumulation in *P. vittata*. Experimental conditions such as medium-textured soil with more clay and higher nutrient content resulted in successful iron scavenging which in turn increased the As release from soil for leaching (Matzen et al. 2022).

1.5 Phytostabilization or Phytoimmobilization

In large, the purpose of phytoremediation is to remove and detoxify the environmental contaminants from the polluted sites with the help of plants having the capacity to accumulate and detoxify the contaminants (Nedjimi 2021). Phytostabilization or phytoimmobilization is also the phytoremediation potential of plants, where remediation is achieved by inactivation or immobilization of contaminants in the metal tolerant plant roots or in the rhizosphere to decrease their bioavailability and to reduce the risk of their mobilization in the ecosystem and food chain (Marques et al. 2009; Gerhardt et al. 2017). The plant roots or the rhizospheric environment restricts the mobility of the contaminants and does not allow the contaminants to cause phytotoxicity. Phytostabilization is a long-term cost-effective bioremediation technique for the immobilization of metalliferous mine tailings (Hammond et al. 2018). The main advantage of phytostabilization in comparison with phytoextraction is that the hazardous biomass which have the contaminants not required. Plant species vary in phytostabilization capabilities; therefore, selection of suitable plant species is crucial to achieve the full potential of phytostabilization. It is evident from the previous research that many plant species have been identified and used for the remediation of metal-contaminated sites (Burges et al. 2018). It has been reported that *Prosopis juliflora* roots grown in compost-amended pyritic mine tailings from a federal Superfund site for 36 months revealed that immobilization of root-associated As(V) on the root epidermis bound to ferric sulfate precipitates resulted in trivalent As(III)–(SR)3 tris-thiolate complexes (Hammond et al. 2018). The efficiency of phytostabilization or phytoimmobilization can be further improved with the help of organic and inorganic amendments (Yan et al. 2020).

1.6 Phytovolatilization

Volatilization is a process in which liquid vaporizes and escapes into the atmosphere. Phytovolatilization is the ability of plants to uptake the pollutants, heavy metals, or other organic contaminants from the soil to release them into the atmosphere in the form of less toxic volatile compounds from the leaves and stem (direct phytovolatilization) by the process of transpiration or from the soil by plant root activities (indirect phytovolatilization) to remediate the contaminated sites (Limmer and Burken 2016; Yan et al. 2020). Phytovolatilization is a suitable phytoremediation approach for the de-contamination of organic contaminants and heavy metals (Yan et al. 2020). In particular, the members of the family Brassicaceae are the best performers as volatilizers of Se (Yan et al. 2020). Natural (algae, sponge, and bacteria) and anthropogenic sources (polymer intermediates, flame retardant intermediates, and wood preservatives) are reported to produce bromophenols and bromoanisoles in the environment (Gribble 2003; Howe et al. 2005; Bidleman et al. 2014, 2017; Koch and Sures 2018; Zhang et al. 2020). Zhang et al. (2020) conducted hydroponic exposure experiments to evaluate the 2,4-dibromophenol (2,4-DBP) and 2,4-dibromoanisole (2,4-DBA) phytovolatilization efficiency of rice plants, and it was noted that aboveground rice tissues showed more bioaccumulation and volatilization of 2,4-DBA in comparison with 2,4-DBP. Furthermore, it has been suggested that rice plants can be better utilized for the phytovolatilization of bromophenols and bromoanisoles (Zhang et al. 2020). Fu et al. (2018) reported the back conversion of methyl triclosan to triclosan in Arabidopsis cells, lettuce, and carrot seedlings while grown on nutrient solution containing methyl triclosan. Environment, especially the soil, is a major sink of polybrominated diphenyl ethers (PBDEs). Xu et al. (2016) observed that brominated diphenyl ethers (BDE-47), hydroxylated PBDEs (6-OH-BDE-47), and methoxylated PBDEs (6-MeO-BDE-47) uptake, translocate, and transform *Zea mays* in hydroponic experiment and reported that root uptake was in the order of BDE-47 > 6-MeO-BDE-47 > 6-OH-BDE-47, whereas 6-OH-BDE-47 showed more acropetal translocation. Furthermore, it was also noted that the transformation of BDE-47 to lower brominated OH/MeO-PBDEs occurred via debromination followed by hydroxylation or methoxylation, whereas no transformation of 6-OH-BDE-47 or 6-MeO-BDE-47 to PBDEs was observed (Xu et al. 2016).

1.7 Rhizodegradation

The surrounding of plant roots is called the rhizosphere, and the degradation of contaminant pollutants (salts, solvents, heavy metals, pesticides, petroleum hydrocarbons, polycyclic aromatic hydrocarbons, halogenated hydrocarbons, etc.) in the plant rhizosphere refers to rhizodegradation or enhanced rhizosphere biodegradation (Liu et al. 2001; Petrová et al. 2017; Keith 2015; Dat and Chang 2017; Sivaram et al. 2020). Plant roots are a major source of vital exudates or rhizodeposits into the rhizosphere soil, such as sterol, organic acid, growth factors, nucleotide, amino acids, sugar, flavanone, and other enzymes, which are essential to maintain the rhizospheric microbial diversity and root microbial activities (Carvalhais et al. 2011; Kim et al. 2010; Phillips et al. 2012; Wang et al. 2014; Lareen et al. 2016). Allamin et al. (2020) studied the potential of *Cajanus cajan* for the remediation of petroleum oily sludge-spiked soil and noted that the population of total heterotrophic bacteria was higher in uncontaminated rhizospheric soil in comparison with petroleum oily sludge-spiked soil, whereas hydrocarbon-utilizing bacteria were significantly higher in contaminated rhizosphere soil. Furthermore, it has been proposed that the potential of *C. cajan* can be exploited for the decontamination of soil contaminated with petroleum oily sludge in ecofriendly and sustainable manner (Allamin et al. 2020). The potential of C3 (*Vigna unguiculata*, *Helianthus annus*, and *Austrodanthonia caespitosa*) and C4 (*Zea mays*, *Sorghum sudanense*, and *Vetiveria zizanoides*) plants for rhizodegradation has been explored using 16S ribosomal RNA pyrosequencing of soil contaminated with polycyclic aromatic hydrocarbons after 60 and 120 days (Sivaram et al. 2020). It has been noted that the population of polycyclic aromatic hydrocarbons degrading bacteria was significantly higher in C4 plant rhizosphere than C3 plant rhizosphere which was further complemented with reduced concentration of polycyclic aromatic hydrocarbons in the remediated soil of C4 plants may due to better efficiency of C4 plants to convert solar energy into biomass than C3 plants (Zhu et al. 2008; Sivaram et al. 2020). The studies of Sivaram et al. (2019) and Aryal and Liakopoulou-Kyriakides (2013) reported the presence of *Phanerochaete chrysosporium*, *Arthrobacter* sp., *Diaphorobacter* sp., *Enterobacter* sp., *Flavobacterium* sp., *Acinetobacter* sp., *Bacillus*, *Pseudomonas* sp., *Stenotrophomonas* sp., *Pseudoxanthomonas* sp., *Sphingomonas* sp., *Polysporus* sp., and *Rhodococcus wratislaviensis* for the degradation of phenanthrene and pyrene in contaminated soils. Rajkumari et al. (2021) studied the potential of *Klebsiella pneumoniae* AWD5 (non-clinical environmental isolate) in the presence of succinate as co-substrate for the rhizodegradation of pyrene in the rhizosphere of *Tagetes erecta* and reported improved root and shoot growth (root length, dry root weight, shoot length, and dry shoot weight) and significantly higher rhizodegradation potential for the degradation of pyrene by 68.61%.

1.8 Rhizofiltration

Rhizofiltration is a phytoremediation mechanism frequently used to decontaminate the inorganic and organic contaminants present in surface, groundwater, or wastewater with the help of roots of tolerant aquatic plants, where roots uptake the contaminants and transfer them to other plant parts for conversion into less toxic compounds (Jadia and Fulekar 2009). A variety of plants such as *Azolla caroliniana*, *Eichhornia crassipes*, *Callitriche lusitanica*, *Callitriche stagnalis*, *Fontinalis antipyretica*, *Lemna minor*, *Callitriche brutia*, *Typha angustifolia*, and *Ranunculus* *trichophyllus* have been employed for rhizofiltration of variety of metals and metalloids such as Fe, Cr, Cu, Cd, Zn, Ni, As, Mn, and U (Favas et al. 2012; Rai 2019; Favas et al. 2012; Pratas et al. 2012; Chandra and Yadav 2010; Kafle et al. 2022). El-Liethy et al. (2022) reported the ability of *Pistia stratiotes* for rhizofiltration of Pb, Zn, and Co in the polluted drain in Egypt and observed seasonal variation in rhizo-filtration of Pb, Zn, and Co as summer for Pb and Co and autumn for Zn. Furthermore, canonical correspondence analysis revealed that the rhizo-filtration potential of *P. stratiotes* and variation in the bacterial abundance was significantly affected by H_2O-dissolved O_2 (El-Liethy et al. 2022).

1.9 Conclusions and Future Perspectives

Phytoremediation (phytodegradation, phytoextraction, phytostabilization, or phyto-immobilization, phytovolatilization, rhizodegradation, and rhizofiltration) of organic and inorganic contaminants from air, soil, and water is an ecofriendly and sustainable approach for cleaning the environment. A variety of plants such as *Austrodanthonia caespitosa*, *Cajanus cajan, Helianthus annus*, *Impatiens glandulifera*, *Ipomea balsamina, Mirabilis jalapa*, *Prosopis juliflora, Pteris vittata, Sedum alfredii, Sorghum sudanense*, *Tegetes patula*, *Vetiveria zizanoides*, *Vigna unguiculata*, *Zea mays*, *Azolla caroliniana*, *Eichhornia crassipes*, *Callitriche lusitanica*, *Callitriche stagnalis*, *Fontinalis antipyretica*, *Lemna minor*, *Callitriche brutia*, *Typha angustifolia*, *Ranunculus trichophyllus* and microbes, and marine diversity have been employed for the remediation of environmental regimes. Further research to enhance the capability of plant and microorganisms employing modern biotechnological tools can help to speed up the process to clean the environment.

Acknowledgements Work on plant abiotic stress tolerance in SSG laboratory was partially supported by University Grants Commission (UGC), Department of Science and Technology (DST), Council of Scientific and Industrial Research (CSIR), Govt. of India. SSG and RG also acknowledge partial support from DBT-BUILDER grant.

References

Afzal M, Khan QM, Sessitsch A (2014) Endophytic bacteria: prospects and applications for the phytoremediation of organic pollutants. Chemosphere 117:232–242

Ali S, Abbas Z, Rizwan M, Zaheer IE, Yavas I, Unay A, Kalderis D (2020) Application of floating aquatic plants in phytoremediation of heavy metals polluted water: a review. Sustainability 12:1927

Allamin IA, Halmi MIE, Yasid NA et al (2020) Rhizodegradation of petroleum oily sludge-contaminated soil using *Cajanus cajan* increases the diversity of soil microbial community. Sci Rep 10:4094. https://doi.org/10.1038/s41598-020-60668-1

Ansari AA, Gill SS, Gill R, Lanza GR, Newman L (Eds) (2015a) Phytoremediation management of environmental contaminants, volume 1, Springer, Cham, ISBN 978-3-319-10394-5, XV, 348. https://doi.org/10.1007/978-3-319-10395-2

Ansari AA, Gill SS, Gill R, Lanza GR, Newman L (Eds) (2015b) Phytoremediation management of environmental contaminants, volume 2, Springer, Cham, ISBN 978-3-319-10968-8, XV, 366. https://doi.org/10.1007/978-3-319-10969-5

Ansari AA, Gill SS, Gill R, Lanza GR, Newman L (Eds) (2016a) Phytoremediation management of environmental contaminants, volume 3, Springer, Cham, ISBN 978-3-319-40146-1, XV, 576. https://doi.org/10.1007/978-3-319-40148-5

Ansari AA, Gill SS, Gill R, Lanza GR, Newman L (Eds) (2016b) Phytoremediation management of environmental contaminants, volume 4, Springer, Cham Switzerland, ISBN 978-3-319-41810-0, XV, 409. https://doi.org/10.1007/978-3-319-41811-7

Ansari AA, Gill SS, Gill R, Lanza GR, Newman L (Eds) (2017) Phytoremediation management of environmental contaminants, volume 5, Springer, Cham, ISBN 978-3-319-52379-8, XIV, 514. https://doi.org/10.1007/978-3-319-52381-1

Ansari AA, Gill SS, Gill R, Lanza GR, Newman L (Eds) (2018) Phytoremediation management of environmental contaminants, volume 6, Springer, Cham, ISBN 978-3-319-99650-9, XV, 476. https://doi.org/10.1007/978-3-319-99651-6

Aryal M, Liakopoulou-Kyriakides M (2013) Biodegradation and kinetics of phenanthrene and pyrene in the presence of nonionic surfactants by Arthrobacter strain Sphe3. Water Air Soil Pollut 224:1426

Banioko B, Eslamian S (2015) Phytoremediation in urban water reuse handbook. Taylor & Francis Group, LLC, pp 1177

Bidleman TF, Agosta K, Andersson A, Haglund P, Nygren O, Ripszam M, Tysklind M (2014) Air-water exchange of brominated anisoles in the Northern Baltic Sea. Environ Sci Technol 48:6124–6132

Bidleman TF, Lunden EB, Hansson K, Laudon H, Nygren O, Tysklind M (2017) Atmospheric transport and deposition of bromoanisoles along a temperate to arctic gradient. Environ Sci Technol 51:10974–10982

Burges A, Alkorta I, Epelde L, Garbisu C (2018) From phytoremediation of soil contaminants to phytomanagement of ecosystem services in metal contaminated sites. Int J Phytoremediation 20:384–397. https://doi.org/10.1080/15226514.2017.1365340

Carvalhais LC et al (2011) Root exudation of sugars, amino acids, and organic acids by maize as affected by nitrogen, phosphorus, potassium, and iron deficiency. J Plant Nutr Soil Sci 174:3–11

Chandra R, Yadav S (2010) Potential of *Typha angustifolia* for phytoremediation of heavy metals from aqueous solution of phenol and melanoidin. Ecol Eng 36:1277–1284

Cherniwchan J (2012) Economic growth, industrialization, and the environment resource. Energy Econ 34:442–467

Coakley S, Cahill G, Enright A-M, O'Rourke B, Petti C (2019) Cadmium hyperaccumulation and translocation in impatiens glandulifera: from foe to friend? Sustainability 11(18):5018. https://doi.org/10.3390/su11185018

Corami A (2017) Soil pollution and phytoremediation In: IIT Roorkee Executive Editor. Environmental Science and Engineering

Corami A (2021) Phytoremediation impacts on water productivity. Water Product J 1(2):13–22

Dat ND, Chang MB (2017) Review on characteristics of PAHs in atmosphere, anthropogenic sources, and control technologies. Sci Total Environ 609:682–693

El-Liethy MA, Dakhil MA, El-Keblawy A, Abdelaal M, Halmy MWA, Elgarhy AH, Kamika I, El-Sherbeny GA, Mwaheb MA (2022) Temporal phytoremediation potential for heavy metals and bacterial abundance in drainage water. Sci Rep 12:8223. https://doi.org/10.1038/s41598-022-11951-w

Favas PJ, Pratas J, Prasad M (2012) Accumulation of arsenic by aquatic plants in large-scale field conditions: opportunities for phytoremediation and bioindication. Sci Total Environ 433:390–397

Fu Q, Liao C, Du X, Schlenk D, Gan J (2018) Back conversion from product to parent: methyl triclosan to triclosan in plants. Environ Sci Technol Lett 3:181–185. https://doi.org/10.1021/acs.estlett.8b00071

Garrison AW, Nzengung VA, Avants JK, Ellington JJ, Jones WJ, Rennels D, Wolfe NL (2000) Phytodegradation of p, p'-DDT and the enantiomers of o, p'-DDT. Environ Sci Technol 34:1663–1670

Gerhardt KE, Gerwing PD, Greenberg BM (2017) Opinion: taking phytoremediation from proven technology to accepted practice. Plant Sci 256:170–185. https://doi.org/10.1016/j.plantsci.2016.11.016

Gribble GW (2003) The diversity of naturally produced organohalogens. Chemosphere 52:289–297

Hammond CM, Root RA, Maier RM (2018) Chorover mechanisms of arsenic sequestration by Prosopis juliflora during the phytostabilization of metalliferous mine tailings. Environ Sci Technol 52:1156–1164. https://doi.org/10.1021/acs.est.7b04363

He Z, Shentu J, Yang X, Baligar VC, Zhang T, Stoffella PJ (2015) Heavy metal contamination of soils: sources, indicators and assessment. J Environ Indicat 9:17–18

Howe PD, Dobson S, Malcolm HM (2005) 2,4,6-Tribromophenol and other simple brominated phenols, Concise International Chemical Assessment Document (CICAD) 66 WHO, Geneva

Jadia CD, Fulekar M (2009) Phytoremediation of heavy metals: recent techniques. Afr J Biotechnol 8(6):921–928

Jagetiya B, Sharma A, Soni A, Khatik UK (2014) Phytoremediation of radionuclides: a report on the state of the art. In: Gupta DK, Walther C (eds) Radionuclide contamination and remediation through plants. Springer, Cham, pp 1–31

Kafle A, Timilsina A, Gautam A, Adhikari K, Bhattarai A, Arya N (2022) Phytoremediation: mechanisms, plant selection and enhancement by natural and synthetic agents. Environ Adv 8:100203. https://doi.org/10.1016/j.envadv.2022.100203

Kamran M, Danish M, Saleem MH, Malik Z, Parveen A, Abbasi GH, Jamil M, Ali S, Afzal S, Riaz M (2021) Application of abscisic acid and 6-benzylaminopurine modulated morpho-physiological and antioxidative defense responses of tomato (*Solanum lycopersicum* L.) by minimizing cobalt uptake. Chemosphere 263:128169

Keith LH (2015) The source of US EPA's sixteen PAH priority pollutants. Polycycl Aromat Compd 35:147–160

Kim S, Lim H, Lee I (2010) Enhanced heavy metal phytoextraction by Echinochloa crusgalli using root exudates. J Biosci Bioeng 109:47–50

Koch C, Sures B (2018) Environmental concentrations and toxicology of 2,4,6-tribromophenol. Environ Pollut 233:706–713

Kohda YHT, Qian Z, Chien MF et al (2021) New evidence of arsenic translocation and accumulation in *Pteris vittata* from real-time imaging using positron-emitting 74As tracer. Sci Rep 11:12149. https://doi.org/10.1038/s41598-021-91374-1

Lareen A, Burton F, Schäfer P (2016) Plant root-microbe communication in shaping root microbiomes. Plant Mol Biol 90:575–587

Li JT, Gurajala HK, Wu LH, van der Ent A, Qiu RL, Baker AJM, Shu WS (2018) Hyperaccumulator plants from China: a synthesis of the current state of knowledge. Environ Sci Technol 52:11980–11994

Limmer M, Burken J (2016) Phytovolatilization of organic contaminants. Environ Sci Technol 50(13):6632–6643. https://doi.org/10.1021/acs.est.5b04113

Lin J, Gao X, Zhao J, Zhang J, Chen S, Lu L (2020) Plant cadmium resistance 2 (SaPCR2) facilitates cadmium efflux in the roots of Hyperaccumulator *Sedum alfredii* Hance. Front Plant Sci 11:568887. https://doi.org/10.3389/fpls.2020.568887

Liu Y, Zhu L, Shen X (2001) Polycyclic aromatic hydrocarbons (PAHs) in indoor and outdoor air of Hangzhou, China. Environ Sci Technol 35:840–844

Liu J, Xin X, Zhou Q (2017a) Phytoremediation of contaminated soils using ornamental plants. Environ Rev 26. https://doi.org/10.1139/er-2017-0022

Liu Y, Zeng G, Zhong H, Wang Z, Liu Z, Cheng M, Liu G, Yang X, Liu S (2017b) Effect of rhamnolipid solubilization on hexadecane bioavailability: enhancement or reduction? J Hazard Mater 322:394–401

Malik Z, Ahmad M, Abassi GH, Dawood M, Hussain A, Jamil M (2017) Agrochemicals and soil microbes: interaction for soil health xenobiotics in the soil environment. Springer, pp 139–152

Marques AP, Rangel AO, Castro PM (2009) Remediation of heavy metal contaminated soils: phytoremediation as a potentially promising clean-up technology. Crit Rev Env Sci Technol 39:622–654. https://doi.org/10.1080/10643380701798272

Matzen SL, Lobo GP, Fakra SC, Kakouridis A, Nico PS, Pallud CE (2022) Arsenic hyperaccumulator Pteris vittata shows reduced biomass in soils with high arsenic and low nutrient availability, leading to increased arsenic leaching from soil. Sci Total Environ 818:151803. https://doi.org/10.1016/j.scitotenv.2021.151803

Mózner Z, Tabi A, Csutora M (2012) Modifying the yield factor based on more efficient use of fertilizer—the environmental impacts of intensive and extensive agricultural practices. Ecol Indicator 16:58–66

Naeem M, Jimenez Bremont JF, Ansari AA, Gill SS (2022) Agrochemicals in soil and environment: impacts and remediation. Springer, Singapore, ISBN: 978-981-16-9309-0; 978-981-16-9310-6, p. XXVI, 612. https://doi.org/10.1007/978-981-16-9310-6

Nedjimi B (2021) Phytoremediation: a sustainable environmental technology for heavy metals decontamination. SN Appl Sci 3:286. https://doi.org/10.1007/s42452-021-04301-4

Petrová Š, Rezek J, Soudek P, Vaněk T (2017) Preliminary study of phytoremediation of brownfield soil contaminated by PAHs. Sci Total Environ 599:572–580

Phillips LA, Greer CW, Farrell RE, Germida JJ (2012) Plant root exudates impact the hydrocarbon degradation potential of a weathered-hydrocarbon contaminated soil. Appl Soil Ecol 52:56–64

Prakash D, Gabani P, Chandel AK, Ronen Z, Singh OV (2013) Bioremediation: a genuine technology to remediate radionuclides from the environment. Microb Biotechnol 6:349–360

Pratas J, Favas PJ, Paulo C, Rodrigues N, Prasad M (2012) Uranium accumulation by aquatic plants from uranium-contaminated water in Central Portugal. Int J Phytoremediation 14:221–234

Rai PK (2019) Heavy metals/metalloids remediation from wastewater using free floating macrophytes of a natural wetland. Environ Technol Innov 15:100393

Rajkumari J, Choudhury Y, Bhattacharjee K, Pandey P (2021) Rhizodegradation of pyrene by a non-pathogenic Klebsiella pneumoniae isolate applied with *Tagetes erecta* L. and changes in the rhizobacterial community. Front Microbiol 12:593023

Rascio N, Navari-Izzo F (2011) Heavy metal hyperaccumulating plants: how and why do they do it? And what makes them so interesting? Plant Sci 180:169–181

Ron EZ, Rosenberg E (2014) Enhanced bioremediation of oil spills in the sea. Curr Opin Biotechnol 27:191–194

Saleem MH, Ali S, Rehman M, Rana MS, Rizwan M, Kamran M, Imran M, Riaz M, Soliman MH, Elkelish A (2020) Influence of phosphorus on copper phytoextraction via modulating cellular organelles in two jute (*Corchorus capsularis* L.) varieties grown in a copper mining soil of Hubei Province, China. Chemosphere 248:126032

Sivaram AK, Logeshwaran P, Lockington R, Naidu R, Megharaj M (2019) Low molecular weight organic acids enhance the high molecular weight polycyclic aromatic hydrocarbons degradation by bacteria. Chemosphere 222:132–140

Sivaram AK, Subashchandrabose SR, Logeshwaran P et al (2020) Rhizodegradation of PAHs differentially altered by C3 and C4 plants. Sci Rep 10:16109. https://doi.org/10.1038/s41598-020-72844-4

Wang Y, Fang L, Lin L, Luan T, Tam NF (2014) Effects of low molecular-weight organic acids and dehydrogenase activity in rhizosphere sediments of mangrove plants on phytoremediation of polycyclic aromatic hydrocarbons. Chemosphere 99:152–159

Wu Z, Banuelos GS, Lin ZQ, Liu Y, Yuan L, Yin X, Li M (2015) Biofortification and phytoremediation of selenium in China. Front Plant Sci 6:136

Wu Q, Zhou H, Tam NF, Tian Y, Tan Y, Zhou S, Li Q, Chen Y, Leung JY (2016) Contamination, toxicity and speciation of heavy metals in an industrialized urban river: implications for the dispersal of heavy metals. Mar Pollut Bull 104:153–161

Xu XH, Wen B, Huang HL, Wang S, Han RX, Zhang SZ (2016) Uptake, translocation and biotransformation kinetics of BDE-47, 6-OH-BDE-47 and 6-MeO-BDE-47 in maize (Zea mays L.). Environ Pollut 208:714–722

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

Yana L, Le QV, Sonne C, Yang Y, Yang H, Gu H, Ma NL, Lam SS, Peng W (2021) Phytoremediation of radionuclides in soil, sediments and water. J Hazard Mater 407:124771

Zaheer IE, Ali S, Saleem MH, Imran M, Alnusairi GS, Alharbi BM, Riaz M, Abbas Z, Rizwan M, Soliman MH (2020) Role of iron–lysine on morpho-physiological traits and combating chromium toxicity in rapeseed (*Brassica napus* L.) plants irrigated with different levels of tannery wastewater. Plant Physiol Biochem 155:70–84

Zhang Q, Kong W, Wei L, Wang Y, Luo Y, Wang P, Liu J, Schnoor JL, Jiang G (2020) Uptake, phytovolatilization, and interconversion of 2,4-dibromophenol and 2,4-dibromoanisole in rice plants. Environ Int 142:105888. https://doi.org/10.1016/j.envint.2020.105888

Zhu XG, Long SP, Ort DR (2008) What is the maximum efficiency with which photosynthesis can convert solar energy into biomass? Curr Opin Biotechnol 19:153–159

Chapter 2
Phytoremediation and Contaminants

Alessia Corami

Abstract The increase in population, industrialisation and urbanisation is the main cause of the huge and deep discharge of contaminants in soil, surface water and groundwater. The origin of contaminants is either natural or anthropogenic. These pollutants could be organic or inorganic. The consequence are environmental problems such as health problems for humans, animals and plants. Water and soil are fundamental resources (e.g., the food supply, energetic resources, or industrial activities). Technological solutions for remediation are very expensive, consume high energy and produce a huge waste after the treatment. This urgent question about the conservation of natural resources and restoration of Brownfield and/or surface water highlights the need to develop and apply alternative technologies such as phytoremediation. This technology is based on the use of plants for removing pollutants in situ and/or reducing the risk of polluted soil, water and air.

Keywords Metals · Organic contaminants · Phytoremediation · Soil · Pollution · Wastewater · Fertilizers · Pesticides · Remediation · Toxicity · Sustainability · Dechlorination · Plants · Bio-degradation · Waters

2.1 Introduction

Rapid industrialization and urbanization have culminated in the pauperization of water, air and land quality, and it has meant an increase of different types of pollutants in the environment, organic and inorganic, natural and anthropogenic ones (Aisien et al. 2010a, b, c; Corami 2017, 2021a). The type of pollution could be point and nonpoint source; the former might be emission, effluents and solid discharge

---

A. Corami (✉)
MIUR, Ministry of University and Research, Rome, Italy
e-mail: alessia.corami@louisiana.edu

L. Newman et al. (eds.), *Phytoremediation*, https://doi.org/10.1007/978-3-031-17988-4_2

from industries, vehicle exhaustion and metals from smelting and mining; the latter might be the use of pesticides/insecticides, disposal of industrial and municipal wastes in agriculture and excessive use of fertilizers (Banioko and Eslamian 2015). In the last years, numerous efforts have been carried out to find a solution, in particular a sustainable solution, to decrease the risk for human health and the environment (Banioko and Eslamian 2015).

Remediation methodology (ex situ and/or in situ) means to remove pollutants or make them less harmful. Techniques for soil remediation usually consist of digging up contaminated soil, removing it and/or capping it to contain the contaminated areas. On the contrary, phytoremediation means removing, stabilizing or transforming the contaminants through the plants and microorganisms in the rhizosphere. Plants can remediate organic and inorganic contaminants, the advantages are: low energy cost and eco-friendly nature; and people reactions are generally positive; On the other hand, remediation requires a long time for the plants to grow and uptake the contaminants (Banioko and Eslamian 2015; Corami 2017). Phytoremediation destroys contaminants or, at least, makes contaminants more innocuous, and sometimes, it is suggested to use phytoremediation instead of leaving a waste site untreated (EPA 2000; Corami 2017, 2021a). Therefore, it is considered an ecologically safe method compared to the previous and environmentally harmful physical and chemical remediation technologies. Important progresses have been made in the last years such as: developing suitable plants for phytoremediation and/or nano-phytoremediation of contaminants. In general, phytoremediation technology is based on the use of plants and rhizosphere microorganisms to remove and transform pollutants in soils, sediments, groundwater and surface water (Corami 2021a; Ali et al. 2020), which might affect the availability and accumulation of heavy metals (HMs) in soil and plants. A huge problem is what to do with biomass, and methods such as incineration, storing or chemical decomposition of contaminated soil are utilized. Phytoremediation has been found to be effective and efficient among environmental technologies, and it also means permanent remediation rather than a different problem. Phytoremediation is currently thought of as an alternative, cost-effective and environmentally acceptable technology for the remediation of contaminated air, land and water. Indeed, the cleanup of contaminated sites and their reuse, minimizing the amount of toxic elements in the food chain, are compulsory (Hooda 2007). Phytoremediation entails the use of plants for decontaminating soil, water and air (Lone et al. 2008). Allenby (1999) states that there is a need for sustainable development in the design of industrial processes, business decisions and strategies.

2.2 Phytoremediation

Phytoremediation is a process in which plants are used in polluted sites, mitigating toxic effects of pollutants by physical, biochemical, biological, chemical and microbiological interactions. Many mechanisms such as accumulation or extraction, degradation, filtration, stabilization and volatilization were employed in phytoremediation (Corami 2017; Favas et al. 2018; Yadav et al. 2018; Gudeppu et al. 2019; UNEP 2019; Vidal et al. 2019; Ansari et al. 2020; Corami 2021a). Results from phytoremediation experiments show that there are differences depending on the different experimental conditions and field experiments. It is quite difficult to state whether one plant species is better than the other species (Brisson and Chazarenc 2009). The choice of plant species is still an open debate, and the type of species used is important to get the best results (Varun et al. 2015; Tripathi et al. 2020).

In addition, contaminants are sorbed by the plant through the nutrient uptake mechanism. These toxic organics are degraded by plants, and inorganic pollutants are sequestrated in vacuoles. Organic pollutants could be metabolised by living organisms, the processes which may occur are immobilization, storage, volatilization, depending on the environmental conditions, plants and the type of organic compound too. Plants absorb xenobiotics mainly through roots reaching the xylem. The availability of an organic compound depends on its physicochemical characteristics (solubility in water, charge, molecular size, etc.) (Campos et al. 2008). Organic compounds are modified when entering the symplast through oxidation, reduction and/or hydrolysis reactions and later through conjugation with glutathione, sugars or organic acids, making contaminants more soluble and simple to be bound by enzymes and proteins (Dietz and Schnoor 2001; Pilon-Smits 2005; Campos et al. 2008). One example is Cytochrome P450 monooxygenases, through the so-called secondary metabolism, reactions from hydroxylation or epoxidation steps. In this step, the potential for phytoremediation was soon recognized through the complexation of phenol coupling, then a ring formation and successively, by the modification or decarboxylation (Campos et al. 2008). In fact, P450s have been combined with the degradation of organochemicals (Doty et al. 2000; Didierjean et al. 2002). Hence, plants sorbed contaminants within plant tissues by diffusion, chemical transformation, conjugation and sequestration from the polluted source (Campos et al. 2008; Komives et al. 2009); moreover, existing genes or transgenic expression of bacterial genes is another way for plant protection (Nwoko et al. 2004; Fernández et al. 2015).

As a matter of fact, Sadowsky (1999) reported that phytoremediation gained attention as a clean-up method for many hazardous organic and inorganic pollutants, such as HMs (Kumar et al. 1995; Salt et al. 1995a; Chaney et al. 1997), chlorinated solvents (Walton et al. 1994; Haby and Crowley 1996), agrochemicals (Anderson et al. 1994; Hoagland et al. 1997; Kruger et al. 1997), polycyclic aromatic hydrocarbons (April and Sims 1990; Reilley et al. 1996), polychlorinated biphenyls (Brazil et al. 1995; Donnely and Fletcher 1995), munitions (Schnoor et al. 1995) and radionuclides (Entry et al. 1996).

Phytoextraction means contaminant uptake by roots and their translocation into the shoots. Contaminants are removed by harvesting the plants. Biomass could be disposable or reused (Ali et al. 2013). Sadowsky (1999) reports that pollutants sequestration within plants is valid for phytoextraction in soil and water with heavy metals contamination (Kumar et al. 1995; Raskin et al. 1997; Chandra and Kumar 2017), such as Cd, Pb, Zn, Cu, Cr, Ni, Se and Hg (Cunningham et al. 1996; Chaney et al. 1997). Phytoextraction can be labelled as continuous phytoextraction (by hyperaccumulator plants) and induced phytoextraction (through a chemical accumulation of metals to crop plants) (Fitz and Wenzel 2002; Corami 2017). Heavy metals are adsorbed and/or absorbed by plant roots via xylem and phloem tissues and then arrive in the harvestable part of the plant. Since plants may have the capacity to uptake and stand different pollutants, many different plants may be used, and this is suitable for media which have been contaminated with more types of pollutants (Banioko and Eslamian 2015). This process could be replicated many times to reduce contamination to acceptable levels. Sometimes, phytomining is allowed so that it is possible to recycle metals; in general, this is reserved for precious metals.

Rhizofiltration is the use of plant roots for absorption, concentration and precipitation of heavy metals from polluted effluents (Dushenkov et al. 1995; Corami 2017; Chandra and Kumar 2017), and it occurs in the rhizosphere and water must be in contact with roots. Rhizofiltration means to trap contaminants in roots and later to shoots. Allowing to harvest the biomass. Later plants could continue the growth/harvest cycle till the suitable level of contamination is reached (Dushenkov et al. 1995; Verma et al. 2008; Fard et al. 2011; Chandra and Kumar 2017; Ali et al. 2020; Ansari et al. 2020); furthermore, biomass is suggested to be used as fuel. The disadvantage is that pollutants are not extracted, so it can take years to clean the medium, and if different contaminants are present, the efficiency decreases.

Phytostabilization is the immobilization of contaminants in soil by absorption and accumulation through the roots, adsorption onto roots, or precipitation within the root zone, preventing a contaminant migration via wind and water erosion, leaching and avoiding the metals from entering the food chain (Baker et al. 1994; Cunningham and Ow 1996; Chandra and Kumar 2017; Ansari et al. 2020). The choice of plants is an important feature for practising phytostabilization-based techniques (Barbafieri et al. 2004; Corami 2017); generally speaking, it is a fundamental aspect of phytoremediation (Lu 2009; Stefani et al. 2011; Ansari et al. 2020). HMs are converted into a less toxic state by special redox enzymes excreted by plants (Ali et al. 2013; Corami 2017), and phytostabilization gathers mainly on sequestering pollutants in the soil near the roots and not in plants.

Phytotransformation or phytodegradation is the rupture of contaminants by metabolic processes within the plant, and they are incorporated into the plant. Degradation might occur outside the plant because compounds are released, which results in their transformation; on the contrary, degradation of microorganisms is considered rhizodegradation. Phytotransformation might also occur in an environment without microorganisms, also in sterile soils, where biodegradation could not occur; unfortunately, toxic intermediate products may form (e.g., PCP was metabolized to tetrachlorocatechol). Hannink et al. (2001) state that genes have encoded a nitroreductase from a bacterium inserted into tobacco, showing a fast removal of trichlorotoluene and raising resistance to the toxic effect of the chemicals. This mechanism allows plants to grow even though the contaminant amount is high for non-treated plants (Burken 2003; Sorek et al. 2008). After organic contaminants uptake, they might be translocated to other plant tissues and later volatilized, they might be degraded, and they might be bound in non-available forms (Salt et al.

1998; Corami 2017). Few organic contaminants appear to be mineralized; in general, a small amount of these pollutants are fully transformed into water and CO_2.

Phytostimulation or rhizodegradation means that microorganisms break organic contaminants in the rhizosphere. Contaminants might reach the rhizosphere in the ground water because of groundwater movement, which might be induced by the transpiration of plants. Plant roots produce exudates, such as sugars, amino acids, organic acids, fatty acids and sterols, which could increase the number of microorganisms. These exudates are different according to the type of plants. Roots might increase soil aeration and soil moisture; therefore, the condition for biodegradation by the microorganism is more favourable (EPA 2000; Corami 2017). Furthermore, rhizospheric microorganisms may accelerate the processes by volatilizing contaminants (Salt et al. 1998; Corami 2017).

Phytovolatilization is the release of contaminants into the atmosphere; the contaminant is uptaken by plant metabolism and released via transpiration. The released contaminants may also be subjected to photodegradation in the atmosphere.

Phytostimulation is considered an intensification of rhizosphere biodegradation or rhizodegradation or plant-assisted bioremediation, where degradation means the rupture of organic contaminants in the soil carried out by microbial activity in the plant root zone.

2.3 Phytoremediation in Water and Wastewater

Unfortunately, lakes and rivers are used as bins for many kinds of waste, including untreated or partially treated municipal sewages, industrial poisons and harmful chemicals. These contaminants leach into the surface and groundwaters and could reach the food chain (Hinrichsen and Tacio 2002). Another big issue is water from formland's runoff because of the presence of different types of pollutants, it is still not possible to waste anymore water. Therefore, contamination is considered heterogeneous, and there are many different points of contamination (French et al. 2006; Corami 2021a). Levine and Asano (2004) write that most of the water, used for municipal purposes, is considered wastewater, but it may be reused after treatment for further applications. They highlight that non-potable water supports public water supplies for irrigation, industrial cooling water, river flow augmentation and other applications.

Domestic waste is among the most common cause for water pollution. The most important factor for water pollution is the kitchen since kitchen wastes enter water bodies and they dissolve in water. It consists of microorganisms and toxic organic and inorganic matter. Phytoremediation shows a high removal rate of pollutants, and the treatment also improves the physical characteristics of the kitchen wastewater such as colour and turbidity. This treated water could be used for gardening and other related purposes (Chandekar and Godboley 2017).

Water below the ground surface is known as groundwater, and it could be polluted or contaminated by human activities and pollutants such as physical, inorganic chemical, organic chemical, bacteriological and radioactive substances. Some of these pollutants are defined as recalcitrant pollutants as they take prolonged time to degrade (Wong 2009). These types of contaminants such as PCBs, persistent organic pollutants (POPs), CPCs, polycyclic aromatic compounds (PAHs) and metals (Ahmadi et al. 2017) could be present also after treatment. Remediation techniques used are pump and treat, air sparging and dual phase extraction (physical), ozone and oxygen gas injection, chemical precipitation, membrane separation, ion exchange, carbon absorption, aqueous chemical oxidation and surfactant-enhanced recovery (chemical) and bioaugmentation, bioventing, biosparging, bioslurping and phytoremediation (biological). Surface waters (rivers, streams and ponds) are easily polluted due to easy access. The main causes of pollution of surface water are run-off, sewage and industrial effluent discharges. Inorganic pollutants are usually not degraded into simple compounds, so these contaminants may be transported or transformed into less toxic forms. Plants grown in inorganic polluted water show different morphological, physiological and biochemical properties, and this could be a useful tool for biomonitoring aquatic system (Zhou et al. 2008; Singh et al. 2012; Fernández et al. 2015). In particular, some species of plants, defined as hyperaccumulators, can absorb metals, but they show slow growth and low biomass production. Plants in the presence of organic pollutants show senescence symptoms – chloroplasts start to degrade and become elongated; chloroplast membranes show degradation; and some chloroplasts become broken (Lucas et al. 2011; Fernandez et al. 2013, 2015). Organic compounds have a large spectrum of chemical compositions and structures, and plants may mineralize them into less toxic compounds, such as CO_2, nitrate, chlorine and ammonia (Cunningham et al. 1996; Fernández et al. 2015). Unfortunately, a high amount of ammonium nitrate and/or other forms of nitrogen increase eutrophication (Glibert et al. 2004; Zhang et al. 2007; Naeem et al. 2014; Ansari et al. 2015). Eutrophication is the amount of nutrients in water and its consequences on aquatic life. Aquatic plants could remove organic nutrients, and they are converted into the substance of the plants as their biomass (El-Kheir et al. 2007). During the phytoremediation through aquatic plants, it is observed that water pH increases allowing the growth of aquatic plants and restoration of the aquatic system (Patel and Kanungo 2010; Kaur et al. 2018; Ansari et al. 2015). Ansari et al. (2015) state that the sustainability of phytoremediation systems is affected by changes in climate, such as pH, temperature and light. In particular, absorption of nutrients and biochemical reactions taking place in living organisms are regulated by pH values; temperature is connected with the functioning of the aquatic system (El-Shafai et al. 2007; Ansari and Khan 2009; Lu et al. 2010; Ansari et al. 2015). It has been carried out experiments on eutrophic waters (overabundance of nutrients) with different amounts of plants and under controlled conditions. Phytoremediation efficiency is species dependent; therefore, the presence of different types of plants is more effective in removing nutrients. By removing regularly aquatic macrophytes and replacing them with fresh plants, the ecosystem could be restored (Ansari et al. 2015). Furthermore, aquatic plants have remediating effects on the removal of heavy metals from wastewater because of the capability of rapid growth on a wide range of pH as stated in Singh et al. (2012), and metals are present in a soluble form.

Phytoremediation shows a high removal rate of pollutants, and the treatment also improves the physical characteristics of the kitchen wastewater, such as colour and turbidity. This treated water could be used for gardening and other related purposes (Chandekar and Godboley 2017).

Ghaly et al. (2005) suggested using wastewater from hydroponic culture as fish feed in aquaculture. Hydroponic wastewater is enriched in nutrients such as N and P. He suggested combining aquaculture and hydroculture techniques, with the double purpose of reducing the pollution caused by fish farming and the demand for fertilizers and avoiding contaminants in surface and ground water. Five plants have been studied; in particular, rye, barley and oat show the ability to reduce the pollution potential of aquaculture wastewater and the potential to be used as fish feed. To use wasteter from hydroponic system for a secondary use in aquaculture must be added Ca, Na, Mn, Fe and fat.

The second use of treated wastewater in agriculture is becoming a recommended practise, and phytoremediation is a very suitable tool. In particular, macrophytes are cost-effective, and they could stand adverse conditions and show high colonisation rates. Indeed, choosing a suitable plant is fundamental to phytoremediation (Truong and Baker 1998; Mashauri et al. 2000; Fonkou et al. 2002; Baskar et al. 2009; Girija et al. 2011; Aisien et al. 2015). Aisien et al. (2015) write about an abattoir in Benin city (Nigeria) and the discharge of wastewaters into water bodies, and these wastewaters have caused an increase in algae growth and consequently the eutrophication phenomenon; reduction of aquatic plants and animals growth; and increase in heavy metals, water odour, foaming, colour, conductivity and temperature. In this case, it is used an integrated approach through macrophytes and microalgae to remediate abattoir wastewaters. The treatment was divided into four steps and each one lasts 7 days. A reduction of organic matter, nutrients and microbial loads is observed. In the end, the water quality indicators are below the limit from WHO/FEPA for discharging wastewater into surface water. The metal amount is decreased because of the aquatic macrophytes and microalgae, which are considered hyperaccumulators. An increase in DO has been observed because of the CO_2 dissolution (Awuah et al. 2004; de Godos et al. 2010); pH decreases because of nutrient absorption, and on the contrary, BOD and COD show a high decrease due to the microbial action. The treatment efficiency by macrophytes and microalgae applied has been very good. In addition, macrophytes could absorb water nutrients turning them into biomass as stated by Souza et al. (2013a, b). Waterbodies flowing in large urban or industrial areas have less amount of dissolved oxygen and an increased level of nutrient concentrations (Zorzal et al. 2005). In general, heavy metals in water are treated with addition of lime or caustic soda to precipitate metal hydroxides. This method is quite costly according the reagent which has been used (United Nations 2003) and then it is necessary to dispose them (Olufunmilayo and Ogunbayo 2012). Olufunmilayo and Ogunbayo (2012) have carried out experiments on three different types of wastewater: metallurgical, textile and pharmaceutical using water hyacinth, which is very efficient in absorbing and accumulating various heavy metals (Von et al. 1999; Rezania et al. 2015) for about 5 weeks. Water hyacinth is effective in decreasing BOD, DO nitrate–nitrogen values. BOD order of efficiency is metallurgical wastewater > textile wastewater > pharmaceutical wastewater; order for DO is slightly different, which is metallurgical wastewater > pharmaceutical wastewater > textile wastewater and for nitrate–nitrogen, the order was textile wastewater > metallurgical wastewater > pharmaceutical wastewater. According to the harvesting during the experimental period, the efficiency of Cd removal is between 93.55% and 95.59%. A Cd release is observed if the time is longer though Lu et al. (2004) have suggested that water hyacinth is effective in treating wastewater with a low Cd concentration. Cu concentration decreases more in textile wastewater than in metallurgical wastewater; iron concentration decreases according to the time, metallurgical wastewater needs 5 weeks, textile wastewater shows a decrease in 3 weeks, and pharmaceutical wastewater decreases during all 5 weeks. It is inferred that water hyacinth could be used for wastewater, and successively, it is suggested to convert the biomass into other products (Rezania et al. 2015). Paz-Alberto and Sigua (2013) report the experiment carried out about the use of water hyacinth in removing ethion (phosphorus pesticide) using non-sterile planted, sterile planted, non-sterile unplanted and sterile unplanted treatment (Xia and Ma 2005). The amount of ethion in plants is about 55–91% in shoots and about 74–81% in roots after a week; this suggests that plant uptake and phytodegradation are the main processes. It is also stated that water hyacinth is a cost-effective and an ecological alternative in accelerating the removal and degradation in case of ethion in agro-industrial wastewater polluted.

Souza et al. (2013a, b) carried out experiments in a greenhouse at 0, 15 for 30 days, and some parameters were controlled such as COD, BOD, ammoniacal nitrogen, total kjeldahl nitrogen, organic nitrogen, total P, pH, DO, EC and T. A high decrease of BOD and COD is observed in 15 days. According the kind of macrophytes, the deacreasing of these parameters is slightly different. The temperature did not show a great difference because of the emerging leaves of *Myriophyllum aquaticum*. In particular, it is noted that in temperate regions, seasonal radiation and temperature variations are well-defined throughout the year, whereas in tropical regions, seasons are not defined very well and show less variations in temperatures (Esteves 1979; Everitt and Burkholder 1991; Madsen and Brix 1997; Souza et al. 2013a, b). This entails a minor variation in the production of biomass in tropical regions than in temperate regions. The highest nitrogen removal is observed after 30 days due to microbiological process and absorption by aquatic plants. Chang et al. (2006) and Souza et al. (2013a, b) state that the assimilation of nitrogen compounds could be amplified by the interaction between macrophytes and bacteria. Bento et al. (2007) have observed that aquatic macrophytes show a great ability to absorb phosphorus, and it could easily return to the water column, in particular in anoxic conditions (Esteves 1998). Water quality could be improved through macrophyte control. This quality level could be maintained through the decomposition process, and therefore, nutrients do not return to the environment.

Actually, phytoremediation programs, based on the use of aquatic macrophytes, have been used in tropical regions with metals (Dias Fernandes et al. 2020), showing high rates of metal removal (85–95%) (Pereira et al. 2011; Martelo and Lara Borrero 2012; Silva et al. 2013) In particular, it highlights the accumulative capacities in an aquatic organism of Cd, Cu and Zn concentrations in wild fish, in particular in fish tissues with Cd level above limits, not suitable for consumption (Ekweozor et al. 2017; Shovon et al. 2017). The capacity of *Echinochloa crusgalli L.* was evaluated at three different times (20, 30 and 45 days). Particularly, an ecotoxicological essay in case of acute or chronic exposure by *Daphnia similis* as a test organism has been carried out. The formation of aerenchyma in roots was observed after 20 days, and this seems to be a strategy in a flooded environment. After 35 days, the number of aerenchyma decreases, which might be due to the fact that plants are adapting to the contaminated environment (Doblas et al. 2017; Dias Fernandes et al. 2020). These endodermal barriers have been created to adapt to the availability and/or toxicity of nutrients. In 16–19 days, the remediation will be achieved. Galiulin et al. (2001) report numerous examples of the use of phytoremediation in contaminated water by metals from ore mining. It is underlined that mining and smelting industries contaminate water in a great measure than soil, and biological availability of metals is related to pH and the amount of organic and inorganic compounds (Zolotukhina and Gavrilenko 1989; Galiulin et al. 2001). It is stated that submerged plants accumulated a great amount of metals than floating or partially submerged plants. This confirm the importance of contact area between plant and aqueous environment. It is suggested a two step-process, firstly the adsorption on the surface and secondly the absorption in plant tissues. Especially, metals form complexes adding ions to the functional groups of organic compounds (carboxyl, amino, imino, hydroxyl, sulfhydryl and keto groups), and macrophyte absorbs metals according to their content in the riverbed sediment, whereas their concentration adsorption is by water.

Hegazy et al. (2011) have studied the capacity of *Typha domingensis* to absorb heavy metals from industrial discharges in surface waters, soils and sediments, in particular, the amount of nitrogen and phosphorous are high, but also cations such as Na^+, Ca^{2+} and Mg^{2+} are abundant, and K^+, Al^{3+}, Fe^{3+}, Zn^{2+} and Pb^{2+} are present. The presence of these cations is due to the industry discharges, in particular iron and steel production for Fe^{3+}; Al^{3+} is attributed to food products and beverage facilities; Zn^{2+} and Pb^{2+} are in excess for electronics and electricity production. It has been valued the translocation factor (TF), TF <1 means metal translocation from root-to-shoot tissue as not an important factor (Ma et al. 2001). In particular, an accumulation of metal ions in roots is observed rather than in other parts of the plants (Satyakala and Jamil 1992; Zaranyika and Ndapwadza 1995; Chandra and Kulshreshtha 2004). It is inferred that changes in pH values are due to root exudates, and this could cause metal precipitation on the root surface through the apoplastic way, that is, through the micropores of cell walls in the root.

Ponce-Hernández et al. (2020) have tested *Typha latifolia*, *Typha angustifolia* and *Salix matsudana* because of their low cost. These plants have been used directly or as precursors of activated carbons to remove metals like Pb(II), Cd(II), Cr(VI), Cu(II), Mn(II) and Zn(II). In particular, *T. latifolia* has been used for Pb(II). It has been observed that pH deeply affects adsorption capacity; at pH = 5, the highest adsorption capacity occurs, and it decreases by varying the pH from 5 to 3 and from 3 to 2. During the adsorption process, pH is kept constant by adding NaOH or HNO_3. This is probably due to H^+ migration from the roots to the solution and Pb(II) has been absorbed by ion exchange. The root absorption capacity also increased with temperature.

Kumar and Chopra (2017) carried out an experiment on municipal wastewater with domestic households and industrial and agricultural activity. This wastewater is enriched with different organic and inorganic contaminants, and it causes eutrophication phenomena in rivers. It is used as an aquatic macrophyte such as *Trapa natans* L. (Bitonti et al. 1996; Alfasane et al. 2011: Mann et al. 2012). The species has a dense and fibrous root system; therefore, the surface area is an optimum medium for absorption and adsorption processes and for microorganism attachment (O'Neill 2006; Lalith et al. 2007; Pandey et al. 2013; Kumar and Chopra 2016, 2017). It has been observed that *T. natans* absorbs in roots, leaves and fruits; in particular, Fe, Mn and Zn are translocated in leaves, and perhaps, this is due to the synthesis of photosynthetic pigments, as also stated by Porra (2002). Lalith et al. (2007) observed that from 15 to 60 days of phytoremediation experiments, the values of fresh weight, dry weight, chlorophyll content and leaf area index of *T. natans* were gradually increased. In the same way, the amount of crude protein, crude fiber, total sugar, total fat and total ash has increased. This aquatic plant efficiently removes macro- and micronutrients and metals. Varun et al. (2015) state that chlorophyll and free proline patterns indicate that most plants have developed strategies to counteract phytotoxicity because of the toxic amount of Cd, Pb and Cu. Growth retardation and a negative effect on plant metabolism (Agrawal and Sharma 2006) and a decrease in biomass production (Phetsombat et al. 2006) are observed; on the contrary, Liphadzi and Kirkham (2006) suggested that the presence of potentially toxic metals in the green parts could be a strategy against herbivores.

Luqman et al. (2013) propose trees as a filter to absorb pollutants from the environment because of large biomass below and above ground (Coder 2011; Ghosh and Singh 2005). It is stated that if water slows slowly because of the presence of vegetation, pollutants could be filtered, thanks to the extended root system (Bose et al. 2008). Crompton (2008) states that natural lands can slow down and filter the water, making it cleaner.

In the last years, the management of arsenic-rich wastewaters has been a major environmental concern, and Jasrotia et al. (2017) have carried out experiments to identify suitable aquatic species (macrophyte and microphyte) to uptake arsenic from water and accumulate into tissue and/or membranes. Phytoextraction mechanism is the preferred one, and water hyacinth has been chosen as macrophyte, and locally algae *Chlorodesmis* sp. and *Cladophora* sp. as microphytes under similar conditions. *Cladophora* sp. can stand extreme arsenic conditions showing high arsenic removal efficiency in 10 days, and pH ranged from 7.2 to 7.5 under ambient temperature; this algae species is suitable to make arsenic wastewater suitable for irrigation. Water hyacinth has survived at 2 mg/L As concentration, conversely Ingole and Bhole (2003) have written that water hyacinth could remove As concentration <10 mg/L; Chlorodesmis sp. withstand over 4 mg/L of arsenic concentration. A difference in pH has been not observed. It varies from 7.3 to 8.4, while COD concentration shows changes. Indeed, for water, a COD removal efficiency of 50% is observed for hyacinth, but As uptake was only 20%, and after the ninth day, desorption started. *Chlorodesmis* sp. could remove about 50–55% of COD and As uptake was about 40–50%. Desorption started from the 11th day. Removal efficiency by COD for *Cladophora* sp. was about 55–60% higher for the first 10 days; later, it became insignificant. The algae behaviour in arsenic water is probably caused by a defence mechanism against oxidative damages inside the cell structure (Pinto et al. 2003; Jasrotia et al. 2017), and As binding is through the biomethylation pathway. This pathway is through reductases and methyltransferases enzymes. This enzyme catalyses the transfer of methyl group from S-adenosylmethionine to trivalent arsenic (Shen et al. 2013).

Many methods have been used for phenol remediation, such as microbial degradation, adsorption on activated carbon, chemical oxidation, incineration and solvent extraction. However, there are many disadvantages like low efficiency and high costs and the products formed are more toxic than phenol itself. Phenol is a compound from industries such as petrochemical, pharmaceutical, plastic and pesticide industry, and it is considered a harmful pollutant and dangerous to human health. González et al. (2006) have applied phytoremediation, through hairy root cultures, the advantages are biochemical and genetic stability as stated in Flores and Curtis (1992). In particular this method is advantageous because the lack of microbiota activity. The method is based on the presence of some enzymes like nitroreductases, glycosyl and glutathione transferases, oxidases, phosphatases, etc.; these enzymes help during the transformation of toxic and xenobiotic compounds; furthermore, plants and microorganisms have several oxidases (laccases and peroxidases) which could help in removing pollutants (Wolfe and Hoehamer 2003). This material (hairy root) is considered as a low-cost enzyme source and the percentage removal increases with H_2O_2; unfortunately, an excess may produce a suicide enzyme inactivation (Arnao et al. 1990). It is suggested the presence of peroxidase with H_2O_2 achieve a phenol chemical removal without roots. In the presence of hairy roots, the treatment efficiency was about 95% in 5 h of treatment, and best results are achieved at a pH of 7.5, but good removal is for a pH range 4.0–9.0. An increase in the temperature (40°–60°) is observed with the removal efficiency. González et al. (2006) state that the optimisation of this method must consider the temperature and pH control, reaction time and the kind of roots to be used to reach a cost-effective method; indeed, tomato hairy roots are able to remove phenol from water.

Other pollutants are antibiotics, used as feed efficiency promoters and to increase the growth of animals, such as livestock destined for human consumption (Gujarathi et al. 2005), and antibiotics are released in waters and soils. Gujarathi et al. (2005) have applied phytoremediation to tetracycline (TC) and oxytetracycline (OTC) in aqueous media using aquatic plants. It is observed that these antibiotics are persistent for a long time; microbes, plants, and animals are exposed to antibiotics in soil, water and sediment, and this may cause antibiotic resistance in bacteria in conventional water. Adams et al. (2002) showed that conventional water treatment is not deeply effective. In fact, aquatic plants have shown a modification of OTC and TC in 24 h, this phenomenon maybe is by a root-secreted enzyme(s)/metabolite(s), perhaps it is involved in antibiotic degradation and/or modification. In particular, it is inferred that according the initial antibiotic concentration the modification decreases, perhaps this modified compound is present in the root exudates, it seems this disappearance is not enzyme catalysed. Unlike, peroxidases have been found to oxidize PAHs (Adler et al. 1994; De Araujo et al. 2002; Miksanova et al. 2001; Criquet et al. 2000; Strycharz and Shetty 2002), it is in higher plants which are able to catalyse oxidation reactions by hydrogen peroxide as in González et al. (2006).

Obinna and Ebere (2019) observed a correlation between the aquatic plant tolerance to organic pollutants and the high amount of contaminant metabolites in the residue fraction of plant cell walls, where enzymatic and metabolic activities may occur. Plant uptake is influenced by physical and chemical properties of organic pollutants, such as hydrophobicity with partition coefficient between octanol and water (KOW), molecular mass, and the partition coefficient between octanol and air (KOA). They suggest a simple uptake of organic pollutants from plants in water and absorption from the air if there is a positive correlation between high *K*OW and low KAO.

Prasad (2011) stated that organic contaminants are water-soluble if they show log Kow < 1, whereas contaminants, showing high sorption to the roots and slow or no translocation to the stems and leaves, have a log Kow > 3.5.

Many studies have demonstrated the effectiveness of organic pollutant and heavy metals remediation. Physicochemical properties of the water contaminants, plants, and the experimental characteristics affect removal rates.

Phytoremediation is a technique that has positive results from wastewater treatment, and this process could be used either with organic or inorganic pollutants.

2.4 Phytoremediation in Soil

In soil, metal pollutants are from industrial areas, mine tailings, fertilizers, animal manures, sewage sludge, pesticides, wastewater irrigation, and metalloids from industrial waste or mine ores (Chen et al. 2000; Khan et al. 2008; Zhang et al. 2010; Vodyanitskii and Plekhanova 2014; Henry et al. 2015; Bolan et al. 2014; Pardo et al. 2014; Pierart et al. 2015; Hettick et al. 2015; Křîbek et al. 2016; Corami 2017). There are also persistent organic pollutants (POP) and polycyclic aromatic compounds (PAHs), pesticides, and herbicides (Gan et al. 2009; Achari et al. 2010; Pateiro-Moure et al. 2013; Ifon et al. 2019). In general, phytoremediation of metals in soil was carried out at military sites, agricultural fields, industrial sites, and mine trailings (Bañuelos and Mayland 2000; Winter Sydnor and Redente 2002; Corami 2021a). Phytoremediation could be successful against macronutrients such as N and P (Horne 2000; Corami 2021a) trace element such as Cr, Cu, Fe, Mn, Mo, and Zn (Lytle et al. 1998); non-essential elements Cd, Co, Fe, Hg, Se, Pb, V, and W (Horne 2000; Blaylock and Huang 2000); and radioactive isotopes ^{238}U, ^{137}Cs, and ^{90}Sr (Dushenkov and Kapulnik 2000; Dushenkov 2003; Hooda 2007). Factors which characterize phytoremediation in soils are metal bioavailability, plant capacity to uptake metals, translocate factor from roots to shoots, and plant–microbe interaction.

Unfortunately, all of these pollutants are non-biodegradable and persistent in the environment. Sarma (2011) showed that metals in soil persist longer than in water or air (Lasat 2002), and their removal is fundamental for protecting the environment (Kim et al. 2004); therefore, hyperaccumulator plants are a fundamental resource, even though they are considered highly metal specific and have a small amount of biomass (Sarma 2011; Corami 2017).

Chandra and Kumar (2017) and Memon and Schröder (2009) classify plant species as follows: metal excluders if a plant can limit heavy metal translocation and maintain low levels in their shoots over a wide range of soil and sludge contaminant levels; metal indicators if a plant can accumulate heavy metals in the aboveground tissue and metal level in the tissue are like the level in soil or sludge, providing information about the impact of contaminants in the environment; and accumulator if they are able to absorb metals in the aboveground tissue over the metal amount in soil.

Sarma (2011) reports that some plants show Al tolerance characteristics (Ma et al. 2001; Pilon-Smits et al. 2009): Co strongly binds to roots; Co and Ni could enter inside the cell through plasma membrane carriers (Pilon-Smith et al. 2009); Cd is adsorbed on root and could be extracted from the soil (Redjala et al. 2011); Se could be accumulated by *Stanley* sp. and *Astragalus* sp. by some specialized transporters (Tamaoki et al. 2008); and Hg binds with sulfur and nitrogen ligands (amino acids) and enters into the cells (Ochiai 1987). Metal bioavailability could depend on the interaction among metals and the form as they are in the soil (Boukirat and Maatoug 2021). Soil physico-chemical parameters also influence metal mobility, bioavailability, and bioaccumulation by plants (Maatoug et al. 2013; Boukirat et al. 2017) and the amount of OM can influence metal mobility too (Tanner and Headley 2011). He et al. (2010) suggest the use of salicylic acid (SA) to protect plants against metals. Application of SA and chemical-assisted phytoremediation reduces the negative effect of heavy metals with an increasing of biomass production (Popova et al. 2009). This acid is biodegradable in soil and can form metal complexes of moderate stability, too (Souza et al. 2013a, b).

Sarwar et al. (2017) suggest the use of biochar with phytoremediation techniques to improve the effectiveness of heavy metals absorption; moreover, biochar increases plant growth and biomass production, too. The increased amount of biomass is due to high nutrients and water holding capacity and cation exchange capacity (CEC) (Liu et al. 2013; Fellet et al. 2014; Ahmadi et al. 2017). According to Elad et al. (2010) biochar influences soil microbial community favouring some microbes and suppressing pathogens.

In general, phytoextraction is the phytoremediation method to achieve best results. Phytoextraction is a process where contaminants are uptaken by plant roots, their translocation within the plants by symplastic and apoplastic pathways (Salt and Rauser 1995; Tandy et al. 2006; Lu et al. 2009).

Apoplastic way is the entrance of metal ions or metal–chelate complex in the root through intercellular spaces, whereas symplastic pathway is a process, dependent on the energy and by specific or generic metal ion carriers or channels (Singh and Santal 2015). Plant roots seem solubilize metals, bound to the soil, by protons from the roots. These metal ions, bound to the soil, are reduced by the roots; metal availability is increased by some enzymes and reductases bind to the plasma membrane (Crowley et al. 1991).

Contaminants are generally removed by harvesting, and this is considered a suitable approach for removing pollutants from soil, sediment, and sludge (Singh et al. 2012; Mojiri et al. 2016). Adler et al. (2000) state that plants are very effective at removing nutrients, and they could absorb high amount of nutrients and store these high levels than required by their metabolism (Luxury Consumption).

Treated wastewater could be used a second time, returning to the environment in excellent condition; therefore, treated wastewater applied to land can importantly lower the cost of these treatments, confronting with other water treatment technologies (Adler et al. 2000, 2003), as already written here. According to Ganesan et al. (2020), the presence of heavy metals in soil and/or water bodies has a consequence on the ecosystem and it is dangerous for agriculture and human health, so the remediation of polluted soil is a huge challenge. Increasing the amount of metals could lead to a loss of soil fertility but most important to soil microbial activity. Depending on well-known features, some plants are more effective in removing aquatic plants, such as water lettuce, Indian mustard, and sunflower are advantageous because of their long feathery leaves, fast growth rate, and high biomass; other characteristic are pH, solar radiation, root depth, and climatic condition (Ganesan et al. 2020), and in particular, soil pH value is one of the main soil factors controlling metal availability (Huang et al. 1997; Paz-Alberto and Sigua 2013). Healthy and fertile agriculture land is the key to food security (Alvernia and Soesilo 2019); in general, heavy metals in soils are due to industrialization and/or fertilizers and pesticides. Furthermore, wastewater sludge has been used as a fertilizer on agriculture soil and also as an amendment in soils. Therefore, soil, water, and crops are enriched by organic pollutants, and it has been found that organic micropollutants are higher in anaerobically digested sludge than in aerobically stabilized sludge, suggesting that organic micropollutants can be partially degraded under aerobic condition and not in anaerobic condition (Schröder et al. 2007).

Paz-Alberto and Sigua (2013) report some examples about the use of *Vetiveria zizanioides* L. in many countries to stabilize waste and slime dams from Pt and Au mines (Knoll 1997), to stabilize landfill and industrial waste sites contaminated with heavy metals such as As, Cd, Cr, Ni, Cu, Pb, and Hg (Truong and Baker 1996), and to control pollution control and stabilize mine tail (Chen et al. 2000).

Boukirat and Maatoug (2021) carried out experiments on Pb-enriched soils, particularly due to the traffic road, through phytoremediation and earthworms which can increase plant biomass, and in some cases, they make contaminants more available. Sizmur and Hodson (2009) state that earthworms influence metal mobility, which is due to organic matter decomposition (Wen et al. 2004). Earthworms undergo the presence of metals, according their ability to adapt to the amount and type of pollutants (Depta et al. 1999), they seems to be more sensitive than invertebrates (Bengtsson et al. 1992). Earthworms decrease soil pH (Cheng and Wong

2002; Huynh 2009; Boukirat 2018) which improves phytoextraction process (Sanders et al. 1986).

Varkey et al. (2012) and Ali et al. (2020) reported that addition of chelating agents to soil enhances phytoextraction, a chemically induced reaction; in general, these agents are gradually added in small doses, but Evangelou et al. (2007) underlined that metal chelators may be toxic for plant microorganisms. About this, Quartacci et al. (2009) have suggested that root exudates play a fundamental role in solubilizing soil to favour metal uptake (Varkey et al. 2012). On the other hand, Kuiper et al. (2004) suggested the blend between plants and microorganism, a fusion between phytoectraction and soil augmentation. In fact, Fuloria et al. (2009) reported that the association of *Brassica juncea* and *Pseudomonas fluorescens* Pf27 allows soil metal bioavailability and plant growth to ameliorate phytoremediation.

Vithanage et al. (2012) have written that a crucial factor for arsenic phytoremediation is using hyperaccumulators, climate and the biomass management. Unfortunately, studies about this phenomenon are rare. It is highlighted that the amount of As (>10 μ/l) exceed human health threshold (WHO 1993). They underlined that phosphorylation is detached by inorganic arsenic and this inhibits the uptake of phosphate, so that inorganic arsenic amount in soils and in water is highly toxic to plants, because it decreases plant growth and affects plant metabolic processes.

Wan et al. (2005) reported, to remediate U, that the presence of carbonate leads to the formation of a stable carbonato-U(VI), if pH ranges from neutral to alkaline conditions. While Weggler et al. (2004) showed that a high chloride concentration in soil solution allows an increase of Cd in soil solution and also Cd uptake from plants. This suggests that the increase of bi(carbonate) concentration is caused by microbial respiration; therefore to stimulate microbial reduction U(VI) to U(IV) is important to consider the amount of organic carbon (OC) and must be considered the presence of ligands which show high affinity for metal cations, chelating them (Van Hullebusch et al. 2005).

Metal bioavailability depends on metal chemical properties, soil properties, environmental condition, and biological activity (Hooda 2007; Corami 2017). CEC is correlated with soil, sand shows more binding site ions; humus concentration is positively correlated with CEC, whereas cation bioavailability is negatively correlated with CEC; and ion bioavailability depends on redox conditions. Metal bioavailability depends on metal chelators released from plants and from bacteria chelators such as organic acids. Phytoremediation could be more effective taking in account all these data; unlikely, aged contaminants are generally less bioavailable and more recalcitrant (Hooda 2007; Corami 2017). Root bacteria and mycorrhiza help to increase metal bioavailability; microorganism organic exudates enhanced bioavailability; and therefore, root absorption is facilitated (Crowley et al. 1991; Burken et al. 2000) also for Fe^{2+} and Mn^{2+} (Barber and Lee 1974; Hooda 2007) and perhaps Cd^{2+} (Salt et al. 1995b). Plant roots and rhizosphere microorganisms can adapt to different soil conditions. Particularly, the presence of phytosiderophores help Fe uptake and may be other metals; organic acids are important in transportation and sequestration, Dal Corso et al. (2019), Kumar et al. (2008) state also that siderophores are able to chelate several metal species, like Mg, Cr(III), Cd, Zn, Cu, Ni, As, Pb, and Mn. Mokea-Niaty et al. (2018) propose the use of *Alchornea cordifolia*, which is tolerant to manganese (Mn) and can extract and accumulate it. This plant shows a strong phytoaccumulating potential in leaves and in roots. Mn is retained in soil by cation exchange reaction forming oxides, hydroxides, and oxyhydroxides or by reaction of ligand exchange. If water in soil is saturated, oxides, hydroxides, and oxyhydroxides of manganese precipitate acting as a new surface on which other substances can be adsorbed (Habeck 2011). In soil, Mn is in divalent and trivalent forms (Iuclid 2000), and in general, a dynamic equilibrium can be established between the valences of the manganese. The divalent form of Mn is dominant in acidic soils and reduction is by organic matter ($pH < 5.5$), whereas in basic soil ($pH > 7$), trivalent form dominates and bacterial oxidation is rapid (Smith and Paterson 1999). Plants absorb Mn mainly in its divalent form, and Mn absorption by plants is favoured by the presence of microorganisms (Adriano 1986; Adriano et al. 2004). *Alchornea cordifolia* absorbs large amounts of Mn at high depth and shows a rapid growth and a capacity to regenerate or modify the soil; observations made in Nigeria have shown that *Alchornea* colonises the degraded mining and petroleum zones in 6 months (Akinbiola et al. 2016).

Sinha et al. (2013) describe the use of trees, shrubs, and grasses as a better alternative for Cr phytoremediation in soils because of Cr-enriched wastewater from leather tanning industries in agricultural fields. Soils show high values of pH, CE, and salinity because of the prolonged use of wastewater from tannery. The success of phytoremediation by trees depends on the amount of contaminants in soil, metal bioavailability, and the contaminant uptake from plants (Garbisu and Alkorta 2001; Lasat 2002); a limited uptake of metals is observed in roots and translocation factor is very low too. Unfortunately, this experiment shows difficulties, and maybe the kind of trees are more suitable for phytostabilization instead of phytoremediation. It is suggested to use trees for timber, and the harvesting may be helpful in removing metal from contaminated soil. One problem about Cr is that high Cr amount is at the top, whereas roots penetrate deep down. Another problem might be the elevated evapotranspiration by trees which reduces the flow of water through the soil, reducing the metal amount that leach from the soil to the water (Pulford and Watson 2003).

Phytostabilization is another processes, through biological activity and soil amendment like phosphates, iron oxides, clay, compost and manure which aid plants during metal sorption phenomenon and at the same time fertilizers help plants growth (Berti et al. 2000; Corami et al. 2005, 2007, 2008a, b; Corami 2006; Mench et al. 2006; Dal Corso et al. 2019), so that contaminated waste is not a product, but the harvested materials and it needs further treatments. Hursthouse (2001) and van Hullebusch et al. (2005) confirm that metallic contaminant remediation can only happen trough their removing from the site or their retention in the solid phase.

Dal Corso et al. (2019) underline that arbuscular mycorrhizae (AM) fungi and phytoextraction can promote rhizo- and endo bacteria (Sessitsch et al. 2013), since AM fungi create a symbiosis with higher plants; therefore, plants could grow in a contaminated site through nutrients such as P and binding metals into roots and making difficult the translocation to the shoots (Dal Corso et al. 2019).

Soil metal pollution is a great challenge affecting human health and consequently environment (Liu et al. 2013); in China, metals are released by mining smelting, chemical industry, and agricultural measures. Leersia hexandra Swartz seems to be efficient in Cr(VI) remediation (Wu 2014). Leersia hexandra Swartz demonstrated a high removal of Cr, Cu, and Ni in mixed polluted water, but is also found that it has a strong tolerance in soil with high metal concentration (Tao Dixun et al. 2010). It is underlined that biomass of Leersia hexandra Swartz is quite small, so genetic engineering could help in improving this characteristic (Liu et al. 2019).

Karczewska et al. (2015) studied how to treat copper, since Cu shows usually a high amount in topsoil; in top soil Cu is bound affecting the area for a long time after the emission is reduced. Unfortunately, Cu is also high in urban soils and in agricultural soils with negative consequences on human health (Wong et al. 2006). One way suggested is the immobilization using amendment or decontamination, removing the excess of Cu. Phytostabilization seems to be the suitable choice, and it aims to diminish the availability of Cu through the right plants (Chaney et al. 1997; Terry and Banuelos 2000; Berti et al. 2000; Raskin and Ensley 1997). Phytostabilization aim is to immobilize metals for a long time in soil in the rizhospere and chemical fixation by amendments.

Other advantages from the use of phytoremediation is that plants help in protecting from wind and water erosion, water percolation down the profile. Moreover, plants stabilize contaminants by sorption on roots surface by exudates and bacteria (Cotter-Howells and Caporn 1996; Mench et al. 2006).

Chen et al. (2015) report that to apply phytoremediation for metal recovery in soil, it is important to determine metal concentration through sampling, to identify the origin of HMs (Micó et al. 2006; Idris 2008; Franco-Uría et al. 2009; Li et al. 2009), and then to choose the appropriate phytoremediation techniques. After the phytoremediation process, it is fundamental to treat the contaminated biomass. Generally to treat the polluted biomass it is suggested the volume reduction (Blaylock and Huang 2000) and/or pyrolisys treatment to recycle metals from the biomass (Bridgwater et al. 1999; Sas-Nowosielska et al. 2004), or incineration of biomass to recycle the metal residue from the ash (Sas-Nowosielska et al. 2004) or incineration to produce energy (Corami 2021b).

Phytomining is a method to recovery mining metals through plants, in particular, when recovery has been considered uneconomical, such as low-grade ores, mill tailings, or mineralized soil (Nedelkoska and Doran 2000). Nickel and thallium have been recovered by hyperaccumulators plants, providing a remediation and at the same time a possible re-use of these two metals in nanoparticles for biomedical applications, sensor, microelectromechanical (MEMS), and/or nanoelectromechanical (NEMS). Phytoming is a method to recovery metals from wastewater and soil, in particular in soil close to mines with high level of metals and allowing their re-use, following the concept of a balanced consumption (Corami 2021b), namely, the minimum use of the resources, the recycling of waste without negative external effects (Seroka-Stolka and Ociepa-Kubicka 2019; Corami 2021b).

Plants can accumulate metals and remove these pollutants from water and soil; these metals, extracted from the environment, could be considered a resource for metallic nanoparticles (Karman et al. 2015). Unfortunately, metals are considered non-renewable resources; therefore, recovering from industrial wastewater could be an alternative. Karman et al. (2015) suggest the use of phytoremediation process to recovery metals starting from (contaminated) biomass and these metals could be used to synthesise nanoparticles, avoiding also a depletion crisis. Recovering metals from contaminated biomass is already studied (Pollmann et al. 2006; Wang and Zhao 2009; Gadd 2010).

Contaminated biomass from phytoremediation is suggested to be valorised as a form of energy (biogas, biofuels, and combustion for energy production and heating), at the same time an important environmental co-benefit, it lets improve the erosion control, soil quality, and functionality, and providing wildlife habitat (Gomes 2012; Pirrera and Pluchino 2017; Song and Park 2017).

2.5 Phytoremediation in Air

Wolverton et al. (1989); Wolverton and Wolverton (1996) started studies about the detoxifying property of houseplants to improve air quality. Wei et al. (2021) state that it is important to choose indoor plants according to plant morphology, composition of epidermis and mesophyll, stomatal density, and size. In general, indoor air contaminants are formaldehyde, benzene, carbon monoxide, carbon dioxide, volatile organic compounds (VOCs), nitrogen oxides, and a variety of aromatics (Davardoost and Kahforoushan 2019). Xu et al. (2018) state that particulate matter (PM) is generally deposited on leaf surface of trees. Selmi et al. (2016) have written that the removal rate of air pollution depends on tree canopy and contaminant amount. McDonald et al. (2007) say that to increase the efficiency of air remediation is important the variety in biomass structure and land management (Jim and Chen 2008); in particular, trees with a wide leaf areas are more effective in removing atmospheric particulate matter (PM) (McDonald et al. 2007; Wei et al. 2021). PM deposition on leaf depends on the adherence between the blade surface and the particles (Wang et al. 2015). Wei et al. (2021) suggest achieving results to use species with a rough wide-surface leaves establishing a suitable environment for microorganism.

Yoo et al. (2006) and Peterson et al. (2015) state that plants, following Calvin cycle, absorb volatile organic compounds (VOCs) by stomata within gas exchange and transforming them in amino acids. Brilli et al. (2018) observe that leaves absorb air pollutants despite stomatal constraints and mesophyll resistance. In this regard, Tardieu et al. (2010) underlined that stomatal porosity is regulated by abscisic acid. In addition, removing indoor pollutants depends on total surface area, anatomical and morphological characteristics, plant chemical properties, and soil matrix characteristics (Irga et al. 2013), and it also depends on the presence, shape, and density of leaf trichomes (Li et al. 2018). Furthermore, Kim et al. (2008) and Orwell et al. (2004) highlight that contaminants removal is due to microbial flora; for example, aromatic hydrocarbons are biodegraded by microbial aerobic pathways (Zhang et al. 2013), such as toluene dioxygenase and toluene methyl mono-oxygenase (Ikem and Adisa 2011).

2.6 Genetic and Phytoremediation

Genetic manipulation could improve efficiency of phytoremediation (Van Huysen et al. 2004); in particular, genes (Danika and Le Duc 2005) from hyperaccumulators could be transferred to fast-growing species enhancing phytoremediation (De Souza et al. 1998).

Arthur et al. (2005) showed that phytoremediation results could be improved by transferring the genes from microorganisms to plants because of their unique metabolic capabilities, suggesting a transgenic remediation. Engineered plants within these new features have shown an increased tolerance against contaminant-resistant microorganisms, improvement in growth, and endurance in degradation of both inorganic and organic contaminants. It is reported the case of transgenic plants, which through a degradation pathway, that occur in some plants and naturally in some bacteria, turn into less toxic and volatile elemental mercury (Hg(0)), starting from organo-mercurial compounds and toxic ionic mercury (Hg(II)). Furthermore, hyper-accumulator plants, thanks to transgenic approach, could improve their metal tolerance and accumulation in fast-growing plants with a large biomass production.

2.7 Conclusions

Plants are particularly advantageous in bioremediation preventing erosion and leaching, avoiding toxic substance diffusion to surrounding areas (USEPA 2004). Dal Corso et al. (2019) state that plants and associated microorganisms are of great concern for their application in polluted soil.

Waste in a cycle might be a resource for another part of the same cycle. The point is to apply the concept of circular economy by the industries to mimic this sustainable closed cycle for the safety of nature, achieving a sustainable development (Olufunmilayo and Ogunbayo 2012).

Phytoremediation is a clean-up technology for contaminated soil and water. To be successful, phytoremediation needs to utilize hyper-accumulator plants to extract toxic metals (Pb, Ni, Cr, Cd, and Zn) and organic contaminants from soil and wastewater. Certain plants are able to accumulate pollutants in the plant roots, to translocate contaminants from the roots to the leafs, and later to the shoots. The contaminant biomass is harvested, and later, it is removed from the site. Avoiding cost for excavation and disposal, topsoil loss generally occurs in traditional remediation techniques.

Unfortunately, phytoremediation would be extremely slow depending on the plant growth rate, while bioremediation depends on plant's total biomass. One of the advantages is that plants also offer a permanent, in situ, nonintrusive method in removing soil/wastewater contaminants (Paz-Alberto and Sigua 2013). One issue is the disposal of the contaminated biomass (Paz-Alberto and Sigua 2007); according to the principle of circular economy, it could be used for the energy production instead of to consider biomass as a waste (Corami 2021b).

A future advantage will be the energy production from contaminated biomass, providing that this land use does not concur for food production. In Sweden, an LCA approach showed that using willow for biofuel remediation, damage to the environment is lower than the traditional excavation-and-refill remediation (Thewys and Kuppens 2008; Gomes 2012). It is also suggested to extract from biomass metals, considering contaminated biomass as a rich ore and applying a conventional ore-processing unit, saving raw materials too (Gomes 2012; Koppolu et al. 2003 part I and part II; Koppolu et al. 2004). Moreover, biochar, the waste from pyrolysis, could be used as amendment to sequester carbon and reducing the CO_2 emission in the atmosphere (Gomes 2012; Lehmann 2007).

Furthermore, to avoid the problem of a long time for phytoremediation and the low amount of biomass, it is suggested to consider the benefit of transgenic approaches using bacterial genes in phytoremediation (Heaton et al. 1998; Rugh et al. 1998). Transgenetic approach consists in mixing hyperaccumulator genomes with high-biomass non-accumulator species, and this seems to become a promising alternative. The transgenetic approach might be achieved utilizing plants with capacity to modify redox status in rhizosphere and/or enhancing root exudation of protons and/or chelators. This might be advantageous in phytovolatilization by trees, thanks to their large root systems and extensive production of litter (Rugh et al. 1998; Krämer and Chardonnens 2001).

Phytoremediation is still a challenge. It could be enhanced by the use of enzymes from plants itself and it is recognized by the potential of biocatalyst in increasing the degradation of contaminants (Singer et al. 2003; Wolfe and Hoehamer 2003; Pilon-Smits 2005).

Phytoremediation is a challenging technology because it is cost-effective, shows increased competence, is environmentally friendly, and follows circular economy principle. Nowadays, remediation of degraded land, wastewater, and soil is only possible by sustainable and eco-friendly technologies. It is a sustainable green technology and a valid cost alternative rather than physicochemical approaches.

References

Achari G, Jakher A, Gupta C, Dhol A, Langford CH (2010) Practical method to extract and dechlorinate PCBs in soils. Pract Period Hazard Toxic Radioact Waste Manage 14:98–103

Adams C, Wang Y, Loftin K, Meyer M (2002) Removal of antibiotics from surface and distilled water in conventional water treatment processes. J Environ Eng 128(3):253–260

Adler PR, Arora R, Ghaouth AE, Glenn DM, Solar JM (1994) Bioremediation of phenolic compounds from water with plant root surface peroxidases. J Environ Qual 23:1113–1117

Adler PR, Harper JK, Takeda F, Wade EM, Summerfelt ST (2000) Economic evaluation of hydroponics and other treatment options for phosphorus removal in aquaculture effluent. HortScience 35(6):993–999

Adler PR, Summerfelt ST, Glenn DM, Takeda F (2003) Mechanistic approach to phytoremediation of water. Ecol Eng 20:251–264

Adriano DC (1986) Introduction. In: Trace elements in the terrestrial environment. Springer, New York, pp 1–45

Adriano DC, Wenzel WW, Vangronsveld J, Bolan NS (2004) Role of assisted natural remediation in environmental cleanup. Geoderma 122(2–4):121–142

Agrawal V, Sharma K (2006) Phytotoxic effects of Cu, Zn, Cd and Pb on *in vitro* regeneration and concomitant protein changes in Holarrhena antidysenterica. Biol Plant 50:307–310

Ahmadi M, Jorfi S, Kujlu R, Ghafari S, Darvishi Cheshmeh Soltani R, Jaafarzadeh Haghighifard N (2017) A novel salt-tolerant bacterial consortium for biodegradation of saline and recalcitrant petrochemical wastewater. J Environ Manag 191:198–208

Aisien ET, Gbegbaje-Das IIE, Aisien FA (2010a) Water quality assessment of river Ethiope in the Niger-Delta Coast of Nigeria. Elec J Env Agricult Food Chem 9:1739–1745

Aisien FA, Faleye O, Aisien ET (2010b) Phytoremediation of heavy metals in aqueous solutions. Leonard J Sci 17:37–46

Aisien ET, Nwatah CV, Aisien FA (2010c) Biological treatment of landfill leachate from Benin City, Nigeria. Elec J Env Agricult Food Chem 9:1701–1705

Aisien ET, Aisien FA, Okoduwa IG (2015) Improved quality of abattoir wastewater through phytoremediation. In: Ansari A, Gill S, Gill R, Lanza G, Newman L (eds) Phytoremediation. Springer, Cham, pp 5–1

Akinbiola S, Awotoye O, Adepoju K, Salami A (2016) Floristic indicators of tropical landuse systems: evidence from mining areas in Southwestern Nigeria. Glob Ecol Conserv 7:141–147

Alfasane MA, Moniruzzaman K, Rahman MM (2011) Biochemical composition of the fruits of water chestnut (*Trapa bispinosa* Roxb). Dhaka University J Biol Sci 20(1):95–98

Ali H, Khan E, Sajad MA (2013) Phytoremediation of heavy metals—concepts and applications. Chemosphere 91(7):869–881

Ali S, Abbas Z, Rizwan M, Zaheer IE, Yavas I, Unay A, Kalderis D (2020) Application of floating aquatic plants in phytoremediation of heavy metals polluted water: a review. Sustainability 12:1927

Allenby BR (1999) Industrial ecology, policy framework and implementation. Prentice Hall, Englewood Cliffs, p 308p

Alvernia P, Soesilo TEB (2019) Phytoremediation as a sustainable way for land rehabilitation of heavy metal contamination. J Phys Conf Ser 1381:1–8

Anderson TA, Kruger EL, Coats JR (1994) Enhanced degradation of a mixture of three herbicides in the rhizosphere of a herbicide-tolerant plant. Chemosphere 28:1551–1557

Ansari AA, Khan FA (2009) Remediation of eutrophied water using Spirodela polyrrhiza L. Shleid in controlled environment. Pan Am J Aquat Sci 4:52–54

Ansari AA, Trivedi S, Khan FA, Gill SS, Perveen R, Dar MI, Abbas ZK, Rehman H (2015) Phytoremediation of eutrophic waters. In: Phytoremediation. Springer, Cham, pp 41–50

Ansari AA, Naeem M, Gill SS, AlZuaibr FM (2020) Phytoremediation of contaminated waters: an eco-friendly technology based on aquatic macrophytes application. Egypt J Aquat Res 46(4):371–376

April W, Sims RC (1990) Evaluation and use of prairie grasses for simulating polycyclic aromatic hydrocarbon treatment in soil. Chemosphere 20:253–265

Arnao MB, Acosta M, del Rio JA, Varón R, García-Cánovas F (1990) Kinetic study on the suicide inactivation of peroxidase by hydrogen peroxide. Biochim Biophys Acta 1041:43–47

Arthur EL, Rice PJ, Rice PJ, Anderson TA, Baladi SM, Henderson KLD, Coats JR (2005) Phytoremediation—an overview. Crit Rev Plant Sci 24:109–122

Awuah E, Oppong-Peprah M, Lubberding HJ, Gijzen HJ (2004) Comparative performance studies of water lettuce, duckweed and algal-based stabilization ponds using low-strength sewage. J Toxicol Environ Health A 67:1727–1739

Baker AJM, McGrath SP, Sidoli CMD, Reeves RD (1994) The possibility of in situ heavy metal decontamination of polluted soils using crops of metal accumulating plants. Resour Conserv Recycl 11:41–49

Banioko B, Eslamian S (2015) Phytoremediation in urban water reuse handbook. Taylor & Francis Group, LLC. 1177 p

Bañuelos GS, Mayland HF (2000) Absorption and distribution of selenium in animals consuming canola grown for selenium phytoremediation. Ecotoxicol Environ Saf 46(3):322–328

Barbafieri M, Tassi E, Rizzi L, Molinar M, Nardella A (2004) Phytoremediation treatability test for an industrial site contaminated by Pb, Zn and As. Soil Sediment Contam 13(2):215

Barber SA, Lee RB (1974) The effect of microorganisms on the absorption of manganese by plants. New Phytol 73:97–106

Baskar G, Deeptha VT, Rahman AA (2009) Treatment of wastewater from kitchen in an institution hostel mess using constructed wetland. Int J Recent Trends Engg 1:54–58

Bengtsson G, Ek H, Rundgren S (1992) Evolutionary response of earthworms to long term metal exposure. Oikos 63:289–297

Bento L, Marotta H, Enrich-Prast A (2007) O papel das macrófitas aquáticas emersas no ciclo do fósforo em lagos rasos. Oecol Bras 4:582–589

Berti WR, Cunningham SD, Scott D (2000) Phytostabilization of metals. In: Phytoremediation of toxic metals: using plants to clean up the environment. Wiley, New York, pp 71–88

Bitonti MB, Cozza R, Wang G, Ruffini-Castiglione M, Mazzuca S, Castiglione S, Sala F, Innocenti AM (1996) Nuclear and genomic changes in floating and submerged buds and leaves of heterophyllous water chestnut (Trapa natans). Physiol Plant 97(1):21–27

Blaylock MJ, Huang JW (2000) Phytoextraction of metals. In: Phytoremediation of toxic metals: using plants to clean up the environment. Wiley, New York, pp 53–70

Bolan N, Kunhikrishnan A, Thangarajan R, Kumpiene J, Park J, Makino T, Kirkham M, Scheckel K (2014) Remediation of heavy metal(loid)s contaminated soils -to mobilize or to immobilize? J Hazard Mater 266:141–166

Bose S, Vedamati J, Rai V, Ramanathan AL (2008) Metal uptake and transport by Tyaha angustata L. grown on metal contaminated waste amended soil: an implication of phytoremediation. Geoderma 145:136–142

Boukirat D (2018) Bioremédiation d'un sol agricole pollué par le plomb à l'aide de l'interaction des macro-invertébrés terrestres (vers de terre : Lumbricus sp) et des céréales (orge commune: Hordeum vulgare). Thèse de doctorat de l'université de Tiaret, Algérie

Boukirat D, Maatoug M (2021) Bioremediation of lead contaminated soils for sustainable agriculture. In: Jhariya, M.K., Meena, R.S., Banerjee, A. (eds) Ecological intensification of natural resources for sustainable agriculture, Springer, Singapore. p 341

Boukirat D, Maatoug M, Zerrouki D, Lahouel H, Heilmeier H, Kharytonov M (2017) Bioremediation of agricultural soil contaminated with lead using interaction: common barley Hordeum Vulgare and earthworm Lumbricus Sp. INMATEH-Agri Eng 51(1):125–134

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

Bridgwater AV, Meier D, Radlein D (1999) An overview of fast pyrolysis of biomass. Org Geochem 30:1479–1493

Brilli F, Fares S, Ghirardo A, de Visser P, Calatayud V, Munoz A, Annesi-Maesano I, Sebastiani F, Alivernini A, Varriale V, Menghini F (2018) Plants for sustainable improvement of indoor air quality. Trends Plant Sci 23(6):507–512

Brisson J, Chazarenc F (2009) Maximizing pollutant removal in constructed wetlands: should we pay more attention to macrophyte species selection? Sci Total Environ 407:3923–3930

Burken JG (2003) Uptake and metabolism of organic compounds: green-liver model. In: Phytoremediation: transformation and control of contaminants, pp 59–84

Burken JG, Shanks JV, Thompson PL (2000) Metabolism of explosives and nitroaromatic compounds. In: Biodegradation of nitroaromatic compounds and explosives, p 239

Campos VM, Merino I, Casado R, Pacios LF, Gómez L (2008) Review. Phytoremediation of organic pollutants. Span J Agric Res 6:38–47

Chandekar N, Godboley B (2017) A review on phytoremediation a sustainable solution for treatment of kitchen wastewater. Int J Sci Res 6(2):1850–1855

Chandra P, Kulshreshtha K (2004) Chromium accumulation and toxicity in aquatic vascular plants. Bot Rev 70(3):313–327

Chandra R, Kumar V (2017) Management phytoremediation of environmental pollutants in phytoremediation: a green sustainable technology for industrial waste. In: Phytoremediation of environmental pollutants. CRC Press, Boca Raton, pp 1–42

Chaney RL, Malik M, Li YM, Brown SL, Brewer EP, Angle JS, Baker AJ (1997) Phytoremediation of soil metals. Curr Opin Biotechnol 8:279–284

Chang H, Yang X, Fang Y, Pu P, Li Z, Rengel Z (2006) In situ nitrogen removal from the eutrofic water by microbiale plant integrated system. JZUS-B 7(7):521–531

Chen HM, Zheng CR, Tu C, Shen ZG (2000) Chemical methods and phytoremediation of soil contaminated with heavy metals. Chemosphere 41(1–2):229–234

Chen J, Chen Y, Shi ZQ, Su Y, Han FX (2015) Phytoremediation to remove metals/metalloids from soils. In: Ansari A, Gill S, Gill R, Lanza G, Newman L (eds) Phytoremediation. Springer, Cham

Cheng J, Wong MH (2002) Effects of earthworms on Zn fractionation in soils. Biol Fertil Soils 36:72–78

Coder KD (2011) Identified benefits of community trees & forests. University of Georgia

Corami A (2006) Phosphate-induced heavy metals immobilization in aqueous solutions and soils. PLINIUS 32

Corami A (2017) Soil pollution and phytoremediation. In: IIT Roorkee Executive, editor. Environmental science and engineering p 1–11

Corami A (2021a) Phytoremediation impacts on water productivity. Water Productivity J 1(2):13–22

Corami A (2021b) Contaminated biomass and circular economy. Acad Lett 2677

Corami A, Ferrini V, Mignardi S (2005) Synthetic phosphates as binding agent of Pb, Zn, Cu and Cd in the environment. World Resour Rev 17(1):61–75

Corami A, Mignardi S, Ferrini V (2007) Copper and zinc decontamination from single- and binary-metal solutions using hydroxyapatite. J Hazard Mater 146(1–2):164–170

Corami A, Mignardi S, Ferrini V (2008a) Removal of lead, copper, zinc and cadmium from water using phosphate rock. Acta Geol Sin 82(6):801–840

Corami A, Mignardi S, Ferrini V (2008b) Cadmium removal from single - and multi-metal (Cd+Pb+Zn+Cu) solutions by sorption on hydroxyapatite. J Colloid Interface Sci 317(2):402–408

Cotter-Howells JD, Caporn S (1996) Remediation of contaminated land by formation of heavy metal phosphates. Appl Geochem 11:335–342

Criquet S, Joner E, Leglize P, Leyval C (2000) Anthracene and mycorrhiza affect the activity of oxidoreductases in the roots and the rhizophere of lucerne (Medicago sativa L.). Biotechnol Lett 22:1733–1737

Crompton JL (2008) Empirical evidence of the contributions of park and conservation lands to environmental sustainability: the key to repositioning the parks field. World Leis J 50(3):154–172

Crowley DE, Wang YC, Reid CPP, Szaniszlo PJ (1991) Mechanisms of iron acquisition from siderophores by microorganisms and plants. Plant Soil 130:179–198

Cunningham SD, Ow DW (1996) Promises and prospects of phytoremediation. Plant Physiol 110(3):715–719

Cunningham SD, Anderson TA, Schwab AP, Hsu FC (1996) Phytoremediation of soils contaminated with organic pollutants. Adv Agron 56:55–114

Dal Corso G, Fasani E, Manara A, Visioli G, Furini A (2019) Heavy metal pollutions: state of the art and innovation in phytoremediation. Int J Mol Sci 20:3412–3425

Danika L, Le Duc TN (2005) Phytoremediation of toxic trace elements in soil and water. J Ind Microbiol Biotechnol 32:514–520

Davardoost F, Kahforoushan D (2019) Modelling the dispersion of volatile organic compounds in indoor environment. Chem Eng Technol 42(3):549–559

De Araujo BS, Charlwood BV, Pletsch M (2002) Tolerance and metabolism of phenol and chloroderivatives by hairy root cultures of Dacus carota L. Environ Pollut 117:329–335

de Godos I, Vargas VA, Blanco S, González MCG, Soto R, García-Encina PA, Becares E, Muñoz R (2010) A comparative evaluation of microalgae for the degradation of piggery wastewater under photosynthetic oxygenation. Bioresour Technol 101(14):5150–5158

De Souza MP, Pilon-Smits EAH, Lytle CM, Hwang S, Tai J, Honma TSU, Yeh L, Terry N (1998) Rate-limiting steps in selenium assimilation and volatilization by Indian mustard. Plant Physiol 117:1487–1494

Depta B, Koscielniak A, Rozen A (1999) Food selection as a mechanism of heavy metal resistance in earthworms. Pedobiologia 43:608–614

Dias Fernandes K, de Campos Roque A, Fonseca AL (2020) Evaluation of ecotoxicity of contaminated water for validation of phytoremediation time. Rev Ambient Água 15(1)

Didierjean L, Gondet L, Perkins R, Lau SM, Schaller H, O'keefe DP, Werck-Reichhart D (2002) Engineering herbicide metabolism in tobacco and Arabidopsis with CYP76B1, a cytochrome P450 enzyme from Jerusalem artichoke. Plant Physiol 130:179–189

Dietz AC, Schnoor JL (2001) Advances in phytoremediation. Environ Health Perspect 109:163–168

Dixun T et al (2010) Absorption and accumulation of chromium, copper and nickel in polluted soil contaminated by electroplating sludge by Leersia hexandra Swartz. J Guilin University Technol 30(01):144–147

Doblas VG, Geldner N, Barberon M (2017) The endodermis, a tightly controlled barrier for nutrients. Curr Opin Plant Biol 39:136–143

Donnely PK, Fletcher JA (1995) PCB metabolism by ectomycorrhizal fungi. Bull Environ Contam Toxicol 54:507–513

Doty SL, Shang TQ, Wilson AM, Tangen J, Westergreen AD, Newman LA, Strand S, Gordon MP (2000) Enhanced metabolism of halogenated hydrocarbons in transgenic plants containing mammalian cytochrome P450 2E1. Proc Natl Acad Sci 97(12):6287–6291

Dushenkov S (2003) Trends in phytoremediation of radionuclides. Plant Soil 249:167–175

Dushenkov S, Kapulnik Y (2000) Phytofiltration of metals. In: Raskin I, Ensley BD (eds) Phytoremediation of toxic metals using plants to clean up the environment. Wiley, New York, pp 89–106

Dushenkov V, Kumar PBAN, Motto H, Raskin I (1995) Rhizofiltration: the use of plants to remove heavy metals from aqueous streams. Environ Sci Technol 29:1239–1245

Ekweozor IKE, Ugbomeh AP, Ogbuehi KA (2017) Zn, Pb, Cr and Cd concentrations in fish, water and sediment from the Azuabie Creek, Port Harcourt. J Appl Sci Environ Manag 21(1):87–91

Elad Y, David DR, Harel YM, Borenshtein M, Kalifa HB, Silber A, Graber ER (2010) Induction of systemic resistance in plants by biochar, a soil-applied carbon sequestering agent. Phytopathology 100(9):913

El-Kheir WA, Ismail G, El-Nour FA, Tawfik T, Hammad D (2007) Assessment of the efficiency of duckweed (Lemna gibba) in wastewater treatment. Int J Agric Biol (Pakistan)

El-Shafai SA, El-Gohary FA, Nasr FA, Van der Steen NP, Gijzen HJ (2007) Nutrient recovery from domestic wastewater using a UASB-duckweed ponds system. Bioresour Technol 98:798–807

Entry JA, Watrud LS, Manasse RS, Vance NC (1996) Phytoremediation and reclamation of soils contaminated with radionuclides. American Chemical Society, Washington, DC 20036 (USA):299–306

EPA [Internet] EPA/600/R-99/107 February 2000. Available from: http://nepis.epa.gov/

Esteves FA (1979) Die Bedeutung Der Aquatischen Makrophyten fur Den Stoffhaushalt Des Schohsees. I. Die Produktion an Biomasse. Arch Hydrobiol Suppl 57:117–143

Esteves FA (1998) Fundamentos de Limnologia, 2nd edn. Interciência, Rio de Janeiro, p 608

Evangelou MWH, Ebel M, Schaeffer A (2007) Chelate-assisted phytoextraction of heavy metals from mn soil. Effect, mechanism, toxicity and fate of chelating agents. Chemosphere 68:989–1003

Everitt DT, Burkholder JM (1991) Seasonal dynamics of macrophyte communities from a stream flowing over granite flatrock in North Carolina, USA. Hydrobiologia 222:159–172

Fard RF, Azimi AA, Bidhendi GRN (2011) Batch kinetics and isotherms for biosorption of cadmium onto biosolids. Desalin Water Treat 28:69–74

Favas PJC, Pratas J, Rodrigues N, D'Souza R, Varun M, Paul MS (2018) Metal(loid) accumulation in aquatic plants of a mining area: potential for water quality biomonitoring and biogeochemical prospecting. Chemosphere 194:158–170

Fellet G, Marmiroli M, Marchiol L (2014) Elements uptake by metal accumulator species grown on mine tailings amended with three types of biochar. Sci Total Environ 468:598–608

Fernandez GL, Fernandez-Pascual M, García-Seco D, Gutierrez-Mañero FJ, Lucas JA (2013) Spent metal working fluids produced alterations on photosynthetic parameters and cell-ultrastructure of leaves and roots of maize plants. J Hazard Mater 260:220–230

Fernández GL, Fernández-Pascual M, Mañero FJG, García JAL (2015) Phytoremediation of contaminated waters to improve water quality. In: Phytoremediation. Springer, Cham, pp 11–26

Fitz WJ, Wenzel WW (2002) Arsenic transformations in the soil-rhizosphere-plant system: fundamentals and potential application to phytoremediation. J Biotechnol 99(3):259–278

Flores HE, Curtis WR (1992) Approaches to understanding and manipulating the biosynthetic potential of plant roots. Ann N Y Acad Sci 665:188–209

Fonkou T, Agendia P, Kengne I, Akoa A, Nya J (2002) Potentials of water lettuce (*Pistia stratiotes*) in domestic sewage treatment with macrophytic lagoon systems in Cameroon. In: Proceedings of International Symposium on Environmental Pollution Control and Waste management, EPCOWM'2002. pp 709–714

Franco-Uría A, López-Mateo C, Roca E, Fernández-Marcos ML (2009) Source identification of heavy metals in pastureland by multivariate analysis in NW Spain. J Hazard Mater 165:1008–1015

French CJ, Dickinson NM, Putwain PD (2006) Woody biomass phytoremediation of contaminated brownfi eld land. Environ Pollut 141:387–395

Fuloria A, Saraswat S, Rai JPN (2009) Effect of *Pseudomonas fluorescence* on metal phytoextraction from contaminated soil by *Brassica juncea*. Chem Ecol 25:385–396

Gadd GM (2010) Metals, minerals and microbes: geomicrobiology and bioremediation. Microbiology 156(3):609–643

Galiulin RV, Bashkin VN, Galiulina RR, Birch P (2001) A critical review: protection from pollution by heavy metals – phytoremediation of industrial wastewater. Land Contam Reclam 9(4):349–358

Gan S, Lau EV, Ng HK (2009) Remediation of soils contaminated with polycyclic aromatic hydrocarbons. J Hazard Mater 172(2–3):532–549

Ganesan S, Panda S, Sinha A, Chettri A (2020) Phytoremediation: sustainable approach for the removal of heavy metals from the environment using plants. Mater Sci Eng 955(1):012096

Garbisu C, Alkorta I (2001) Phytoextraction: a cost-effective plant-based technology for the removal of metals from the environment. Bioresour Technol 77:229–236

Ghaly AE, Kamal M, Mahmoud NS (2005) Phytoremediation of aquaculture wastewater for water recycling and production of fish feed. Environ Int 31:1–13

Ghosh M, Singh SP (2005) A review on phytoremediation of heavy metals and utilization of its byproducts. Appl Ecol Environ Res 3(1):1–18

Girija N, Pillai SS, Koshy M (2011) Potential of *Vetiver* for phytoremediation of waste in retting area. The Ecoscan 1:267–273

Glibert PM, Heil CA, Hollander D, Revilla M, Hoare A, Alexander J, Murasko S (2004) Evidence for dissolved organic nitrogen and phosphorus uptake during a cyanobacterial bloom in Florida Bay. Mar Ecol Prog Ser 280:73–83

Gomes HI (2012) Phytoremediation for bioenergy: challenges and opportunities. Environ Technol Rev 1(1):59–66

González PS, Capozucca CE, Tigierm HA, Milrad SR, Agostini E (2006) Phytoremediation of phenol from wastewater, by peroxidases of tomato hairy root cultures. Enzym Microb Technol 39(4):647–653

Gudeppu M, Varier KM, Chinnasamy A, Thangarajan S, Balasubramanian J, Li Y, Ganjendran B (2019) Nanobiotechnology approach for the remediation of environmental hazards generated from industrial waste. In: Rajendran S, Naushad M, Raju K, Boukherroub R (eds) Emerging nanostructured materials for energy and environmental science, Environmental chemistry for a sustainable world, vol 23. Springer, Cham

Gujarathi NP, Haney BJ, Linden JC (2005) Phytoremediation potential of *Myriophyllum aquaticum* and *Pistia stratiotes* to modify antibiotic growth promoters, tetracycline, and oxytetracycline, in aqueous wastewater systems. Int J Phytoremediation 7:99–112

Habeck M (2011) Toxicological profile for manganese agency for toxic substances and disease registry. United States public health service

Haby PA, Crowley DE (1996) Biodegradation of 3-chlorobenzoate as affected by rhizodeposition and selected carbon substrates. J Environ Qual 25:304–310

Hannink N, Rosser SJ, French CE, Basran A, Murray JA, Nicklin S, Bruce NC (2001) Phytodetoxification of TNT by transgenic plants expressing a bacterial nitroreductase. Nat Biotechnol 19(12):1168–1172

He J, Ren Y, Pan X, Yan Y, Zhu C, Jiang D (2010) Salicylic acid alleviates the toxicity effect of cadmium on germination, seedling growth, and amylase activity of rice. J Plant Nutr Soil Sci 173:300–305

Heaton ACP, Rugh CL, Wang N-j, Meagher RB (1998) Phytoremediation of mercury- and methylmercury-polluted soils using genetically engineered plants. J Soil Contam 7(4)

Hegazy AK, Abdel-Ghani NT, El-Chaghaby GA (2011) Phytoremediation of industrial wastewater potentiality by Typha domingensis. Int J Environ Sci Technol 8(3):639–648

Henry H, Naujokas MF, Attanayake C, Basta NT, Cheng Z, Hettiarachchi GM, Maddaloni M, Schadt M, Schekel KG (2015) Bioavailability-based In situ remediation to meet future Lead (Pb) standards in urban soils and gardens. Environ Sci Technol 49(15):8948–8958

Hettick BE, Cañas-Carrell JE, French AD, Klein DM (2015) Arsenic: a review of the element's toxicity, plant interactions, and potential methods of remediation. J Agric Food Chem 63(32):7097–7107

Hinrichsen D, Tacio H (2002) The coming freshwater crisis is already here. The linkages between population and water. Woodrow Wilson International Center for Scholars, Washington, DC, pp 1–26

Hoagland RE, Zablotowicz RM, Locke MA (1997) An integrated phytoremediation strategy for chloracetamide herbicides in soil. In: Kruger EL, Anderson TA, Coats JR (eds) Phytoremediation of soil and water contaminants, vol 664. American Chemical Society, Washington, D.C., pp 92–105

Hooda V (2007) Phytoremediation of toxic metals from soil and waste water. J Environ Biol 28(2):367–376

Horne AJ (2000) Phytoremediation by constructed wetlands. In: Terry N, Bañuelos G (eds) Phytoremediation of contaminated soil and water. Lewis, Boca Raton, pp 13–40

Huang JW, Chen J, Berti WR, Cunningham SD (1997) Phytoremediation of lead-contaminated soils: role of synthetic chelates in lead phytoextraction. Environ Sci Technol 31(3):800–805

Hursthouse AS (2001) The relevance of speciation in the remediation of soils and sediments contaminated by metallic elements—an overview and examples from Central Scotland, UK. J Environ Monit 3:49–60

Huynh TMD (2009) Impact des métaux lourds sur les interactions plante/ver de terre/microflore tellurique. (Doctoral dissertation, Université Paris-Est)

Idris AM (2008) Combining multivariate analysis and geochemical approaches for assessing heavy metal level in sediments from Sudanese harbors along the Red Sea coast. Microchem J 90:159–163

Ifon BE, Togbé ACF, Sewedo Tometin LA, Suanon F, Yessoufou A (2019) Metal-contaminated soil remediation: phytoremediation, chemical leaching and electrochemical remediation. In: Metals in soil-contamination and remediation. IntechOpen, London, pp 534–554

Ikem A, Adisa S (2011) Runoff effect on eutrophic lake water quality and heavy metal distribution in recent littoral sediment. Chemosphere 82(2):259–267

Ingole NW, Bhole AG (2003) Removal of heavy metals from aqueous solution by water hyacinth (Eichhornia crassipes). J Water 53(2):119–128

Irga PJ, Torpy FR, Burchett MD (2013) Can hydroculture be used to enhance the performance of indoor plants for the removal of air pollutants? Atmos Environ 77:267–271

Iuclid F (2000) International uniform chemical information database. European Commission ISPRA CD ROM

Jasrotia S, Kansal A, Mehra A (2017) Performance of aquatic plant species for phytoremediation of arsenic-contaminated water. Appl Water Sci 7:889–896

Jim CY, Chen WY (2008) Assessing the ecosystem service of air pollutant removal by urban trees in Guangzhou (China). J Environ Manag 88(4):665–676

Karczewska A, Mocek A, Goliński P, Mleczek M (2015) Phytoremediation of copper-contaminated soil. In: Phytoremediation. Springer, Cham, pp 143–170

Karman SB, Diah SZM, Gebeshuber IC (2015) Raw materials synthesis from heavy metal industry effluents with bioremediation and phytomining: a biomimetic resource management approach. Adv Mater Sci Eng pp 1–22

Kaur M, Kumar M, Sachdeva S, Purib SK (2018) Aquatic weeds as the next generation feedstock for sustainablebioenergy production Bioresource Technology 251:390–402

Khan S, Cao Q, Zheng MY, Huang ZY, Zhu GY (2008) Health risks of potentially toxic elements in contaminated soils and food crops irrigated with wastewater in Beijing, China. Environ Pollut 152(3):686–692

Kim S, Jee JH, Kang JC (2004) Cadmium accumulation and elimination in tissues of juvenile olive flounder, Paralichthys olivaceus after sub-chronic cadmium exposure. Environ Pollut 127(1):117–123

Kim KJ, Song JS, Yoo EH, Son KC, Kays SJ (2008) Efficiency of volatile formaldehyde removal by indoor plants: contribution of aerial plant parts versus the root-zone. J Am Soc Horticult Sci 133(4):521–526

Knoll C (1997) Rehabilitation with vetiver. African Mining 2(2):43

Komives T, Gullner G, Bittsanszky A, Pascal S, Laurent F (2009) Phytoremediation of persistent organic pollutants. Cereal Res Commun 37:537–540

Koppolu L, Agblevor FA, Clements LD (2003) Pyrolysis as a technique for separating heavy metals from hyperaccumulators. Part II: Lab-scale pyrolysis of synthetic hyperaccumulator biomass. Biomass Bioenergy 25:651–663

Koppolu L, Prasad R, Clements LD (2004) Pyrolysis as a technique for separating heavy metals from hyperaccumulators. Part III: Pilot-scale pyrolysis of synthetic hyperaccumulator biomass. Biomass Bioenergy 26(5):463–472

Krämer U, Chardonnens AN (2001) The use of transgenic plants in the bioremediation of soils contaminated with trace elements. Appl Microbiol Biotechnol 55:661–672

Kříbek B, Majer V, Knésl I, Keder J, Mapani B, Kamona F, Mihaljevič M, Ettler V, Penížel V, Vaněk A, Sracek O (2016) Contamination of soil and grass in the Tsumeb smelter area, Namibia: Modeling of contaminants dispersion and ground geochemical verification. Appl Geochem 64:75–91

Kruger EL, Anhalt JC, Sorenson D, Nelson B, Chouhy AL, Anderson TA, Coats JR. Atrazine degradation in pesticide-contaminated soils: phytoremediation potential. In: Kruger EL, Anderson TA, Coats JR. Phytoremediation of soil and water contaminants. American Chemical Society, Washington, D.C. 1997;64:54–64

Kuiper I, Kravchenko LV, Bloemberg GV, Lugtenberg BJ (2004) Rhizoremediation: a beneficial plant microbe interaction. Mol Plant Microbe Interact 17:6–15

Kumar V, Chopra AK (2016) Reduction of pollution load of paper mill effluent by phytoremediation technique using water caltrop (*Trapa natans* L.). Cogent Environ Sci 2:1153–1216

Kumar V, Chopra AK (2017) Phytoremediation potential of water caltrop (*Trapa natans* L.) using municipal wastewater of activated sludge process based municipal wastewater treatment plant. Environ Technol 39(1):12–23

Kumar PB, Dushenkov V, Motto H, Raskin I (1995) Phytoextraction: the use of plants to remove heavy metals from soils. Environ Sci Technol 29:1232–1238

Kumar KV, Singh N, Behl HM, Srivastava S (2008) Influence of plant growth promoting bacteria and its mutant on heavy metal toxicity in Brassica juncea grown in fly ash amended soil. Chemosphere 72:678–683

Lalith S, Susumu A, Akihiro S, Aminul H (2007) Variation in growth and yield performance of seventeen water chestnut accessions (Trapa spp.) collected from Asia and Europe. Plant Prod Sci 10(3):372–379

Lasat MM (2002) Phytoextraction of toxic metals: a review of biological mechanisms. J Environ Qual 31(1):109–120

Lehmann J (2007) Bioenergy in the black. Front Ecol Environ 5(7):381–387

Levine AD, Asano T (2004) Recovering sustainable water from wastewater. Environ Sci Technol 1:201A–208A

Li J, He M, Han W, Gu F (2009) Analysis and assessment on heavy metal sources in the coastal soils developed from alluvial deposits using multivariate statistical methods. J Hazard Mater 164:976–981

Li S, Tosens T, Harley PC, Jiang YF, Kanagendran A, Grosberg M, Jaamets K, Niinemets U (2018) Glandular trichomes as a barrier against atmospheric oxidative stress: relationships with ozone-uptake, leaf damage, and emission of LOX products across a diverse set of species. Plant Cell Environ 41(6):1263–1277

Liphadzi MS, Kirkham MB (2006) Heavy-metal displacement in chelate- treated soil with sludge during phytoremediation. J Plant Nutr Soil Sci 169(6):737–744

Liu X, Zhang A, Ji C, Joseph S, Bian R, Li L, PazeFerreiro J (2013) Biochar's effect on crop productivity and the dependence on experimental conditions- a meta-analysis of literature data. Plant Soil 373:583–594

Liu Z, Lin H, Cai T, Chen K, Lin Y, Xi Y, Chhuond K (2019) Effects of phytoremediation on industrial wastewater. IOP Conf Series: Earth and Environmental Science 371(032011)

Lone MI, He Z-L, Stoffella PJ, Yang X-E (2008) Phytoremediation of heavy metal polluted soils and water: progresses and perspectives. J Zhejiang Univ Sci B 9(3):210–220

Lu Q (2009) Evaluation of aquatic plants for phytoremediation of eutrophic storm waters. Ph.D Thesis. University of Florida

Lu X, Kruatrachue M, Pokethitiyook P, Homyok K (2004) Removal of cadmium and zinc by water hyacinth, Eichhornia crassipes. Sci Asia 30:93–103

Lu LL, Tian SK, Yang XE, Li TQ, He ZL (2009) Cadmium uptake and xylem loading are active processes in the hyperaccumulator Sedum alfredii. J Plant Physiol 166(6):579–587

Lu Q, He ZL, Graetz DA, Stoffella PJ, Yang X (2010) Phytoremediation to remove nutrients and improve eutrophic storm waters using water lettuce (*Pistia stratiotes* L.). Environ Sci Pollut Res 17:84–96

Lucas GJA, Grijalbo L, Ramos B, Gutierrez Mañero FJ (2011) Procedimiento para la reducción de la DQO de efluentes líquidos aceitosos mediante fitorremediación con maíz-esparto; su aplicación al tratamiento detaladrinas agotadas. Patent No. 2. Spanish Office of Patents. pp 350–433

Luqman M, Butt TM, Tanvir A, Atiq M, Hussan MZY, Yaseen M (2013) Phytoremediation of polluted water by trees: a review. Int J Agric Res 1(2):22–25

Lytle CM, Lytle FW, Yang N, Qian H, Hansen D, Zayed A, Terry N (1998) Reduction of Cr(VI) to Cr(III) by wetland plants: potential for in situ heavy metal detoxification. Environ Sci Technol 32:3087–3093

Ma LQ, Komar KM, Tu C, Zhang W, Cai Y, Kennelly ED (2001) A fern that hyperaccumulates arsenic. Nature Biotechnol 409:579–579

Maatoug M, Amirat M, Zerrouki D, Ait Hammou M (2013) Decontamination of agricultural soil polluted with lead using the common barley (Hordium vulgare). Arab Gulf J Sci Res 31(1):23–35

Madsen TV, Brix H (1997) Growth, photosynthesis and acclimation by two submerged macrophytes in relation to temperature. Oecologia 110:320–327

Mann S, Gupta D, Gupta V, Gupta RK (2012) Evaluation of nutritional, phytochemical and antioxidant potential of *Trapa bispinosa* roxb. fruits. Int J Pharm Pharm Sci 4(1):432–436

Martelo J, Lara Borrero JA (2012) Macrófitas flotantes en el tratamiento de aguas residuales: una revisión del estado del arte. Ingeniería y ciencia 8(15):221–243

Mashauri DA, Mulungu DMM, Abdulhussein BS (2000) Constructed wetland at the University of Dar Es Salaam. Water Res 34:1135–1144

McDonald AG, Bealey WJ, Fowler D, Dragosits U, Skiba U, Smith RI, Donovan RG, Brett HE, Hewitt CN, Nemitz E (2007) Quantifying the effect of urban tree planting on concentrations and depositions of PM10 in two UK conurbations. Atmos Environ 41(38):8455–8467

Memon AR, Schröder P (2009) Implications of metal accumulation mechanisms to phytoremediation. Environ Sci Pollut Res 16:162–175

Mench M, Vangronsveld J, Bleeker P, Ruttens A, Geebelen W, Lepp N (2006) Phytostabilisation of metal-contaminated sites. In: Morel JL, Echevarria G, Goncharova N (eds) Phytoremediation of metal-contaminated soils. Springer, Dordrecht, pp 109–190

Micó C, Recatalá L, Peris M, Sánchez J (2006) Assessing heavy metal sources in agricultural soils of an European Mediterranean area by multivariate analysis. Chemosphere 65:863–872

Miksanova M, Hudecek J, Paca J, Stiborova M (2001) To the mechanism of horseradish peroxidases-mediated degradation of a recalcitrant dye Remazol brilliant blue R. Collect Czech Chem Commun 66:663–675

Mojiri A, Ziyang L, Tajuddin RM, Farraji H, Alifar N (2016) Co-treatment of landfill leachate and municipal wastewater using the ZELIAC/zeolite constructed wetland system. J Environ Manag 166:124–130

Mokea-Niaty A, Medza-Mve SD, Lepengue AN, Moupela C, Ognalaga M, Mboumba P, Toussaint A, M'batchi B (2018) *Alchornea cordifolia* (Schumach. & Thonn.) Müll. Arg: a potential plant for phytoremediation of manganese polluted soils. Int J Adv Res 1(1):328–337

Naeem M, Idrees M, Khan MMA, Moinuddin MA, Ansari AA (2014) Task of mineral nutrients in eutrophication. In: Ansari AA, Gill SS (eds) Eutrophication: causes, consequences and control, vol 2. Springer, The Netherlands, pp 223–237

Nedelkoska TV, Doran PM (2000) Hyperaccumulation of cadmium by hairy roots of *Thlaspi caerulescens*. Biotechnol Bioeng 67:607–615

Nwoko CO, Okeke PN, Ac-Chukwuocha N (2004) Preliminary studies on nutrient removal potential of selected aquatic plants. J Discov Innovat Afr Acad Sci 16(3):133–136

O'Neill CR (2006) Water chestnut (Trapa natans) in the Northeast. NYSG Invasive Species Fact sheet Series: 06-1

Obinna IB, Ebere EC (2019) Phytoremediation of polluted waterbodies with aquatic plants: recent progress on heavy metal and organic pollutants analytical methods. Environ Chem J 17:1–10

Ochiai EI (1987) General principles of biochemistry of the elements. Springer, Boston

Olufunmilayo TA, Ogunbayo AO (2012) Achieving environmental sustainability in wastewater treatment by phytoremediation with water hyacinth (*Eichhornia Crassipes*). J Sustain Develop 5(7):80

Orwell RL, Wood RA, Tarran J, Torpy F, Burchett MD (2004) Removal of benzene by the indoor plant/substrate microcosm and implications for air quality. Water Soil Air Pollut 157(1–4):193–207

Pandey S, Mewada A, Thakur M (2013) Rapid biosynthesis of silver nanoparticles by exploiting the reducing potential of Trapa bispinosa peel extract. J Nanosci p 1–9

Pardo T, Clemente R, Alvarenga P, Bernal MP (2014) Efficiency of soil organic and inorganic amendments on the remediation of a contaminated mine soil: II. Biological and ecotoxicological evaluation. Chemosphere 107:101–108

Pateiro-Moure M, Arias-Estévez M, Simal-Gándara J (2013) Critical review on the environmental fate of quaternary ammoniumherbicides in soils devoted to vineyards. Environ Sci Technol 47(10):4984–4998

Patel DK, Kanungo VK (2010) Phytoremediation potential of Duckweed (*Lemna minor* L: a tiny aquatic plant) in the removal of pollutants from domestic wastewater with special reference to nutrients. Bioscan 5:355–358

Paz-Alberto M, Sigua GC (2013) Phytoremediation: a green technology to remove environmental pollutants. Am J Clim Chang 2:71–86

Paz-Alberto M, Sigua GC, Baui BG, Prudente JA (2007) Phytoextraction of lead-contaminated soil using vetiver grass (*Vetiveria zizanioides* L.), cogon grass (*Imperata cylindrica* L.) and carabao grass (*Pas palum conjugatum* L.). Environ Sci Pollut Res 14(7):498–504

Pereira FJ, Castro EM, Oliveira CP, Pasqual M (2011) Mecanismos anatômicos e fisiológicos de planta de aguapé para a tolerância à contaminação por Arsênio. Planta Daninha 29(2):259–267

Peterson G, Jones T, Rispoli D, Stitt D, Haddadi S, Niri V. Monitoring volatile organic compound removal by common indoor plants using solid phase microextraction and gas chromatography-mass spectrometry. 2015

Phetsombat S, Kruatrachue M, Pokethitiyook P, Upatham S (2006) Toxicity and bioaccumulation of cadmium and lead in Salvinia cucullata. J Environ Biol 27(4):645–652

Pierart A, Shahid M, Séjalon- Delmas N, Dumat C (2015) Antimony bioavailability: knowledge and research perspectives for sustainable agricultures. J Hazard Mater 289:219–234

Pilon-Smits E (2005) Phytoremediation. Annu Rev Plant Biol 56:15–39

Pilon-Smits EAH, Quinn CF, Tapken W, Malagoli M, Schiavon M (2009) Physiological functions of beneficial elements. Curr Opin Plant Biol 12(3):267–274

Pinto E, Sigaud-kutner TCS, Leitão MAS, Okamoto OK, Morse D, Colepicolo P (2003) Heavy metal induced oxidative stress in algae 1. J Phycol 39(6):1008–1018

Pirrera G, Pluchino A (2017) Phytoremediation for ecological restauration and industrial ecology. Procedia Environ Sci Eng Manage 4:273–286

Pollmann K, Raff J, Merroun M, Fahmy K, Selenska-Pobell S (2006) Metal binding by bacteria from uranium mining waste piles and its technological applications. Biotechnol Adv 24(1):58–68

Ponce-Hernández A, Maldonado-Miranda JJ, Medellin-Castillo NA, Alonso-Castro AJ, Carranza-Alvarez C (2020) Phytoremediation technology: sustainable solution for cleaning up of recalcitrant pollutants from disturbed environs. In: Bioremediation and biotechnology, vol 3. Springer, Cham, pp 245–268

Popova LP, Maslenkova LT, Yordanova RY, Ivanova AP, Krantev AP, Szalai G (2009) Exogenous treatment with salicylic acid attenuates cadmium toxicity in pea seedlings. Plant Physiol Biochem 47:224–231

Porra RJ (2002) The chequered history of the development and use of simultaneous equations for the accurate determination of chlorophylls *a* and *b*. Photosynth Res 73:149–156

Prasad MNV (2011) A state-of-the-art report on bioremediation, its applications to contaminated sites in India. Ministry of Environment & Forests, Government of India

Pulford ID, Watson C (2003) Phytoremediation of heavy metal-contaminated land by trees—a review. Environment international 29(4):529–540

Quartacci MF, Irtelli B, Gonnelli C, Gabbrielli R, Navari-Izzo F (2009) Naturally assisted metal phytoextraction by *Brassica carinata*: role of root exudate. Environ Pollut 157:2697–2703

Raskin I, Ensley BD (1997) Phytoremediation of toxic metals: using plants to clean up the environment. Curr Opin Biotechnol 8(2):221–226

Raskin I, Smith RD, Salt DE (1997) Phytoremediation of metals: using plants to remove pollutants from the environment. Curr Opin Biotechnol 8:221–226

Redjala T, Zelko I, Sterckeman T, Legué V, Lux A (2011) Relationship between root structure and root cadmium uptake in maize. Environ Exp Bot 71:241–248

Reilley KA, Banks MK, Schwab AP (1996) Dissipation of polycyclic aromatic hydrocarbons in the rhizosphere Journal of Environemtal Quality

Rezania S, Ponraj M, Talaiekhozani A, Mohamad SE, Din MFM, Taib SM, Sabbagh F, Sairan FM (2015) Perspectives of phytoremediation using water hyacinth for removal of heavy metals, organic and inorganic pollutants in wastewater. J Environ Manag 163:125–133

Rugh CL, Senecoff JF, Meagher RB, Merkle SA (1998) Development of transgenic yellow poplar for mercury phytoremediation. Nat Biotechnol 16(10):925–928

Sadowsky M (1999) Phytoremediation: past and future practises. Proceedings of the 8th international symposium on microbial ecology Halifax Canada. pp 1–7

Salt DE, Rauser WE (1995) MgeATP dependent transport of phytochelatins across tonoplast of oat roots. Plant Physiol 107:1293–1301

Salt DE, Smith RD, Raskin I (1998) Phytoremediation Annual Review of Plant Phisiology and Plant Biology 49:643–668

Salt DE, Blaylock M, Kumar NP, Dushenkov V, Ensley BD, Chet I, Raskin I (1995a) Phytoremediation: a novel strategy for the removal of toxic metals from the environment using plants. Bio/Technol 13:468–474

Salt DE, Blaylock M, Kumar PBAN, Dushenkov V, Ensley BD, Chet I, Raskin I (1995b) Phytoremediation: a novel strategy for the removal of toxic metals from the environment using plants. Biotechnol 13:468–475

Sanders JR, McGrath SP, Adams TM (1986) Zinc, copper and nickel concentrations in ryegrass grown on sewage sludge-contaminated soils of different pH. J Sci Food Agric 37:961–968

Sarma H (2011) Metal hyperaccumulation in plants: a review focusing on phytoremediation technology. J Environ Sci Technol 4(2):118–138

Sarwar N, Imran M, Shaheen MR, Ishaque W, Kamran MA, Matloob A, Rehim A, Hussain S (2017) Phytoremediation strategies for soils contaminated with heavy metals: modifications and future perspectives. Chemosphere 171:710–721

Sas-Nowosielska A, Kucharski R, Małkowski E, Pogrzeba M, Kuperberg JM, Kryński K (2004) Phytoextraction crop disposal—an unsolved problem. Environ Pollut 128:373–379

Satyakala G, Jamil K (1992) Chromium-induced biochemical changes in Eichhornia crassipes (Mart) solms and Pistia stratiotes L. Bull Environ Contam Toxicol 8(6):921–928

Schnoor JL, Licht LA, McCutcheon SC, Wolfe NL, Carreira LH (1995) Phytoremediation of organic and nutrient contaminants. Environ Sci Technol 29:318–323

Schröder P, Navarro-Aviñó J, Azaizeh H, Golan Goldhirsh A, DiGregorio S, Komives T, Langergraber G, Lenz A, Maestri E, Memon AR, Ranalli A, Sebastiani L, Smrcek S, Vanek T, Vuilleumier S, Wissing F (2007) Using phytoremediation technologies to upgrade waste water treatment in europe. Environ Sci Pollut Res 14(7):490–497

Selmi W, Weber C, Riviere E, Blond N, Mehdi L, Nowak D (2016) Air pollution removal by trees in public green spaces in Strasbourg city. France. Urban For Urban Green 17:192–201

Seroka-Stolka O, Ociepa-Kubicka A (2019) Green logistics and circular economy. Transportation Research Procedia 39:471–479

Sessitsch A, Kufner M, Kidd P, Vangronsveld J, Wenzel WW, Fallman 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

Shen S, Li XF, Cullen WR, Weinfield M, Le XC (2013) Arsenic binding to proteins. Chem Rev 113(10):7769–7792

Shovon MNH, Majumdar BC, Rahman Z (2017) Heavy metals (lead, cadmium and nickel) concentration in different organs of three commonly consumed fishes in Bangladesh. Fish Aquac J 8(3):1–6

Silva AS, Techio VH, Castro EM, Faria MR, Palmieri MJ (2013) Reproductive, cellular, and anatomical alterations in Pistia stratiotes L. plants exposed to cadmium. Water Air Soil Pollut 224:1465–1477

Singer AC, Crowley DE, Thompson IP (2003) Secondary plant metabolites in phytoremediation and biotransformation. Trends Biotechnol 21(3):123–130

Singh NP, Santal AR (2015) Phytoremediation of heavy metals: the use of green approaches to clean the environment. In: Ansari A, Gill S, Gill R, Lanza G, Newman L (eds) Phytoremediation. Springer, Cham

Singh D, Tiwari A, Gupta R (2012) Phytoremediation of lead from wastewater using aquatic plants. J Agric Technol 8(1):1–11

Sinha S, Mishra R, Sinam G, Mallick S, Gupta A (2013) Comparative evaluation of metal phytoremediation potential of trees, grasses and flowering plants from tannery wastewater contaminated soil in relation with physicochemical properties. Soil Sediment Contam 22(8):958–983

Sizmur A, Hodson ME (2009) Do earthworms impact mobility and availability in soil? A review. Environ Pollut 159:1981–1989

Smith KA, Paterson JE (1999) Mangan und Cobalt. In: Alloway BJ (ed) Schwermetalle in Böden. Springer, Berlin, Heidelberg

Song U, Park H (2017) Importance of biomass management acts and policies after phytoremediation. J Ecol Environ 41:13

Sorek A, Atzmon N, Dahan O, Gerstl Z, Kushisin L, Laor Y, Migelgrin U, Nasser A, Ronen D, Tsechansky L, Weisbrod N, Graber ER (2008) Phytoscreening: the use of trees for discovering subsurface contamination by VOCs. Environ Sci Technol 42(2):536–542

Souza LA, Piotto FA, Nogueirol RC, Azevedo RA (2013a) Use of nonehyperaccumulator plant species for the phytoextraction of heavy metals using chelating agents. Sci Agric 70(4):290–295

Souza FA, Dziedzic M, Cubas SA, Maranho LT (2013b) Restoration of polluted waters by phytoremediation using Myriophyllum aquaticum (Vell.) Verdc., Haloragaceae. J Environ Manag 120:5–9

Stefani GD, Tocchetto D, Salvato M, Borin M (2011) Performance of a floating treatment wetland for in-stream water amelioration in NE Italy. Hydrobiologia 674:157–167

Strycharz S, Shetty K (2002) Effect of Agrobacterium rhizogenes on phenolic content of Menthapulegium elite clonal line for phytoremediation applications. Process Biochem 38:287–293

Tamaoki M, Freeman JL, Pilon-Smits EAH (2008) Cooperative ethylene and jasmonic acid signaling regulates selenite resistance in Arabidopsis. Plant Physiol 146(3):1219–1230

Tandy S, Schulin R, Nowack B (2006) The influence of EDDS on the uptake of heavy metals in hydroponically grown sunflowers. Chemosphere 62(9):1454–1463

Tanner CC, Headley TR (2011) Components of floating emergent macrophyte treatment wetlands influencing removal of storm water pollutants. Ecol Eng 37(3):474–486

Tardieu F, Parent B, Simonneau T (2010) Control of leaf growth by abscisic acid: hydraulic or non-hydraulic processes? Plant Cell Environ 33(4):636–647

Terry N, Banuelos G (2000) Phytoremediation of contaminated soil and water. Edited by Terry N, Banuelos GS. CRC Press Lewis, Boca Raton. 408 p

Thewys T, Kuppens T (2008) Economics of willow pyrolysis after phytoextraction. Int J Phytoremediation 10:561–583

Tripathi S, Sing VP, Srivastava P, Singh R, Devi SD, Kumar A, Bhadouria R (2020) Phytoremediation of organic pollutants: current status and future directions. Abatement Environ Pollut:81–105

Truong PN, Baker D (1996) Vetiver grass system for environmental protection. Royal development projects protection. Tech Bull 1998(1)

Truong P, Baker D (1998) Vetiver grass system for environmental protection. Pacific Rim Vetiver Network, Office of the Royal Development Projects Board

UNEP (2019) UNEP (Undated) Phytoremediation: an environmentally sound technology for pollution prevention, control and remediation. An introductory guide to decision-makers. Newsletter and Technical Publications Freshwater Management Series No. 2 United Nations Environment Programme Division of Technology, Industry, and Economics. http://www.unep.or.jp/Ietc/Publications/Freshwater/FMS2/1.asp. Assessed 18 Aug 2019

United Nations, UN (2003) Wastewater treatment technologies: a general review. United Nations, New York

United States Environmental Protection Agency (USEPA) (2004) Hazard summary. Lead compounds. http://www.epa.gov/ttn/atw/hlthef/lead.html

Van Hullebusch E, Piet NLL, Tabak HH (2005) Developments in bioremediation of soils and sediments polluted with metals and radionuclides. 3. Influence of chemical speciation and bioavailability on contaminants immobilization/mobilization bio-processes. Rev Environ Sci Bio/Technol 4:185–212

Van Huysen T, Terry N, Pilon-Smith EAH (2004) Exploring the selenium phytoremediation potential of transgenic Indian mustard overexpressing ATP sulfurylase or cystathionine-gamma-synthase. Int J Phytoremediation 6(2):111–118

Varkey M, Lal N, Khan ZH (2012) Phytoremediation: strategies to enhance the potential for toxic metal remediation of brassica oilseed species. In: Phytotechnologies: remediation of environmental contaminants. Taylor and Francis, New York, pp 293–308

Varun M, D'Souza R, Favas PJC, Pratas J, Paul MS (2015) Utilization and supplementation of phytoextraction potential of some terrestrial plants in metal-contaminated soils. In: Ansari AA et al (eds) Phytoremediation. Springer, Cham, pp 177–200

Verma VK, Tewari S, Rai JPN (2008) Ion exchange during heavy metal biosorption from aqueous solution by dried biomass of macrophytes. Bioresour Technol 99:1932–1938

Vidal CF, Oliveira JA, da Silva AA, Ribeiro C, Farnese FDS (2019) Phytoremediation of arsenite-contaminated environments: is Pistia stratiotes L. a useful tool? Ecol Indic 104:794–801

Vithanage M, Dabrowska BB, Mukherjee AB, Sandhi A (2012) Arsenic uptake by plants and possible phytoremediation applications: a brief overview. Environ Chem Lett 10(3):217–224

Vodyanitskii YN, Plekhanova IO (2014) Biogeochemistry of potentially toxic elements in contaminated excessively moistened soils (analytical review). Eurasian Soil Sci 47(3):153–161

Von WN, Klair S, Bansal S, Briat JF, Khodr H, Shiori T, Leigh RA, Hider RC (1999) Nicotianamine chelates both Fe (III) and Fe (II). Implications for metal transport in plants. Plant Physiol 119:1109–1111

Walton BT, Guthrie EA, Hoylman AM (1994) Toxicant degradation in the rhizosphere. In: Anderson TA, Coats JR (eds) Bioremediation through rhizosphere technology, vol 563. American Chemical Society, Washington, D.C., pp 11–26

Wan J, Tokunaga TK, Brodie E, Wang Z, Zheng Z, Herman D, Hazen TC, Firestone MK, Sutton SR (2005) Reoxidation of bio-reduced uranium under reducing conditions. Environ Sci Technol 39:6162–6169

Wang S, Zhao X (2009) On the potential of biological treatment for arsenic contaminated soils and groundwater. J Environ Manag 90(8):2367–2376

Wang L, Gong HL, Liao WB, Wang Z (2015) Accumulation of particles on the surface of leaves during leaf expansion. Sci Total Environ 532:420–434

Weggler K, McLaughlin MJ, Graham RD (2004) Effect of chloride in soil solution on the plant availability of bio-solid borne cadmium. J Environ Qual 33:496–504

Wei Z, Van Le Q, Peng W, Yang Y, Yang H, Gu H, Lam SS, Sonne C (2021) A review on phytoremediation of contaminants in air, water and soil. J Hazard Mater 403:123658

Wen B, Hu X, Liu Y, Wang W, Feng M, Shan X (2004) The role of earthworms (Eisenia fetida) in influencing bioavailability of heavy metals in soils. Biol Fertil Soils 40:181–187

WHO (1993) Arsenic in drinking water, world health organisation factsheet 210. World Health Organisation, Geneva

Winter Sydnor ME, Redente EF (2002) Reclamation of high elevation, acidic mine waste with organic amendments and topsoil. J Environ Qual 31:1528–1537

Wolfe NL, Hoehamer CF (2003) Enzymes used by plants and microorganisms to detoxify organic compounds. In: Mc. Cutcheon SC, Schnoor JL (eds) Phytoremediation: transformation and control of contaminants. Wiley, USA, pp 159–187

Wolverton BC, Wolverton JD (1996) Interior plants: their influence on airborne microbes inside energyefficient buildings. Journal of the Mississippi Academy of Sciences 41(2):99–105

Wolverton BC, Johnson A, Bounds K (1989) Interior landscape plants for indoor air pollution abatement: final report. National Aeronautics and Space Administration

Wong Argüelles C (2009) Estudio de organismos acuáticos macrobentónicos como indicadores de la contaminación por metales pesados en ríos de la huasteca potosina. REPOSITORIO NACIONAL CONACYT

Wong CS, Li X, Thornton I (2006) Urban environmental geochemistry of trace metals. Environ Pollut 142:1–16

Wu Q (2014) Study on the purification performance of Cr(VI) polluted water by Lishihe Constructed Wetland. J Environ Eng 8(02):536–540

Xia H, Ma X (2005) Phytremediation of ethion by water hyacinth (*Echhornia crassipes*) from water. Bioresour Technol 97(8):1050–1054

Xu YS, Xu W, Mo L, Heal MR, Xu XW, Yu XX (2018) Quantifying particulate matter accumulated on leaves by 17 species of urban trees in Beijing, China. Environ Sci Pollut Res 25(13):12545–12556

Yadav KK, Gupta N, Kumar A, Reece LM, Singh N, Rezania S, Khan SA (2018) Mechanistic understanding and holistic approach of phytoremediation: a review on application and future prospects. Ecol Eng 120:274–298

Yoo MH, Kwon YJ, Son KC, Kays SJ (2006) Efficacy of indoor plants for the removal of single and mixed volatile organic pollutants and physiological effects of the volatiles on the plants. J Am Soc Hortic Sci 131(4):452–458

Zaranyika MF, Ndapwadza T (1995) Uptake of Ni, Zn, Fe, Co, Cr, Pb, Cu and Cd by water hyacinth (*Eichhornia crassipes*) in Mukuvsi and rivers, Zimbabwe. J Environ Sci Health A 30(1):1157–1169

Zhang X, Liu P, Yang Y, Chen W (2007) Phytoremediation of urban wastewater by model wetlands with ornamental hydrophytes. J Environ Sci China 19:902–909

Zhang KM, Liu YZ, Wang H (2010) Use of single extraction methods to predict bioavailability of potentially-toxic elements in polluted soils to rice. Commun Soil Sci Plant Anal 41:820–831

Zhang H, Pennisi SV, Kays SJ, Habteselassie MY (2013) Isolation and identification of toluene-metabolizing bacteria from rhizospheres of two indoor plants. Water Air Soil Pollut 224(9):1648

Zhou Q, Zhang J, Fu J, Shi J, Jiang G (2008) Biomonitoring: an appealing tool for assessment of metal pollution in the aquatic ecosystem. Anal Chim Acta 606:135–150

Zolotukhina EY, Gavrilenko EE (1989) Heavy metals in aquatic plants: accumulation and toxicity. Biol Sci 9:93–106

Zorzal FMB, Elias JL, Elias JVV, Jachic J, Medina AS (2005) Caracterização da bacia hidrográfica do rio Barigui e Curitiba. In: Congresso Brasileiro de Engenharia Sanitária e Ambiental

Chapter 3
Phytoremediation by Wild Weeds: A Natural Asset

Sabreen Bashir, Madhuri Girdhar, Vikram Srivastava, and Anand Mohan

Abstract The diverse activities of humans have changed the composition and organization of soil which have resulted in the contamination of our environment. A number of methods have been used to get rid of these contaminants from our environment, but majority of the methods are expensive and non-effective and do not give desired results. The technique of phytoremediation includes the use of either plants or plant products to clean the contaminated sites. Phytoremediation takes advantage of plant's natural ability to take up, collect, store, or degrade the inorganic and organic substances. It is an economical and natural green technology, which helps us in removing the toxic elements from our environment by making use of wild weeds or small herbal plants. It offers a promising tool for the hyperaccumulation of various heavy metals such as lead, nickel, chromium, arsenic, mercury, etc. Thus, plants having an inherent capacity to accumulate heavy metals in their roots or their shoots can form phytochelates and can convert toxic metals into stable compounds.

Keywords Phytoremediation · Metal excluders · Wild weeds · Hyperaccumulation · Metal tolerance

3.1 Introduction

Increase in human population leading to over exploitation of natural resources as well as degradation of the environment in terms of soil, air and water by different natural and anthropogenic activities has resulted in much damage to property and human health. Heavy metal pollution is one such problem that is emerging very fast.

S. Bashir · M. Girdhar · A. Mohan (✉)
School of Bioengineering and Biosciences, Lovely Professional, University, Phagwara, Punjab, India

V. Srivastava
Department of Biomedical Sciences, Iowa State University, Ames, IA, USA

L. Newman et al. (eds.), *Phytoremediation*, https://doi.org/10.1007/978-3-031-17988-4_3

To deal with heavy metal pollution, various techniques are employed. Most of these are very costly, time consuming, less effective and are not environment friendly. Therefore, to deal with heavy metal stress, a green technology called phytoremediation has been undertaken recently that is based on the use of green plants to decontaminate the contaminated soil and water. There are more than four hundred plant families that act as hyperaccumulator plants (Girdhar et al. 2014a, b). Leafy vegetables are among one of them. However, they are the part of food chain and consumed by human beings, so if they accumulate heavy metals in their leaves, they can pose risk to human health. Instead of leafy vegetables, weeds can be a good option as they produce large biomass and also grow very fast under any type of environmental stress (Archary et al. 2017).

Pollution of environment in terms of soil, water and air is imposing a serious impact on humans and other components of the environment (Xiao et al. 2017). There are different types of pollutants in our environment. One such pollutant is heavy metals. Heavy metal pollution can become the cause of human deaths (Jarup et al. 2003). Scientists all around the world are more concerned about heavy metal pollution because of their much toxic effects on all biotic components of environment, their long-term persistence in the nature, and their easy entrance into the food chain (Wang et al. 2006; Archary et al. 2017).

Heavy metal pollution is caused by both anthropogenic as well as natural activities, but natural activities can be remediated by nature itself. On the other hand, anthropogenic activities such as mining, smelting, electroplating, and agricultural use of metal. are irreparable by nature (Mohan et al. 2019). Therefore, from time to time, different remediation techniques are used by various researchers to remediate heavy metal polluted sites. Such soils can be treated by chemical methods, acid percolation, soil treatment by washing, segregation of pollutants by physical methods or biochemical treatments of soil, etc. (Hashim et al. 2011; Tangahu et al. 2011). For correction of ground waters, use of microbes, adsorption or biosorption methods can be used (Hashim et al. 2011). However, the problem of using these methods is that these methods are very costly and need long time for treatment and are not environment friendly (Tangahu et al. 2011; Susarla et al. 2002). An alternate approach to the above problems is the use of plants to correct heavy metal polluted sites. This approach to make soil contamination free is called Phytoremediation or 'Green Technology'. This technique is not very costly; in addition, it is eco-friendly and gives long-term results (Chaney et al. 2005). The plants and wild weeds used in this technique store heavy metals in their root, stem, and leave and thus can act as hyperaccumulator plants (Baker et al. 2020).

3.2 Phytoremediation and Its Techniques

Plant treatment, which has become more popular in the last 10 years, is a passive technology related to soil reclamation in which plants are used to remove contaminants from an area or restore them (Raskin et al. 1997).

Salt et al. (1998) have divided phytoremediation techniques into phytoextraction, phytodegradation, rhizofiltration, phytostabilization, phytovolatilization, and rhizodegradation, as shown in Fig. 3.1.

(a) Phytoextraction

This technique, also known as vegetal assimilation, is used to absorb inorganic and organic pollutants by the roots and branches of plants. In this method, the plants which have the ability to absorb metals are selected to remove contaminants from soil and thus recover the contaminated sites.

Since the application of this technology takes more time than other techniques, it is very difficult to apply it to heavily polluted areas. In addition, a plant that grows in this ecosystem must be selected. It should also be non-seasonal, as they will be later harvested. They are then burned in incinerator after harvesting (Royer and Smith 1995). This method, known as phytomining, helps to obtain ores that are uneconomical to cultivate. In USA, gold and nickel are being recovered with this method (Pivetz 2001).

After comparing the plants which were utilized in this method with others, it was found that they are able to accumulate pollutant elements more than 100 times. A total of 400 species that have the ability to accumulate heavy metals along with family Euphorbiaceae, Scrophulariaceae, Asteraceae, Lamiaceae, and Brassicaceae are identified in this method. The residues can be isolated by drying, incineration, annealing, and recycling into organometallic minerals from the harvested plants (Memon et al. 2001).

(b) Phytodegradation (Vegetal Degradation)

In phytodegradation method, organic pollutants are broken down by compounds which are produced by the plants via metabolism. This method can apply to soils,

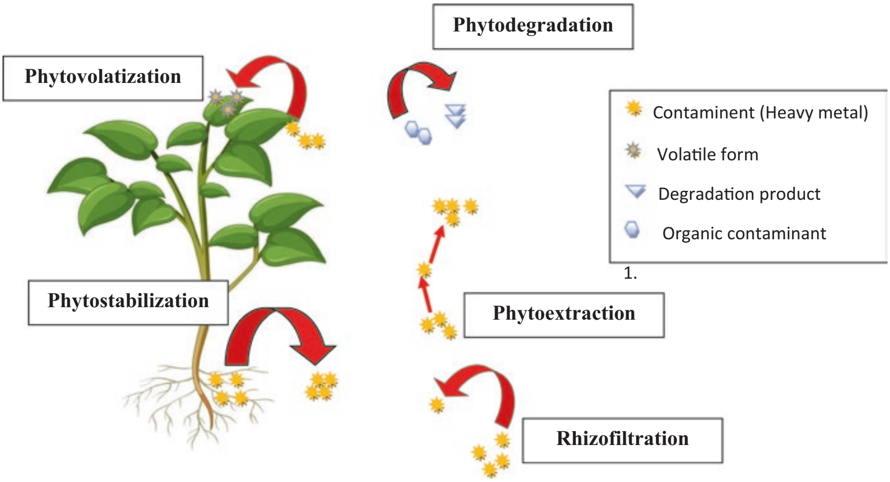


Fig. 3.1 Representation of phytoremediation and its techniques

clays, sediments and groundwater. Occurrence of degradation and reduction inside the plant body as a physiological process without depending on micro-organisms is the chief advantage of this approach. On the other hand, the appearance of intermediate and final products is toxic and difficult to detect which creates a drawback (Pivetz 2001).

Plant's uptake of the organic compounds depends on the plant type, the time of residence of the contaminant in the soil, and chemical and physical properties of the soil. It is difficult to absorb soluble compounds. Herbicides, chlorinated solvents, trichloroethane (TCE) and other toxic substances are broken down by the plant enzymes (Memon et al. 2001).

(c) Phytostabilization

Phytostabilization is used in the stabilization of soil. Such plants possess the ability for high levels of metal tolerance and also use sorption, sedimentation complexation, or reduction in metal valences for immobilizing the metals. In the soil, the contamination factors occur because of the contaminant immobilization around plant roots, cohesion or sedimentation around the roots or their accumulation by the roots (Mirsal 2004).

(d) Phytovolatilization (Vegetal Evaporation)

Conversion of more toxic compounds (containing mercury) to forms which are less toxic is the chief aspect of this method. However, a major drawback of this method is the possibility of releasing these harmful and toxic materials in the atmosphere. Pollutants can be removed from plants through evaporation or transpiration. Since, water transportation occurs from roots to leaves, the contaminants are released by the process of evaporation or by volatilization into the air. Poplar tree shows this mechanism (Royer and Smith 1995).

Heavy metals are absorbed and converted to gaseous form by the process of phytovolatization and then released into the atmosphere by some plants such as *Arabidopsis thaliana* and *Brassica juncea* (Wang et al. 2007).

(e) Rhizodegradation

In this method, degradation occurs with the help of roots. Root decay is a process in which organic matter present in the soil around the roots of the plant is broken down by the activity of microbes. Sugars, organic acids, amino acids, sterols, fatty acids, growth factors, nucleotides, flavones and enzymes secreted by the roots affect the microbial activity in the area around the roots. The destruction of contaminants in their natural environment is the chief advantage of rhizome decomposition (Yildiz 2008).

The contaminants which can be dissolved by the method of rhizodegradation include polychlorinated pentachlorophenol, surfactants, total petroleum hydrocarbons, ethylbenzene, benzene, pesticides (herbicides and insecticides), toluene, xylene, polycyclic aromatic hydrocarbons, chlorinated solvents (TCE and TCA), and biphenyls (PCB). Red berries (*Morusrubra L.*), peppermint (*Menthaspicata L.*), mace (*Typhalatifolia L.*), and alfalfa (*Medicago sativa L.*) can be utilized in the rhizome digestion (Pulford and Watson 2003).

(f) Rhizofiltration

In this method, the roots are used for filtration in which the contaminants stick to the roots of the plants or are being absorbed by the roots according to the biotic and abiotic process. The contaminants during this process may either be taken or transported by the plant. It is important to maintain the contaminant immobilization in or on the plants. Later, we can take the contaminants by using various methods from the plants. Rhizofiltration method is used to clean surface waters, underground water and also waste waters (Sogut et al. 2002).

Water contaminated with metals or radioactive substances is cleaned by using rhizofiltration. In this method, the plants used are grown on the contaminated soil directly and also contaminant adaptation is ensured. Instead of growing in soil, the plants are initially grown in clean water hydroponically and then the rooted plants are shifted to contaminated water to help them adjust in their new environment. The plants are harvested when their roots become saturated. The land and water plants are given an opportunity to be utilized through this method. In addition to being utilized in natural environments, this method is also used in ponds, tanks, and basins (Salt and Smith 1998).

Over more than 100 families of plants have been reported to act as hyperaccumulator families and the most common among these are Brassicaceae, Fabaceae, Asteracecae, Poaceae, Euphorbiaceae, etc. (Sarma et al. 2011). It is also reported that plants belonging to a particular region should be used for green technology than exotic or alien plant species because of better growth and survival rate of native species (Yoon et al. 2006). The various heavy metals include Cr, Ca, Pb, Ni, Cu, Zn, etc., that can be remediated by using wild weeds and cultivated plants (Kaur et al. 2020).

Leafy vegetables show high amount of metal uptake (Saglan et al. 2013; Chang et al. 2014), but these are the part of food chain, so metals accumulated by them can enter human body also. Plants that can be used to accumulate heavy metals must be fast growing having high amount of biomass and must have the ability to absorb heavy metals from their very low concentration. Weeds are the plants that show these characters. Thus, they can be utilized for the phytoremediation of soils contaminated with heavy metals (Khankhane and Varshney 2008; Lum et al. 2014). There also is no risk to the health of humans because weeds do not make a part of the food chain.

3.3 Type of Plant Responses Against Metal Tolerance

Plants show three types of responses (Fig. 3.2) while growing on metal contaminated soils (Raskin et al. 1994). These responses include:

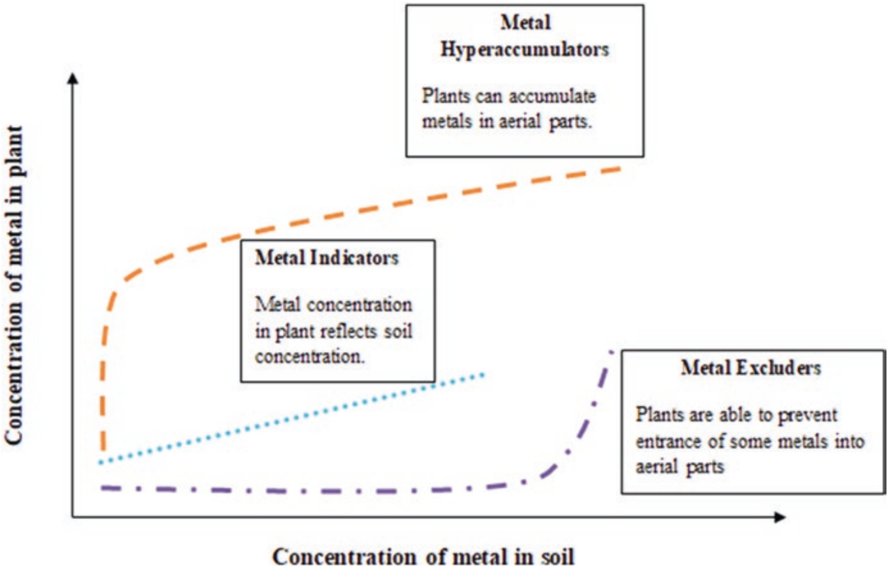


Fig. 3.2 Plant responses to an increase in the concentration of metals in soil

(a) Metal excluders: plants that do not allow metals to enter into their roots and other parts.
(b) Metal indicators: these are such plants which store the metals in their aerial parts and tolerate it by making chelators.
(c) Hyperaccumulators: such plants that have the ability to accumulate 100 times more heavy metals in their roots, stem, and leaves than in the soil. Plants accumulating more than 1000 mg/g of Cu, Cd Cr, Pb, Ni, Ca and 10,000 mg/g of Zn or Mn are considered as hyperaccumulator plants (Baker & Brooks 1989).

Weeds are defined in many ways. According to JethroTull (1731), weeds are the plants that grow in places where they are not required. There are nearly 350 families of flowering plants, out of which 12 plant families include world's most important weeds (Holm et al. 1977). These are Solanaceae, Malvaceae, Euphorbiaceae, Fabaceae, Amaranthaceae, Asteraceae, Poaceae, Cyperaceae, Polygonaceae, Brassicaceae, Convolvulaceae, and Chenopodiaceae.

3.4 Review of Phytoremediation Capability of Some Wild Weeds

Girdhar et al. (2014a, b) studied the phytoremediation capabilities of three wild weed varieties, i.e., *Solanum nigrum, Cannabis sativa,* and *Chenopodium album* on their four morphological parameters-pollen fertility, length of shoot, area of the leaf and number of branches, using lead, chromium, cadmium, copper and nickel as heavy metals at 5, 10, 50, 100, 200, 300 and 350 ppm concentration. *Cannabis sativa* was confirmed as good hyperaccumulator weed. They also concluded that all other weeds have the capability to store heavy metals in their parts and were also showing normal growth and reproduction (Girdhar et al. 2014a, b).

A total of 24 wild plants belonging to 7 different families from 44 contaminated soils were studied by Abou-Shanab et al. (2017) for their phytoremediation potential by using copper, zinc, nickel, lead and chromium as heavy metals on the basis of translocation factor (TF) and bioaccumulation factor (BF). From their study, they concluded that no wild plant species acted as hyperaccumulator species but *Amaranthus* species, *M. parviflora*, *C. ambrosioides* and *L. serriola* could be used for phytoextraction of Pb, Zn, Cu and Ni respectively, having high TF and *C. bonariensis, L. serriola, G. coronaria,* and *C. ambrosioides* could be used for phytostabilization due to high BF.

Hyperaccumulator nature of *Parthenium hysterophorus* for cadmium as heavy metal was studied by Sanghamitra et al. The value for TF was more than 1 showing that this species can be used for phytoextraction of heavy metals from the contaminated soils (Sanghamitra et al. 2011). It was reported and confirmed that *Solanum nigrum* L. is Cd hyperaccumulator weed plant. They also studied the enhanced remediation effect of *Solanum nigrum* in soils contaminated with multi-metals such as Zn, Cu, Cd and Pb. Their results indicated that phytoremediation ability of *Solanumnigrum* was not affected by presence of many heavy metals (Yu et al. 2015).

Phytoremediation ability of four weeds, i.e., *Taraxacum officinale, Solanum nigrum, Abutilon theophrasti,* and *Portulaca oleracea* in Cd contaminated soils was studied by Hammami et al. The parameters used by them for checking phytoremediation ability of these four weeds were translocation factor (TF), bioconcentration factor (BCF), and translocation efficiency (TE%). From the study, they concluded that *Taraxacum officinale* and *Solanum nigrum* can accumulate high amounts of Cd in their parts without showing much damage (Hammami et al. 2016).

Subah & Srinivas (2017) studied the phytoremediation ability of eight weed plants in the benthic lake sludge Hyderabad containing Ni, As, Cr, Fe, Cu, Pb, Zn and Cd in terms of bioaccumulation factor (BCF). Weeds selected for the study were *Cyperus alopecuroides, Amaranthus viridus, Euphorbia geniculata, Polygonum glabrum, Parthenium hysterophorus, Ipomea carnea, Eucalyptus globulus,* and *Ricinus communis*. All the weeds showed high BCF content for Ni followed by Cd, As, Cu, Cr, Pd, Zn and Fe metals. High BCF increases the ability of plants to collect heavy metals in its aerial parts.

Chinmayee et al. (2012) conducted a greenhouse experiment on *Amaranthus spinosus* for knowing its phytoremediation ability on the basis of BCF and TF using Cu, Zn, Cr, Pb and Cd. The values for BCF and TF were above 1 showing that *A. spinosus* can act as an agent for heavy metal accumulation and translocation. BCF shows the index factor that determines the amount of accumulated metal in the plant roots with respect to its amount in the soil (Yoon et al. 2006). TF shows the ratio of heavy metal amount in the shoots to that of roots of a plant (Li et al. 2007). For a species to be hyperaccumulator, its BCF and TF should be more than 1.

Twenty four wild weeds belonging to nine families were studied for their hyperaccumulative properties by Wei et al. (2009) using Cd, Pb, Cu and Zn. The research confirmed that *Rorippa globosa* is a hyperaccumulator weed of Cd with more than 100 mg/kg of Cd in its stem and leaves.

A study made by Subhashini et al. (2017) found the heavy metal uptake potential of *Acalypha indica, Abutilon indicum, and Physalis minima* for Pb, Ni, Cd and Cr metals for 60 days. It confirmed that Pb can be accumulated by *A. inidica* and *P. minima,* Cr by *A. indica* and *A. indicum* and Ni by *A. indica.* They also pointed out that soils contaminated by above given heavy metals can be decontaminated by growing these wild weeds.

3.5 Role of Heavy Metal Tolerance Genes

Overexpression of few genes which are involved in the uptake and translocation of heavy metals in plants is useful to enchant the effect of phytoremediation process (Table 3.1) (Mani & Kumar 2014; Das et al. 2016). There are several families of genes that can be overexpressed as metal transporters, metal chelators and as part of antioxidant machinery (Koźmińska et al. 2018).

The following are in the category of metal transporters:

(i) ATP Binding Cassette (ABC family) found in vacuolar membrane help in increasing movement of Cd and Cu by phytoextraction and phytostabilization.
(ii) Cation diffusion facilitator gene family which is responsible for encoding metal transport protein. Plants which possess these genes accumulate and show tolerance to heavy metals in addition to producing large amount of living metal.
(iii) ZRT/IRT gene family expressing ZIP proteins for Zn and Fe accumulation.

The following are in the category of metal chelators:

(i) Phytochelatins.
(ii) Metallothioneins (MTs) are included. Several studies are available in the literature showing high tolerance ability of plants to heavy metals that largely express MTs genes (Leszczyszyn et al. 2013).

Following are in the category of antioxidant machinery:

(i) Superoxide dismutase (SOD)
(ii) Ascorbate peroxidase (APX)
(iii) Catalase (CAT)
(iv) Glutathione-S-transferase (GST) are overexpressed under various abiotic stresses. Mechanism of stress tolerance at molecular level in hyperaccumulative plants can be known on the basis of identifying some stress tolerance genes in them. Singh et al. (2016) found the over expression of heavy metal tolerance genes during movement of heavy metals from roots to shoot resulting

Table 3.1 Some key genes/proteins that are found to be involved in response between heavy metals and plant hormones (Saini et al. 2021)

Heavy Metal	Gene/protein in plants	Mechanism	Reference
Cd	YDK1,GH3.3, MES7, MES17, GH3.17,NIT2, AUX/IAA,CYP71A13	Auxin biosynthesis modulation by up-regulating IAOX biosynthetic pathway genes while down-regulating the genes which are involved in the methylation and conjugation of auxin and also repression of auxin signaling, thus alleviating the Cd toxicity.	Pacenza et al. (2021)
Cd	PIN4, YUCCA8, YUCCA6, PIN1a, PIN1c, YUCCA9	Increased concentration of auxin and alleviated high metal stress were observed as a result of up-regulated auxin biosynthesis and transport genes by the selenium.	Luo et al. (2019)
As/Cd	PIN5b,ASA2, AUX1, YUCCA2	Formation of lateral roots was negatively affected by change in expression of transport genes and auxin biosynthesis genes.	Ronzan et al. (2018)
Cd	YUCCA6	The gene expression of YUCCA6 was increased, in response to Cd stress, which resulted in auxin accumulation and hence enhancing the adventitious and lateral root density.	Fattorini et al. (2017)
As	YUCCA6	The root architecture was found to be affected due to decreased levels of auxin which was a result of down-regulation of the gene YUCCA6.	Krishnamurthy and Rathinasabapathi (2013)
Cd	OsPIN, OsYUCCA, OsARF, OsCDK, OsMAPK, OsIAA	Auxin-related genes were negatively regulated by altered MAPK signaling thus decreasing the growth of roots.	Zhao et al. (2013)
Cd	GH3	Reduce in the content of auxin and conjugation of auxin was promoted by elevated GH3 activity while also improving lignin and peroxidase activity.	Elobeid et al. (2012)
Cd	SHY2	Increase in levels of SHY2 results in negative regulation of PIN 1,3, 7 genes which in turn inhibit the transport of auxin to the root apex.	Bruno et al. (2017)

(continued)

Table 3.1 (continued)

Heavy Metal	Gene/protein in plants	Mechanism	Reference
As	Transgenic CK-deficient plants	Thiol compounds, which include glutathione and phytochelatins mediate arsenic sequestration which result in increase in stress tolerance.	Mohan et al. (2016)
Zn	IPT	The tobacco plants with IPT gene transformation showed better transpiration and photosynthesis due to increase in cytokinin levels.	Pavlíkov'a et al. (2014)
Cd	CKX	Cytokinin levels were modulated by up-regulating the CKX gene in roots and down-regulating the genes in the shoots.	Vitti et al. (2013)
Cd	IPT	The levels of cytokinin in shoots were improved due to increased transcript levels of IPT gene.	Vitti et al. (2013)
Cd	Cytokinin oxidase	The levels of cytokinin were decreased as a result of increased activity of cytokinin oxidase.	Veselov et al. (2003)
As	GA20ox,GA2ox, CIGR,GID1L2	GA responsive defensive pathways might be evoked in response to As stress resulted due to GA signaling genes modulation.	Di et al. (2021)
Cd, Mo	α-Amylase and β-amylase, acid phosphatase and alkaline phosphatase.	Due to increase in activities of various hydrolytic enzymes, germination of seeds was improved.	Amri et al. (2016)
Cd	IRT1	Decrease in the uptake of Cd by down-regulating IRT1 which is a Cd transporter gene.	Zhu et al. (2012)
As	GA2ox9, GA2ox3	Increased levels of GA possibly due to up-regulation of response to stress.	Huang et al. (2012)
Cr	glutamine 2-oxoglutarate aminotransferase (GOGAT), glutamine synthetase (GS) and Nitrate reductase (NR)	The enzymes responsible for nitrogen assimilation show reduced activity which results in altered levels of nitrogen.	Gangwar et al. (2011)
Cr	Glutamate dehydrogenase (GDH)	Increase in GDH enzyme activity modulates assimilation of NH_4^+	Gangwar et al. (2011)

(continued)

Table 3.1 (continued)

Heavy Metal	Gene/protein in plants	Mechanism	Reference
Zn	Ethylene signaling defective mutants ein2–1 and etr1–3	Antioxidant enzymes such as SOD, CAT, APX and POD show improved activities.	Khan et al. (2019a)
Zn	APX,SOD, GPX, GST, GR,	Mechanisms related to defense such as increased proline content are activated in addition to enhanced ROS homeostasis.	Khan et al. (2019b)
Cd	Ethylene signaling mutant ein2–1 and ein 2–5 and Ethylene biosynthesis double knockout acs2–1/6–1.	Down-regulates RBOH expression upon Cd exposure, thus controls the levels of ROS in mutants.	Keunen et al. (2015)
Cr	ACS2, ACS1, ACO5, EIN3;4, ACO4,	Root growth is inhibited by signaling and stimulating the production of ethylene under the stress of Cr.	Trinh et al. (2014)
Cr	ACO4,ACO2, ERF1, ETR2, ACS6ACS2	Signaling and biosynthesis of ethylene is triggered.	Schellingen et al. (2014)
Hg	Ethylene insensitive ein2–5 mutants	Production of ROS and expression of the genes related to ethylene which are required for improved high metal stress are reduced.	Montero-Palmero et al. (2014)
Pb	Ethylene signaling mutant ein2–1	Reducing the synthesis of GSH by Down-regulating the GSH1 gene.	Cao et al. (2009)
As	EIN3;5, ACS2,ACS1, ACO4, ACO5, ACO3, EIN3;3, EIN3;4, ACO6,	Improvement in the ethylene biosynthesis and signaling.	Huang et al. (2012)
Co	CAT, APX, POD,SOD	Better detoxification of ROS.	Kamran et al. (2021)
Cd	AAO,NCED, ZEP	Levels of ABA are improved and thus alleviating the toxicity of Cd.	Lu et al. (2020)
Pb	ABCG40, ABCC1.1,NRAMP1.4, PCS1.1, FRD3.1,	Increase in the uptake, transport and detoxification of Pb and also shows increase in the antioxidant activities of POD, CAT, APX enzymes.	Shi et al. (2019)
Zn	ZIP	Regulates metal transport across cell membrane, thus modulating the uptake and accumulation of Zn.	Song et al. (2019)
Zn	NRAMP3,YSL, PCR2	Many genes related to detoxification showed increase in the expression when ABA and Zn were applied together.	Song et al. (2019)

(continued)

Table 3.1 (continued)

Heavy Metal	Gene/protein in plants	Mechanism	Reference
Cd	NCED4	Increase in the biosynthesis of ABA for high metal alleviation.	Tan et al. (2017)
As	PP2C4,NCED3,NCED2, bZIP10, bZIP12,ABA4,PP2C5.	Reduced root growth under As exposure resulting from increase in the ABA biosynthesis and signaling.	Huang et al. (2012)
Cd	Mn-SOD, Cu/Zn-SOD, CAT1, CAT2, CAT3Fe-SOD	Detoxification of ROS increases.	Sharma et al. (2018)
Cd	Nitrate reductase	Modulates metabolism of nitrogen.	Singh and Prasad (2017)
Cr	APX, Cu/Zn-SOD, Mn-SOD, GR,CAT	Activates the antioxidant defence of plants and thus show enhancement in their growth.	Sharma et al. (2016)
Al	CAT,P5CS, APX, SODPOD.	Improves osmoregulation and detoxification of ROS detoxification.	Madhan et al. (2014)
Cd	BR6ox,DWARF1, DWARF4	High metal stress triggers BR-signalling pathway by maintaining BR homeostasis.	Villiers et al. (2012)
Cr	CAT, SOD, GPX, GR	Improved antioxidant defense against toxicity of high metals.	Choudhary et al. (2012)
Zn	SOD, CAT, GR, POD, APX	Improved detoxification of ROS.	Sharma et al. (2007)
Cr	MYB1	Influence of development of lateral roots and strengthening the antioxidant defense due to MYB1 crosstalk with auxin and salicylic acid.	Tiwari et al. (2020)
Cd	SIPK	Improved endogenous levels of salicylic acid by up-regulating SIPK gene.	Tajti et al. (2019)
Pb	ZmSAMD, ZmACS6	Regulation of metabolism of methionine.	Zanganeh et al. (2018)
As	CYP71AV1, ALDH1, ADS, DBR2	Levels of artemisinin, an important secondary plant metabolite increases.	Kumari et al. (2018)
Cd	SOD, CAT, GR, GPX, APX	Detoxification of ROS which gets collected in response to Cd stress.	Gu et al. (2018), Lu et al. (2020)
Ni	Carbonic anhydrase	Enhanced the rate of photosynthesis.	Yusuf et al. (2012)
Cd	Rubisco and phosphenolphyruvate carboxylase enzymes	Improved traits of the process of photosynthesis.	Moussa and El-Gamal (2010)

(continued)

Table 3.1 (continued)

Heavy Metal	Gene/protein in plants	Mechanism	Reference
Pb	HMAs, PCS1, PCS2, ABCC1	Decrease in Pb translocation to the above ground parts of the plant.	Salavati et al. (2021)
As	OPR, JAZ, LOX	Variation in Jasmonic acid signaling genes which activate many HM responsive stress adaptive pathways.	Di et al. (2021)
Cd	JA-deficient spr2 mutant	Elevation in sensitivity for Cd stress.	Zhao et al. (2016)
As	Lypoxygenase (LOX)	Increase in jasmonic acid biosynthesis.	Farooq et al. (2016)
As	SOD, APX, CAT, POD	Detoxification of ROS which gets accumulated in response to Cd stress.	Farooq et al. (2016)
As	JA biosynthesis and signaling genes	Up-regulating the response to As stress which in turn may activate many high metal stress adaptive pathways.	Huang et al. (2012)
Cd/Cu	Gamma-glutamylcysteinesynthetase, glutathione synthetase	Increase in the glutathione biosynthesis.	Xiang and Oliver (1998)

in less destruction to the plant. Role of some antioxidant enzymes like GR has been found recently against various stressful conditions like salt stress, temperature stress, heavy metal stress, etc. (Yannarelli et al. 2007). Some of the findings showing role of these enzymes and stress tolerance genes produced by them are discussed ahead.

A study was conducted by Ahmad et al. on *Cannabis sativa* (hemp) to find out its phytoremediation potential on the basis of identification of two heavy metal stress tolerance genes such as glutathione disulfide reductase (GSR) and phospholipase D-alpha (PLD alpha). The researchers concluded that due to the presence of these genes, *C. sativa* could accumulate 1530 mg/kg of Cu, 151 mg/kg of Cd, and 123 mg/kg of Ni in its leaves from the soils contaminated with these heavy metals (Ahmed et al. 2016). Another group of researchers studied the phytoremediation capacity of eight wild weeds, i.e., *Xanthium strumarium, Spilanthes paniculata, Eclipta alba, Ageratum conyzoides, Euphorbia hirta, Amaranthus hybridus, Solanum nigrum,* and *Peppromia pellucida* with Cu, Cd, Ni, Zn, and Pb as heavy metals. The study concluded that *A. hybridus, S. nigrum, E.hirta* and *X. strumarium* show high metal uptake then other weeds having more non-enzymatic antioxidants like carboxylic acid and amino acids etc. that can bind with heavy metals and detoxify them (Clemens et al. 2001). The amount of super oxide radicals and antioxidant enzymes such as SOD, APX, GST, CAT, POD, etc., was also high in all the studied wild plants, which shows their high metal uptaking nature (Singh et al. 2016).

3.6 Conclusion

Pollution of environment in terms of heavy metals is recent cause of concern. Human health and food security are at high priority. Taking this in view, different wild weeds are employed to phytoremediate heavy metal polluted sites. Wild weeds show all the characters to act as hyperaccumulators. They are fast growing, producing large amount of living metal and accumulating heavy metals in their plant parts that can be harvested. Some types of genes are over expressed in these plants that help them in storing heavy metals in their harvestable parts. To deal with adverse effects of heavy metal toxicity on plants, application of a number of plant hormones exogenously has been used successfully. Primarily, these hormones help in strengthening the antioxidant defenses of plants which are exposed to heavy metals. In addition, plants tolerance to heavy metal stress mediated by phytohormones involve other major mechanisms, such as the reduction of biosorption of various heavy metals, improvement in the process of photosynthesis and gas exchange characteristics, osmotic regulation, production of GSH, induction of meta-transporters, etc. As we move forward, the big challenge is understanding the crosstalk between phytohormone and heavy metal signaling. In future, more number of wild weeds should be exploited for their heavy metal accumulative nature in heavily polluted areas.

References

Abou-Shanab RA, Tammam AA, El-Aggan WH, Mubarak MM (2017) Phytoremediation potential of wild plants collected from heavy metals contaminated soils. Int J Geol Agri Environ Sci 5

Achary MS, Satpathy KK, Panigrahi S, Mohanty AK, Padhi RK, Biswas S, Prabhu RK, Vijayalakshmi S, Panigrahy RC (2017) Concentration of heavy metals in the food chain components of the nearshore coastal waters of Kalpakkam, southeast coast of India. Food Control 72:232–243

Ahmad R, Tehsin Z, Malik ST, Asad SA, Shahzad M, Bilal M, Shah MM, Khan SA (2016) Phytoremediation potential of hemp (Cannabis sativa L.): identification and characterization of heavy metals responsive genes. CLEAN–Soil, Air, Water 44(2):195–201

Amri B, Khamassi K, Ali MB, da Silva JA, Kaab LB (2016) Effects of gibberellic acid on the process of organic reserve mobilization in barley grains germinated in the presence of cadmium and molybdenum. S Afr J Bot 106:35–40

Baker AJ, Brooks R (1989) Terrestrial higher plants which hyperaccumulate metallic elements. A review of their distribution, ecology and phytochemistry. Biorecovery 1(2):81–126

Baker AJ, McGrath SP, Reeves RD, Smith JA (2020) Metal hyperaccumulator plants: a review of the ecology and physiology of a biological resource for phytoremediation of metal-polluted soils. Phytoremediat Contamin Soil Water 25:85–107

Bruno L, Pacenza M, Forgione I, Lamerton LR, Greco M, Chiappetta A, Bitonti MB (2017) In Arabidopsis thaliana cadmium impact on the growth of primary root by altering SCR expression and auxin-cytokinin cross-talk. Front Plant Sci 8:1323

Cao S, Chen Z, Liu G, Jiang L, Yuan H, Ren G, Bian X, Jian H, Ma X (2009) The Arabidopsis Ethylene-Insensitive 2 gene is required for lead resistance. Plant Physiol Biochem 47(4):308–312

Chaney RL, Angle JS, McIntosh MS, Reeves RD, Li YM, Brewer EP, Chen KY, Roseberg RJ, Perner H, Synkowski EC, Broadhurst CL (2005) Using hyperaccumulator plants to phytoextract soil Ni and Cd. Z Naturforsch C 60(3–4):190–198

Chang CY, Yu HY, Chen JJ, Li FB, Zhang HH, Liu CP (2014) Accumulation of heavy metals in leaf vegetables from agricultural soils and associated potential health risks in the Pearl River Delta, South China. Environ Monit Assess 186(3):1547–1560

Chinmayee MD, Mahesh B, Pradesh S, Mini I (2012) SwapnaTS.The assessment of phytoremediation potential of invasive weed *Amaranthus spinosus* L. Appl Biochem Biotechnol 167(6):1550–1559

Choudhary SP, Kanwar M, Bhardwaj R, Yu JQ, Tran LS (2012) Chromium stress mitigation by polyamine-brassinosteroid application involves phytohormonal and physiological strategies in *Raphanus sativus* L. PLoS One 7(3):e33210

Clemens S (2001) Developing tools for phytoremediation: towards a molecular understanding of plant metal tolerance and accumulation. Int J Occup Med Environ Health 14(3):235–239

Das N, Bhattacharya S, Maiti MK (2016) Enhanced cadmium accumulation and tolerance in transgenic tobacco overexpressing rice metal tolerance protein gene OsMTP1 is promising for phytoremediation. Plant Physiol Biochem 105:297–309

Di X, Zheng F, Norton GJ, Beesley L, Zhang Z, Lin H, Zhi S, Liu X, Ding Y (2021) Physiological responses and transcriptome analyses of upland rice following exposure to arsenite and arsenate. Environ Exp Bot 183:104366

Elobeid M, Göbel C, Feussner I, Polle A (2012) Cadmium interferes with auxin physiology and lignification in poplar. J Exp Bot 63(3):1413–1421

Farooq MA, Gill RA, Islam F, Ali B, Liu H, Xu J, He S, Zhou W (2016) Methyl jasmonate regulates antioxidant defense and suppresses arsenic uptake in *Brassica napus* L. Front Plant Sci 7:468

Fattorini L, Ronzan M, Piacentini D, Della Rovere F, De Virgilio C, Sofo A, Altamura MM, Falasca G (2017) Cadmium and arsenic affect quiescent centre formation and maintenance in Arabidopsis thaliana post-embryonic roots disrupting auxin biosynthesis and transport. Environ Exp Bot 144:37–48

Gangwar S, Singh VP, Srivastava PK (2011) MauryaJN.Modification of chromium (VI) phytotoxicity by exogenous gibberellic acid application in *Pisum sativum* (L.) seedlings. Acta Physiol Plant 33(4):1385–1397

Girdhar M, Sharma NR, Rehman H, Kumar A, Mohan A (2014a) Comparative assessment for hyperaccumulatory and phytoremediation capability of three wild weeds. 3 Biotech 4(6):579–589

Girdhar M, Singh S, Rasool HI, Srivastava V, Mohan A (2014b) Evaluating different weeds for phytoremediation potential available in tannery polluted area by conducting pot and hydroponic experiments. Curr World Environ 9(1):156

Gu CS, Yang YH, Shao YF, Wu KW, Liu ZL (2018) The effects of exogenous salicylic acid on alleviating cadmium toxicity in *Nymphaea tetragona* Georgi. S Afr J Bot 114:267–271

Hammami H, Parsa M, Mohassel MH, Rahimi S, Mijani S (2016) Weeds ability to phytoremediate cadmium-contaminated soil. Int J Phytoremediation 18(1):48–53

Hashim MA, Mukhopadhyay S, Sahu JN, Sengupta B (2011) Remediation technologies for heavy metal contaminated groundwater. J Environ Manag 92(10):2355–2388

Holm LG, Plucknett DL, Pancho JV, Herberger JP (1977) Distribution and biology. The world's worst weeds. The University Press of Hawaii, Honolulu

Huang TL, Nguyen QT, Fu SF, Lin CY, Chen YC, Huang HJ (2012) Transcriptomic changes and signalling pathways induced by arsenic stress in rice roots. Plant Mol Biol 80(6):587–608

Järup L (2003) Hazards of heavy metal contamination. Br Med Bull 68(1):167–182

Kamran M, Danish M, Saleem MH, Malik Z, Parveen A, Abbasi GH, Jamil M, Ali S, Afzal S, Riaz M, Rizwan M (2021) Application of abscisic acid and 6-benzylaminopurine modulated morpho-physiological and antioxidative defense responses of tomato (*Solanum lycopersicum* L.) by minimizing cobalt uptake. Chemosphere 263:128–169

Kaur N, Girdhar M, Mohan A (2020) Toxic effects ofhexavalent chromium on physiological and biochemical parameters of *Cyperus iria* (Rice Flatsedge)–A weed plant. Plant Cell Biotechnol Mol Biol 17:67–73

Keunen E, Schellingen K, Van Der Straeten D, Remans T, Colpaert J, Vangronsveld J, Cuypers A (2015) Alternative oxidase1a modulates the oxidative challenge during moderate Cd exposure in *Arabidopsis thaliana* leaves. J Exp Bot 66(10):2967–2977

Khan AR, Wakeel A, Muhammad N, Liu B, Wu M, Liu Y, Ali I, Zaidi SH, Azhar W, Song G, Wu J (2019a) Involvement of ethylene signaling in zinc oxide nanoparticle-mediated biochemical changes in *Arabidopsis thaliana* leaves. Environ Sci Nano 6(1):341–355

Khan MI, Jahan B, Alajmi MF, Rehman MT, Khan NA (2019b) Exogenously-sourced ethylene modulates defense mechanisms and promotes tolerance to zinc stress in mustard (*Brassica juncea* L.). Plants 8(12):540

Khankhane PJ, Varshney JG (2008) Accumulation of heavy metals by weeds grown along drains of Jabalpur. Indian J Weed Sci 40(1&2):55–59

Koźmińska A, Wiszniewska A, Hanus-Fajerska E, Muszyńska E (2018) Recent strategies of increasing metal tolerance and phytoremediation potential using genetic transformation of plants. Plant Biotechnol Rep 12(1):1–4

Kumari A, Pandey N, Pandey-Rai S (2018) Exogenous salicylic acid-mediated modulation of arsenic stress tolerance with enhanced accumulation of secondary metabolites and improved size of glandular trichomes in *Artemisia annua* L. Protoplasma 255(1):139–152

Leszczyszyn OI, Imam HT, Blindauer CA (2013) Diversity and distribution of plant metallothioneins: a review of structure, properties and functions. Metallomics 5(9):1146–1169

Li MS, Luo YP, Su ZY (2007) Heavy metal concentrations in soils and plant accumulation in a restored manganese mineland in Guangxi. South China Environ Pollut 147(1):168–175

Lu Q, Chen S, Li Y, Zheng F, He B, Gu M (2020) Exogenous abscisic acid (ABA) promotes cadmium (Cd) accumulation in *Sedum alfredii* Hance by regulating the expression of Cd stress response genes. Environ Sci Pollut Res 27(8):8719–8731

Lum AF, Ngwa ES, Chikoye D, Suh CE (2014) Phytoremediation potential of weeds in heavy metal contaminated soils of the Bassa Industrial Zone of Douala. Cameroon Int J Phytoremediation 16(3):302–319

Luo Y, Wei Y, Sun S, Wang J, Wang W, Han D, Shao H, Jia H, Fu Y (2019) Selenium modulates the level of auxin to alleviate the toxicity of cadmium in tobacco. Int J Mol Sci 20(15):3772

Madhan M, Mahesh K, Rao SS (2014) Effect of 24-epibrassinolide on aluminium stress induced inhibition of seed germination and seedling growth of *Cajanus cajan* (L.) Millsp. Int J Multidiscipl Current Res 2:286–290

Mani D, Kumar C (2014) Biotechnological advances in bioremediation of heavy metals contaminated ecosystems: an overview with special reference to phytoremediation. Int J Environ Sci Technol 11(3):843–872

Memon AR, Aktoprakligil D, Özdemir A, Vertii A (2001) Heavy metal accumulation and detoxification mechanisms in plants. Turk J Bot 25(3):111–121

Mirsal IA (2004) Soil pollution: origin, monitoring and remediation, vol 1, Ist edn. Springer, pp 5–11

Mohan TC, Castrillo G, Navarro C, Zarco-Fernández S, Ramireddy E, Mateo C, Zamarreño AM, Paz-Ares J, Muñoz R, García-Mina JM, Hernández LE (2016) Cytokinin determines thiol-mediated arsenic tolerance and accumulation. Plant Physiol 171(2):1418–1426

Mohan A, Kaur R, Girdhar M (2019) Analysis of ability of chenopodium album for remediation of heavy metal degraded soil. Res J Pharm Technol 12(10):4851–4856

Montero-Palmero MB, Martín-Barranco A, Escobar C, Hernández LE (2014) Early transcriptional responses to mercury: a role for ethylene in mercury-induced stress. New Phytol 201(1):116–130

Moussa HR, El-Gamal SM (2010) Effect of salicylic acid pretreatment on cadmium toxicity in wheat. Biologia Plantarum 54(2):315–320

Pacenza M, Muto A, Chiappetta A, Mariotti L, Talarico E, Picciarelli P, Picardi E, Bruno L, Bitonti MB (2021) In Arabidopsis thaliana Cd differentially impacts on hormone genetic pathways in the methylation defective ddc mutant compared to wild type. Sci Rep 11(1):1–7

Pavlíková D, Pavlík M, Procházková D, Zemanová V, Hnilička F, Wilhelmová N (2014) Nitrogen metabolism and gas exchange parameters associated with zinc stress in tobacco expressing an ipt gene for cytokinin synthesis. J Plant Physiol 171(7):559–564

Pivetz BE (2001) Phytoremediation of contaminated soil and ground water at hazardous waste sites.US Environmental Protection Agency, Office of Research and Development, Office of Solid Waste and Emergency Response

Pulford ID, Watson C (2003) Phytoremediation of heavy metal-contaminated land by trees—a review. Environ Int 29(4):529–540

Raskin I, Kumar PN, Dushenkov S, Salt DE (1994) Bioconcentration of heavy metals by plants. Curr Opin Biotechnol 5(3):285–290

Raskin I, Smith RD, Salt DE (1997) Phytoremediation of metals: using plants to remove pollutants from the environment. Curr Opin Biotechnol 8(2):221–226

Ronzan M, Piacentini D, Fattorini L, Della Rovere F, Eiche E, Riemann M, Altamura MM, Falasca G (2018) Cadmium and arsenic affect root development in *Oryza sativa* L. negatively interacting with auxin. Environ Exp Bot 151:64–75

Royer MD, Smith LA (1995) Contaminants and remedial options at selected metals contaminated sites-a technical resource document. Environmental Protection Agency, Cincinnati

Saglam C (2013) Heavy metal accumulation in the edible parts of some cultivated plants and media samples from a volcanic region in Southern Turkey. Ekoloji 22(86):1–8

Saini S, Kaur N, Pati PK (2021) Phytohormones: key players in the modulation of heavy metal stress tolerance in plants. Ecotoxicol Environ Saf 223:112578

Salavati J, Fallah H, Niknejad Y, Tari DB (2021) Methyl jasmonate ameliorates lead toxicity in *Oryza sativa* by modulating chlorophyll metabolism, antioxidative capacity and metal translocation. Physiol Mol Biol Plants 27(5):1089–1104

Salt DE, Smith RD, Raskin I (1998) Phytoremediation. Annu Rev Plant Biol 49(1):643–668

Sanghamitra K, PrasadaRao PV, Naidu GR (2011) Heavy metal tolerance of weed species and their accumulations by phytoextraction. Indian J Sci Technol 4(3):285–290

Sarma H (2011) Metal hyperaccumulation in plants: a review focusing on phytoremediation technology. J Environ Sci Technol 4(2):118–138

Schellingen K, Van Der Straeten D, Vandenbussche F, Prinsen E, Remans T, Vangronsveld J, Cuypers A (2014) Cadmium-induced ethylene production and responses in Arabidopsis thaliana rely on ACS2 and ACS6 gene expression. BMC Plant Biol 14(1):1–4

Sharma P, Bhardwaj R (2007) Effects of 24-epibrassinolide on growth and metal uptake in *Brassica juncea* L. under copper metal stress. Acta Physiol Plant 29(3):259–263

Sharma P, Kumar A, Bhardwaj R (2016) Plant steroidal hormone epibrassinolide regulate–heavy metal stress tolerance in *Oryza sativa* L. by modulating antioxidant defense expression. Environ Exp Bot 122:1–9

Sharma I, Sharma A, Pati P, Bhardwaj R (2018) Brassinosteroids reciprocates heavy metals induced oxidative stress in radish by regulating the expression of key antioxidant enzyme genes. Braz Arch Biol Technol 14:61

Shi WG, Liu W, Yu W, Zhang Y, Ding S, Li H, Mrak T, Kraigher H, Luo ZB (2019) Abscisic acid enhances lead translocation from the roots to the leaves and alleviates its toxicity in Populus× canescens. J Hazard Mater 362:275–285

Singh S, Prasad SM (2017) Effects of 28-homobrassinoloid on key physiological attributes of *Solanum lycopersicum* seedlings under cadmium stress: photosynthesis and nitrogen metabolism. Plant Growth Regul 82(1):161–173

Singh A, Prasad SM, Singh S, Singh M (2016) Phytoremediation potential of weed plants' oxidative biomarker and antioxidant responses. Chem Ecol 32(7):684–706

Söğüt Z, Zaimoğlu BZ, Erdoğan R, Doğan S (2002) Su KalitesininArttırılmasındaBitkiKullanımı (YeşilIslah-Phytoremediation), Türkiye'ninKıyıveDenizalanları IV. UlusalKonferansı, pp 5–8

Song C, Yan Y, Rosado A, Zhang Z, Castellarin SD (2019) ABA alleviates uptake and accumulation of zinc in grapevine (*Vitis vinifera* L.) by inducing expression of ZIP and detoxification-related genes. Front Plant Sci 10:872

Subah S, Srinivas N (2017) Phytoremediation potential of weedy plants in heavy metal contaminated benthic lake sludge. Int J Appl Eng Res 12:4534–4538

Subhashini V, Swamy AV, Harika D, Venkateswararao K (2017) Phytoremediation of heavy metals contaminated soils. Int J Curr Microbiol App Sci 5:19–30

Susarla S, Medina VF, McCutcheon SC (2002) Phytoremediation: an ecological solution to organic chemical contamination. Ecol Eng 18(5):647–658

Tajti J, Németh E, Glatz G, Janda T, Pál M (2019) Pattern of changes in salicylic acid-induced protein kinase (SIPK) gene expression and salicylic acid accumulation in wheat under cadmium exposure. Plant Biol 21(6):1176–1180

Tan M, Cheng D, Yang Y, Zhang G, Qin M, Chen J, Chen Y, Jiang M (2017) Co-expression network analysis of the transcriptomes of rice roots exposed to various cadmium stresses reveals universal cadmium-responsive genes. BMC Plant Biol 17(1):1–8

Tangahu BV, Sheikh Abdullah SR, 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 1:2011

Tiwari P, Indoliya Y, Chauhan AS, Singh P, Singh PK, Singh PC, Srivastava S, Pande V, Chakrabarty D (2020) Auxin-salicylic acid cross-talk ameliorates OsMYB–R1 mediated defense towards heavy metal, drought and fungal stress. J Hazard Mater 399:122811

Trinh NN, Huang TL, Chi WC, Fu SF, Chen CC, Huang HJ (2014) Chromium stress response effect on signal transduction and expression of signaling genes in rice. Physiol Plant 150(2):205–224

Veselov D, Kudoyarova G, Symonyan M, Veselov S (2003) Effect of cadmium on ion uptake, transpiration and cytokinin content in wheat seedlings. Bulg J Plant Physiol 29(3–4):353–359

Villiers F, Jourdain A, Bastien O, Leonhardt N, Fujioka S, Tichtincky G, Parcy F, Bourguignon J, Hugouvieux V (2012) Evidence for functional interaction between brassinosteroids and cadmium response in Arabidopsis thaliana. J Exp Bot 63(3):1185–1200

Vitti A, Nuzzaci M, Scopa A, Tataranni G, Remans T, Vangronsveld J, Sofo A (2013) Auxin and cytokinin metabolism and root morphological modifications in Arabidopsis thaliana seedlings infected with Cucumber mosaic virus (CMV) or exposed to cadmium. Int J Mol Sci 14(4):6889–6902

Wang G, Su MY, Chen YH, Lin FF, Luo D, Gao SF (2006) Transfer characteristics of cadmium and lead from soil to the edible parts of six vegetable species in southeastern China. Environ Pollut 144(1):127–135

Wang FY, Lin XG, Yin R (2007) Inoculation with arbuscular mycorrhizal fungus *Acaulospora mellea* decreases Cu phytoextraction by maize from Cu-contaminated soil. Pedobiologia 51(2):99–109

Wei S, Zhou Q, Xiao H, Yang C, Hu Y, Ren L (2009) Hyperaccumulative property comparison of 24 weed species to heavy metals using a pot culture experiment. Environ Monit Assess 152(1):299–307

Xiang C, Oliver DJ (1998) Glutathione metabolic genes coordinately respond to heavy metals and jasmonic acid in Arabidopsis. Plant Cell 10(9):1539–1550

Xiao R, Wang S, Li R, Wang JJ, Zhang Z (2017) Soil heavy metal contamination and health risks associated with artisanal gold mining in Tongguan, Shaanxi. China Ecotoxicol Environ Safety 141:17–24

Yannarelli GG, Fernández-Alvarez AJ, Santa-Cruz DM, Tomaro ML (2007) Glutathione reductase activity and isoforms in leaves and roots of wheat plants subjected to cadmium stress. Phytochemistry 68(4):505–512

Yıldız N (2008) Principles of plant nutrition and disorders of plant nutrition in plants. Erzurum: Atatürk University Agricultural Faculty. Eser Offset Printing, p 304

Yoon J, Cao X, Zhou Q, Ma LQ (2006) Accumulation of Pb, Cu, and Zn in native plants growing on a contaminated Florida site. Sci Total Environ 368(2–3):456–464

Yu C, Peng X, Yan H, Li X, Zhou Z, Yan T (2015) Phytoremediation ability of *Solanum nigrum* L. to Cd-contaminated soils with high levels of Cu, Zn, and Pb. Water Air Soil Pollut 226(5):1–10

Yusuf M, Fariduddin Q, Varshney P, Ahmad A (2012) Salicylic acid minimizes nickel and/or salinity-induced toxicity in Indian mustard (*Brassica juncea*) through an improved antioxidant system. Environ Sci Pollut Res 19(1):8–18

Zanganeh R, Jamei R, Rahmani F (2018) Impacts of seed priming with salicylic acid and sodium hydrosulfide on possible metabolic pathway of two amino acids in maize plant under lead stress. Mol Biol Res Commun 7(2):83

Zhao FY, Hu F, Zhang SY, Wang K, Zhang CR, Liu T (2013) MAPKs regulate root growth by influencing auxin signaling and cell cycle-related gene expression in cadmium-stressed rice. Environ Sci Pollut Res 20(8):5449–5460

Zhao S, Ma Q, Xu X, Li G, Hao L (2016) Tomato jasmonic acid-deficient mutant spr2 seedling response to cadmium stress. J Plant Growth Regul 35(3):603–610

Zhu XF, Jiang T, Wang ZW, Lei GJ, Shi YZ, Li GX, ZhengS J (2012) Gibberellic acid alleviates cadmium toxicity by reducing nitric oxide accumulation and expression of IRT1 in Arabidopsis thaliana. J Hazard Mater 239:302–307

Chapter 4
Phytoremediation: Sustainable and Organic Technology for the Removal of Heavy Metal Contaminants

Ganesan Subbulakshmi, R. Thiruneelakandan, and G. Padma Priya

Abstract Environmental pollution is one of the major threats faced by the planet earth. There are different methods of removing toxic substances, from water, air, and soil. Out of them, phytoremediation can be defined as an innovative as well as a greener way to reduce toxins from the environment. Phytoremediation is an emerging technology that can be applied for the removal of both organic and inorganic pollutants present in water, air, and soil by using green plants. Using phytoremediation techniques removal of heavy metal contaminants. This method is an economically feasible method which is only powered by solar energy and is simple to manage, and due to that, the cost of maintenance is low. Moreover, this can provide a sustainable way to improve the economies of developing counties as well. Therefore, phytoremediation can be considered as a promising eco-friendly solution to the environmental pollution.

Keywords Environmental pollution · Contaminants · Toxin · Phytoremediation · Plant species

4.1 Introduction

Bioremediation is the process by which natural living organisms are used to remove contaminants in soil and ground water. It is an environmental friendly method to remove pollutants from the environment (Belouchrani et al. 2016). Bioremediation

G. Subbulakshmi (✉) · G. P. Priya
Department of Chemistry, Jain University, Bangalore, Karnataka, India
e-mail: g.subbulakshmi@jainuniversity.ac.in

R. Thiruneelakandan
Department of Chemistry University, College of Engineering Bit Campus, Anna University Tiruchirappalli, Tiruchirappalli, Tamil Nadu, India

L. Newman et al. (eds.), *Phytoremediation*, https://doi.org/10.1007/978-3-031-17988-4_4

can be aerobic or anaerobic and also bioremediation can be done as in-situ bioremediation and ex-situ bioremediation. Among bioremediation techniques, phytoremediation is a major technique that is used to remove pollutants from the environment (Burges et al. 2018). Phytoremediation is the process of using higher plants for the removal of contaminants from soil and ground water. Specific plants are cultivated at the sides of polluted soil. These plants are capable of stimulating the biodegradation of pollutants in the soil adjacent to the roots (Enyoh et al. 2018). Although phytoremediation is an environmentally friendly method to remove contaminants, it takes several years. If we provide optimal conditions like nutrients supply, temperature, and aeration, we can enhance phytoremediation (Indah 2019). Ground water and soil can be polluted by petroleum hydrocarbons, pesticide, weedicides, heavy metalizes, etc. As they are non-biodegradable, they are accumulated in the environment. In addition, these can cause so much of problems, because they enter through food chains and accumulate in the human body. After the industrialization, the use of chemicals in agriculture has increased, and therefore, the addition of chemicals to the environment is very high. Therefore, we have to remove those toxic materials from the environment. Although there are different methods to remove these chemicals from the environment, they are highly expensive and not environmentally friendly; phytoremediation is one of the best solutions to remove toxic materials from the environment. Phytoremediation sources of growings plants can be wetlands, reed beds and floating plant systems. Phytoremediation occurs by phytoextraction, phytodegradation, and phytostabilization. Phytoextraction is a method in which plants accumulate the contaminants and utilize them for processing (Koptsik 2014). Phytodegradation is a process in which plants convert toxic materials in the environment into less toxic materials. In phytostabilization the contaminants present in collodial form can be precipitated and absorbed by plant tissues. Both organic and inorganic contaminants can be removed by phytoremediation (Liu and Wu 2018). Organic pollutants can be removed by phytodegradation. Organic pollutants present in the soil and water should be easily available for the plants to degrade. In phytodegradation, the breakdown of complex compounds to smaller constituents which are less toxic. And then, those compounds are absorbed by the plants. Rhizosphere bacteria help in phytodegradation (Lu 2018). As soil, air and water are major controllers of the environment (Mai et al. 2017). humans cannot live without them therefore; we have to protect them otherwise homeostasis of the earth will collapse and will arise so many problems. so that we have to take actions to remove pollutants from soil, air and water as they are already polluted from human activities (Mekawy et al. 2018). Therefore, we can use phytoremediation as a solution for the removal of toxic materials from the environment (Ng and Chan 2017).

4.2 Phytoremediation to Improve the Quality of Air

The quality of air can be improved by utilizing a number of plant species, including trees, shrubs, and vines. For example, the regions of North Katowice in Poland and Tabriz in Iran grew trees to tackle the growing particulate matter present in the air as a result of air pollution (Safauldeen 2019). Out of the many plant species grown in these regions, two species proved to be effective phytoremediation sources:

1. *Parthenocissus quiquefolia*
2. *Betula pendula*

Both these species used their wax to trap particulate matter from the air environment, thereby reducing the concentration of pollutants present in the air. The study also showed that the ability of the plant species to remediate the air environment was directly dependent on the type of leaves that the plant has (Schwantes 2019). Following were some of the observations made regarding this study:

1. Plant with leaves having greater surface area work better in absorbing the particulate matter. For example, *Wedelia trilobata*, with wider leaves, is a better phytoremediator than *Syzigium oleina*, with smaller leaves.
2. Plant species that have needle shaped leaves are better in absorption when compared to plants with wide leaves.
3. Plants with high concentration of abaxial stomata per unit area can capture more amount of particulate matter, e.g., *Muntingia calabura*.

While it has been made clear from this study that plant species having different features with regard to their leaves have different capacities to remediate the quality of air, the remediation capacity also additionally depends on the location in which phytoremediation is carried out.

The plant species that showed high levels of absorption and entrapment of particulate matter in regions such as roads where traffic is rampant could not display the same effectiveness in regions around industries (Valadi et al. 2019). These species include *Loropetalum chinense* and *Cinnamomum japonicum*.

The APTI or Air Pollution Tolerance Indices for plants used in phytoremediation is suggested to be greater than 10.83 for effective phytoremediation to occur.

4.3 Phytoremediation to Improve the Quality of Water

The main technique that was used for the phytoremediation of polluted water was rhizofiltration. This process involves the use of plant species to capture and remove the pollutants that are present in water. (Wang et al. 2012). These pollutants mainly include heavy metals, such as lead, copper, nickel, etc.:

1. Roots of Indian mustard—removes cadmium, chromium, and zinc.
2. Sunflower (*Helianthus annuus*)—removes lead, uranium, Caesium-137, and Strontium-90 that are mainly present in hydroponic solutions.

The ability of *Lemna minor* L. to phytoremediate polluted water was tested using a nutrient-added solution. It showed positive results for selenium, copper, and cadmium. The pot experiment from Wang was utilized for testing plant species from wetlands to check for their remediation properties. The five species that were tested included:

1. Duckweed (*Lemna minor* L.)
2. Water hyacinth
3. Water dropwort
4. Sharp dock
5. Calamus

From the above plant species that were tested, it was observed that both water hyacinth and duckweed showed remediation and entrapment of cadmium. Water dropwort showed successful entrapment and accumulation of Mercury. Sharp dock was able to successfully absorb and accumulate phosphorus, and Calamus showed successful entrapment of lead. Hydroponic experiments were used to determine the ability of water hyacinth (*Eichhornia crassipes*) to phytoremediate solutions containing 5 mg/L of metals such as arsenic, chromium, and Mercury (Yuan et al. 2017). The results showed that Arsenic showed an uptake of 26 mg/kg, mercury an uptake of 327 mg/kg, and chromium an uptake of 108 mg/kg.

4.4 Phytoremediation to Improve the Quality of Soil

Some of the common methods of phytoremediation to restore the pristine quality of soil include the following processes:

1. Leaching
2. Flocculation
3. Microfiltration
4. Reverse osmosis
5. Valence transformation
6. Volatilization

Experiments were conducted to test the effectiveness of chemicals such as EDTA, ammonium sulfate, and citric acid. These chemicals mainly served as chelating agents and showed positive results in the removal or phytoremediation of polluted soil by the accumulation of lead, uranium, cadmium, and zinc. The study also showed that phytoremediation activity was reduced when the pH of the soil was reduced, hence allowing the accumulation of higher concentrations of pollutants or heavy metals (Zhang et al. 2017). Phytoextraction experiments to extract pollutants present in the soil showed positive results for the seedlings of *Brassica juncea*. The main plant root microbes involved in this process were *Pseudomonas* and *Bacillus*. It was also observed that the plant species were effectively able to phytoremediate the soil when there was a presence of higher moisture content in the soil.

4.5 Results and Discussion

Major environmental and human problems are caused by soil and water contamination with toxic metals. With lot of research in the field of heavy metal contaminants removal, phytoremediation technique is a viable method for ecofriendly environment. Nearly 1.4 million square meter of areas is estimated to be contaminated according to the European Environment Agency. Environmental restoration and construction were carried out by bioengineering. The results show that the soil which was used for the sorption experiments was slightly acidic (sample 1), while sample 2 soil was alkaline. The pH range of sample 1 was 6.12 and that of sample 2 was 7.60. The organic content for carbon was11.9 and 12.1 kg-1. In both soils, the N and P (nitrogen and phosphorus) contents were low. This shows that some nutrients should be supplied for the growth of plants. The absorption pattern was similar in both the samples taken for the experiment. An increase in the amount of Pb and Cu absorbed with increasing amounts of Pb and Cu absorbed. The above said concept is applicable for the removal of transition metals like Cd and Zn; these was observed as a decrease in the amounts of metals absorbed in case of 25 $\mathrm{mgkg}-^{1}$, and in the case of 50 $\mathrm{mgkg}-^{1}$, these shows the increase in adsorption for both metals and an increase in absorption was seen for Zn in 100 $\mathrm{mgkg}-^{1}$, and a negative adsorption was seen for Cd. This chapter indicates the sources of heavy metal pollution, types of phytoremediation, and plants used for phytoremediation techniques. Phytoremediation techniques like phytostabilization, phytovolatilization, and phytohydraulic control are vigorous research methods adopted over the past decades for contaminated soil and water.

4.6 Conclusions

While there have been positive aspects related to the use of phytoremediation for the treatment and restoration of polluted air, soil, and water, there is still a need for more research into the plants used for this process. Genetic variations in the plant species need to be studied to a greater extent to clearly obtain the accumulating power of these species. With the advancement in the field of biology, the ability of a plant species to recognize and entrap a particular heavy metal due to the presence of a specific gene being studied. This information can help us further test the production of hybrid breeds that have the genes to recognize the desired heavy metal that needs to be removed by accumulation. The lower costs involved in the use of this process as well as its environmentally sustainable nature contributes significantly to the large-scale use of phytoremediation techniques to treat air, soil, and water. However, the process is slower when compared to industrial remediation methods. More research into this concept will definitely tell us how we can precisely utilize phytoremediation for the remediation of air, soil, and water.

References

Belouchrani AS, Mameri N, Abdi N, Grib H, Lounici H, Drouiche N (2016) Ecol Eng 95:43–49

Burges A, Alkorta I, Epelde L, Garbisu C (2018) Int J Phytoremed 20:384–397

Enyoh CE, Verla AW, Egejuru NJ (2018) Int J Environ Anal Chem 5:1–9

Indah S (2019) J Environ Manag 263:763–769

Koptsik G (2014) Eurasian Soil Sci 47:923–939

Liu N, Wu Z (2018) Environ Sci Pollut Res 25:4934–4941

Lu B (2018) Ecol Eng 110:18–26

Mai D, Wen R, Cao W, Yuan B, Liu Y, Liu Q, Qian G (2017) ACS Sustain Chem Eng 5:3499–3508

Mekawy AMM, Assaha DVM, Munehiro R (2018) Environ Exp Bot 147:157–166

Ng Y S and Chan D J C 2017 Elsevier Ltd15 pp107–115

Safauldeen SH (2019) J Ecol Eng 20:177–187

Schwantes D (2019) Int J Phytoremed Taylor Francis 21:714–723

Valadi AS, Hatamzadeh A, Sedaghathoor S (2019) Environ Sci Pollut Res 26:21340–21350

Wang J, Feng X, Anderson CW, Xing Y, Shang L (2012) J Hazard Mater 221:1–18

Yuan Z, Yi H, Wang T, Zhang Y, Zhu X, Yao J (2017) Environ Sci Pollut Res 24:21877–21884

Zhang L, Huang X, Cao Y, Xin Y, Ding L (2017) ACS Sensors 2:1821–1830

Chapter 5
Structure and Function of Heavy Metal Transporting ATPases in *Brassica* Species

Abdulrezzak Memon and Nuriye Meraklı

Abstract Heavy metal pollution adversely affects soil ecology, agricultural production, and groundwater quality and ultimately harms the health of living organisms in the food chain. Soils or waters contaminated with heavy metals affect plant growth and yield and often lead to the production of harmful metabolites. Hyperaccumulator plants possess various cellular mechanisms responsible for detoxifying heavy metals from the cell and providing tolerance to metal stress. Much progress has been achieved in the last decade to elucidate the molecular mechanisms of metal tolerance and accumulation in accumulator plants. However, the detailed mechanism of hyperaccumulation in plants is still not well characterized. Therefore, there is an urgent need to develop practical tools and systems for studies on metal accumulations in plants at the molecular level. Genomic analysis of the *Arabidopsis* genome helped in the identification of many transporters. P_{1B}–heavy metal ATPases (HMAs) are one of the significant transporters belonging to the family of P-type ATPases involved in heavy metal homeostasis in the cell. Eight genes (AtHMA1–AtHMA8) have been identified in the *Arabidopsis* genome. This chapter intends to elucidate the heavy metal tolerance and accumulation mechanisms in the *Brassicaceae* family with the role of the HMAs (HMA1–HMA8) in response to heavy metal stress. The role and function of HMA transporters in *A. thaliana* have been clearly defined. In this paper, we utilized the genomic knowledge of Arabidopsis thaliana to understand the role of these metal transporter ATPases in other species in Brassicaceae. We performed the phylogenetic analysis, multiple sequence alignments, 3D structure prediction, and validation to investigate the interacting proteins present in different plant species, including agriculturally important crop species in Brassica. Studies on these protein–protein interactions are most important to understand the complexity of the function of HMA proteins. This chapter provides the recent development in heavy metal transporting ATPases in metal transport and translocation in the accumulator

---

A. Memon (✉) · N. Meraklı
Department of Molecular Biology and Genetics, Arts and Science Faculty, Usak University, Usak, Turkey
e-mail: armemon@usak.edu.tr

L. Newman et al. (eds.), *Phytoremediation*, https://doi.org/10.1007/978-3-031-17988-4_5

plants. It will help the researchers to understand the role of these transporters in detoxifying the toxic metals from the cells of accumulator plants. Further research on gene cloning, gene expression, and generating new super accumulator plants for phytoremediation is required to efficiently remediate contaminated soils from toxic heavy metals.

Keywords Hyperaccumulator plants · P_{1B}-heavy metal ATPase · phylogenetic analysis · MEME motif analysis · protein 3D structure analysis · phytoremediation

5.1 Introduction

The term "heavy metals" refers to any metallic element with a relatively high density (greater than 5 g/cm^3) and is toxic or poisonous even at low concentrations. Heavy metals (HMs) are functionally classified into two categories: (i) essential metals such as copper (Cu), iron (Fe), and zinc (Zn) and (ii) non-essential metals such as cadmium (Cd), lead (Pb), and mercury (Hg) (Ozturk et al. 2012; Pinto and Ferreira 2015; Memon et al. 2021). Both these classes are essential for plant growth. Recently, this requires more attention because heavy metals above their normal ranges are highly toxic to both plant and animal life (Van der Zaal et al. 1999; Dehkordi et al. 2010). Anything that does not fall in a normal and optimal concentration range may affect plant growth and result in toxicity symptoms. The toxic amount of heavy metals in the soil adversely affects soil ecology, reduces agricultural production or product quality, deteriorates groundwater quality, and ultimately harms living organisms' health.

Plants are capable of various cellular mechanisms, and thus, they can contribute to the detoxification of heavy metals, providing tolerance to metal stress. For effective phytoextraction of metals from the soil, plants rapidly transport these metal through roots to shoots and sublocalize in the vacuolar compartment or deposit them in the trichome in the leaves (Memon et al. 2001). The transport of the metals in the cell takes place either through an apoplastic or symplastic system. Metals are first bound to the cell wall and then transported through the plasma membrane to the cytosol and the other compartments of the cell. Especially, a large amount of the metal is stored in the vacuole in the elemental form or bound to some organic acids (Memon 2019). In accumulator plants, heavy metals are efficiently translocated from roots to shoots through efficient xylem loading. This transport process is controlled by the expression of transporter genes responsible for root-to-shoot transport (Memon and Schröder 2009).

Plants are capable of various cellular mechanisms and can detoxify heavy metals by either compartmentalizing metals at the subcellular level or depositing them in leaf trichomes in innocuous form. Some plant species can accumulate and detoxify the large amounts of heavy metals present in the soil (Memon et al. 2001; Memon and Schröder 2009; Memon and Zahirovic 2014). The natural phenomenon of heavy metal tolerance became of most significant concern and interest in plant research to study the gene expression and regulation in some well-known accumulator plants such as *Arabidopsis halleri, Noccaea caerulescens, Pteris vittata,* and *Brassica juncea.* In addition, HM toxicity may block essential functional groups of enzymes, disrupt the structural appearance of biomolecules, generate oxidative stress, etc. (Hall 2002; Mills et al. 2005; Kraemer 2009; Meraklı et al. 2022).

5.2 Metal Hyperaccumulator Plants for Phytoremediation

To solve the heavy metal pollution problem, researchers have come up with various methods of soil decontamination (Salt et al. 1995, 1998). One of the most promising and affordable methods is phytoremediation, removing contaminants from soil using plants (Salt et al. 1998; Memon 2016). A specific group of plants has shown a great potential to absorb and translocate metals from roots to shoots and is termed hyperaccumulators (Baker and Whiting 2002; Chaney et al. 2007; Sytar et al. 2021). The common traits that distinguish hyperaccumulators from other plants are a higher capacity for metal absorption from the soil, an effective root-to-shoot translocation, and a better ability to accumulate and store heavy metals in the leaves (Memon et al. 2001; Rascio and Navari-Izzo 2011). Heavy metal accumulator plants have developed several detoxification mechanisms in the cell, such as metal chelation and sequestration, metal storage in the vacuolar compartment, and excreting metal in the trichomes of the leaves (Memon et al. 2001; Memon 2020). Because of their high metal accumulation capacity in their shoot, these hyperaccumulator plants are considered important candidates for phytoremediation. Among the hyperaccumulator plants, the family *Brassicaceae* represents the highest number of accumulator species (Anjum et al. 2012). Out of these, two species have explicitly been drawn into the focus of researchers and emerged as models for this process, for example, *Noccaea caerulescens* and *Arabidopsis halleri* (Memon and Schröder 2009; Meyer and Verbruggen 2012; Koch and German 2013). An interesting finding is that the process of hyperaccumulation does not depend on novel genes but rather on genes that are also commonly present in non-hyper accumulators but only differently expressed and regulated (Verbruggen et al. 2009). The distinctive characteristic of hyperaccumulator plants is to translocate toxic metals from roots to shoots efficiently, sub-compartmentalize them in the cell and keep the metal away from the metabolic processes (Van der Ent et al. 2013; Sytar et al. 2021). A set of functional genes such as P-type ATPase, ZIP, and NRAMP are crucial in plant cell metal homeostasis (Hall and Williams 2003; Williams and Mills 2005; Memon 2016). For instance, P1B-ATPases, also known as heavy metal ATPases (HMAs), play a critical role in phytoremediation via the long-distance transport of various metals between plant organs (Colangelo and Guerinot 2006). In recent years, significant scientific progress has been made in understanding the molecular mechanisms of metal uptake and transport in hyperaccumulator plants, including several members of the *Brassicaceae* family.

5.3 Heavy Metal ATPases in Metal Transport

Significant progress has been made elucidating metal uptake, accumulation, and tolerance mechanisms in plants (Mills et al. 2005; Rhee et al. 2003). However, the hyperaccumulation mechanism in plants is still not well characterized. Therefore, there is a considerable need to develop some practical tools and systems for studies on metal accumulations in plants on the molecular level. *Arabidopsis thaliana,* a non-accumulator plant in Brassicaceae, is used as a model for higher plant research. The knowledge of metal transporter genes from the Arabidopsis genome will be of great importance and could be easily applied to other plants in Brassicaceae because around 25% of the reported hyperaccumulator species belong to this family (Rhee et al. 2003; Claus et al. 2013; Iqbal et al. 2013; Pinto and Ferreira 2015). Heavy metals in the accumulator plants are transported through several different transporters located in the plasma membrane, tonoplast, and chloroplast membranes. Among these transporters, P-type metal transport ATPases play a significant role in compartmentalizing metals in the cell and preventing the toxic effect of heavy metals in the cytoplasm for basic cell function (Ducic and Polle 2005).

Heavy metal transporting ATPases (HMAs) are membrane-bound proteins having 6–8 predicted transmembrane helices (Axelsen and Palmgren 2001; Smith et al. 2014). They contain 31 amino acids (aa) of heavy metal-associated domain featuring GMTCxxC, a short C-terminal domain, and a very long N-terminal domain (Bull and Cox 1994).

Here, we intend to elucidate the heavy metal tolerance and accumulation mechanisms in the plant species in the *Brassicaceae* family with the role of the HMAs (HMA1–HMA8) in response to heavy metal stress. The phylogenetic relationships of the HMA1–HMA8 proteins from *Brassica* spp., *A. thaliana*, *A. halleri,* and *Noccaea caerulescens* (*Thlaspi caerulescens*) were assessed using multiple sequence alignment and phylogenetic tree construction (Fig. 5.1). Using different bioinformatics tools, we have identified eight heavy metal transporter genes (HMA1–8) in different plant species in *Brassicaceae* [three *Arabidopsis* spp., four *Brassica* spp., and *Noccacea caerulescens* (*Thlaspi caerulescens*)]. The phylogenetic relationships among HMAs were established using the MEGA X program for phylogenetic tree construction, and the relative similarity rates among the genes and plant spp. were estimated (Fig. 5.1). HMA1–8 protein sequences from *Arabidopsis thaliana*, *Arabidopsis halleri, Arabidopsis lyrata, Brassica napus, Brassica rapa, Brassica juncea, Brassica oleracea,* and *Noccaea caerulescens* (*Thlaspi caerulescens*) were retrieved from NCBI and UniProt, and a phylogenetic tree was constructed. The phylogenetic tree shows the evolutionary relationship of HMA1–8 transporters using a Neighbour-joining tree without distance corrections. In Fig. 5.1,

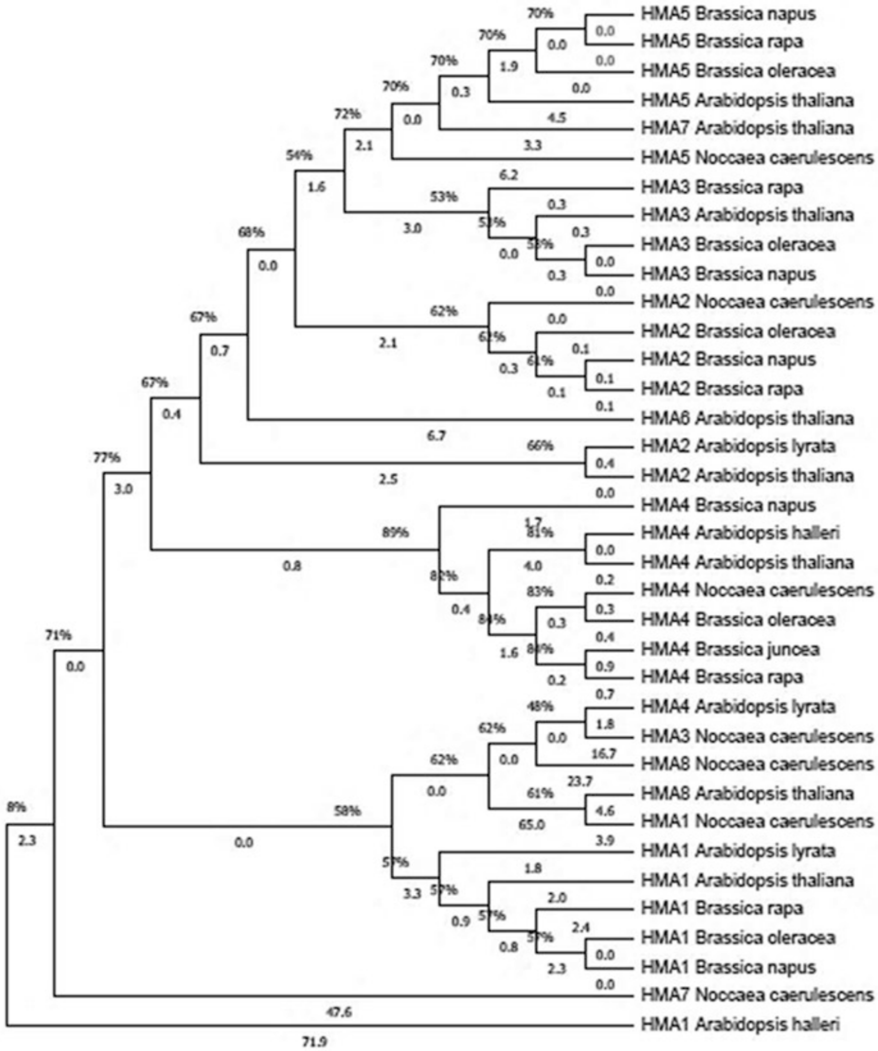


Fig. 5.1 Protein sequences of HMA1–8 family transporters from different plant species from the *Brassicaceae* family were obtained from NCBI and UniProt. The protein sequence IDs are AtHMA1 (Q9M3H5), AhHMA1 (Q70IH7), AlHMA1 (XP_020875667), NcHMA1 (JAU82411), BrHMA1 (XP_009137459), BnHMA1 (XP_022573707), BoHMA1 (XP_013595810), AtHMA2 (Q9SZW4), AlHMA2 (XP_002867367), BrHMA2 (XP_009128090), BnHMA2 (XP_013748024), BoHMA2 (XP_013609995), NcHMA2 (JAU82907.1), AtHMA3 (P0CW78), AhHMA3 (AJ556182), AlHMA3 (XM_002867320), BrHMA3 (XP_009137892), BnHMA3 (XP_013752152), BoHMA3 (XP_013591300), NcHMA3 (A0A1J3HSX9), AtHMA4 (AT2G19110), AhHMA4 (ABB29495), AlHMA4 (XP_020869480), BrHMA4 (XP_009150707), BjHMA4 (AFJ94635), BnHMA4 (XP_022561353), BoHMA4 (XP_013629797), NcHMA4 (JAU89865), AtHMA5 (OAP12074), BrHMA5 (XP_009112946), BnHMA5 (XP_013748077), BoHMA5 (XP_013606061), NcHMA5 (JAU39366), AtHMA6 (AT4G33520), AtHMA7 (NP_199292), NcHMA7 (JAU79906), AtHMA8 (NP_001031920), and NcHMA8 (JAU85510). The neighbor-joining phylogenetic tree was constructed using MEGAX after CLUSTALW alignment of the full-length amino acid sequences of heavy metal ATPases in different plant species in *Brassicaceae*. The tree is unrooted, and its branch length represents the relative evolutionary distances between the input proteins

we observe two sister groups, one group being AhHMA1 and NcHMA7, and the other one HMA1–8, each having a common ancestor. BoHMA5, AtHMA5, and AtHMA7 share a common ancestry with BnHMA5 and BrHMA5, and similarly, BrHMA3 and AtHMA3 share their ancestry with BoHMA3 and BnHMA3. NcHMA2 and BoHMA2 share a common ancestry with BnHMA2 and BrHMA2, and similarly, BrHMA3 and AtHMA3 share their ancestry with BoHMA3 and BnHMA3. On the other hand, AtHMA2 and AlHMA2 share a common ancestry with AtHMA6, BrHMA2, BnHMA2, BoHMA2, NcHMA2, BnHMA3, BoHMA3, AtHMA3, BrHMA3, NcHMA5, AtHMA7, AtHMA5, BoHMA5, BrHMA5, and BnHMA5.

HMA1–8 sequences from *A. thaliana* were compared to its homologs in other species in *Brassicaceae*; for example, *B. juncea*, *B. rapa, B. napus, B. oleacea, A. lyrata, A. halleri,* and *N. caerulescens*. Phylogenetic analysis showed a very close relationship of BnHMA1 to BoHMA1; AtHMA1 to NcHMA8; AtHMA2 toAlHMA2; BrHMA2 toBnHMA2; BnHMA3 to BoHMA3; AtHMA4 to AhHMA4; BoHMA4 to NcHMA4; BjHMA4 to BrHMA4; and AlHMA4 to NcHMA3. HMA transporters are divided into the Cu/Ca/Zn/Cd/Co-ATPases group, the Zn/Cd/Pb/Co-ATPases group, and the Cu-ATPases group (Hermand et al. 2014). BnHMA2 and BnHMA4 are reported to belong in the Cu/Ca/Zn/Cd/Co-ATPases group. It is inferred from the phylogenetic tree analysis that HMA4 in *A. thaliana*, *A. halleri,* and *B. napus* are closely evolutionary related and are homologs to each other. HMA2 in *Brassica* and *Arabidopsis* phylogenetically was closely related, and showed similar distribution patterns in the phylogenetic tree. NcHMA4 and BoHMA4, BjHMA4 and BrHMA4, and AtHMA4 and AhHMA4 were placed in different groups.

5.4 Genomic Structure of Metal ATPases Identified from Different Plant Species in *Brassicaceae*

A detailed bioinformatics analysis was carried out using several tools and databases to understand heavy metal ATPases' genomic structure and function and their interaction with other metal transporters. Genomic sequencing analysis of the *Arabidopsis* genome helped to identify many reported transporters. A wide variety of transporters belong to the family of heavy metal ATPases that regulate heavy HM homeostasis in the plant cell (Eren and Arguello 2004; Ozturk et al. 2012; Iqbal et al. 2013). HMA transporters belong to the P-type ATPase protein family that has a role in transporting the cations using ATP as an energy source (Memon and Yatazawa 1988; Memon 2020). One of the subgroups of P-type ATPases known as P_{1B} metal ATPases plays a vital role in transporting heavy metals, including many toxic metals such as Cu, Zn, Cd, and Pb in accumulator plants (see Table 5.1). Genome-wide analysis of Arabidopsis (*Arabidopsis thaliana*) (Cobbett et al. 2003), rice (*Oryza sativa*) (Takahashi et al. 2012), Populus (*Populus trichocarpa*) (Li et al. 2015), soybean

Table 5.1 List and general characteristics of the HMA1–HMA8 proteins identified in different plant species in *Brassicaceae* (classification according to protein function)

Organism	Gene name (HMA1–8)	Accession number	Molecular weight	Length of sequence (aa)	Location	Molecular function	Metal	References
A. thaliana	HMA1	Q9M3H5	88.189	819	Chloroplast Envelope/ Membrane/ Plastid	Copper-exporting ATPase activity, ATPase activity	Cu Zn Cd Ca Co	Mayer et al. (1999), Seigneurin-Berny et al. (2006), Kim et al. (2009), Higuchi et al. (2009), Moreno et al. (2008), Olsen et al. (2016)
A. halleri	HMA1	Q70IH7/AJ580403	19.184	182	Membrane	ATP Binding; ATPase activity	Cd/ Zn	Becher et al. (2004), Zorrig et al. (2011)
A. lyrata	HMA1	XP_020875667	88.648	826	Chloroplast envelope, Membrane	ATP Binding; P-type zinc transporter activity; Metal ion binding	Cd/ Zn	Hu et al. (2011)
N. caerulescens	HMA1	JAU82411	93.383	866	Chloroplast	ATP Binding; Metal ion binding; P-type zinc transporter activity	Cd/ Zn	Blande et al. (2017)
B. rapa	HMA1	XP_009137459	87.626	818	Chloroplast, Membrane	ATP Binding; Metal binding	Cd/ Zn	Wang et al. (2011), Zhang et al. (2018), Wu et al. (2019)
B. napus	HMA1	XP_022573707	87.581	817	Chloroplast	ATP Binding; Metal ion binding	Cd/ Zn	Li et al. (2018), Zhang et al. 2020

(continued)

Table 5.1 (continued)

Organism	Gene name (HMA1–8)	Accession number	Molecular weight	Length of sequence (aa)	Location	Molecular function	Metal	References
B. oleracea	HMA1	XP_013595810	87.525	817	Chloroplast envelope, Membrane	P-type zinc transporter activity; ATP binding; Metal ion binding	Cd/Zn	Parkin et al. (2014)
A. thaliana	HMA2	Q9SZW4	120.2	951	Plasma membrane	P-type zinc transporter activity; ATP Binding	Zn Cd Cu	Hussain (2004) Wong and Cobbett (2009), Wong et al. (2009), Wu et al. (2015)
A. lyrata	HMA2	XP_002867367	101.031	944	Membrane	ATP Binding; Metal ion binding	Cd/Zn	Hu et al. (2011)
B. rapa	HMA2	XP_009128090	94.127	872	Plasma membrane	ATP Binding; Metal ion binding	Cd/Zn	Wang et al. (2011), Yu et al. (2017), Wu et al. (2019)
B. napus	HMA2-like	XP_013748024/ XP_013748024.1	95.574	886	–	ATP Binding; Metal binding	Cd/Zn	Wu et al. (2015), Li et al. (2018), Zhang et al. (2020)
B. oleracea	HMA2	XP_013609995	95.343	883	Plasma Membrane	ATP Binding; Metal ion binding	Cd/Zn	Parkin et al. (2014)
N. caerulescens	HMA2	JAU82907	104.484	974	Membrane	ATP Binding; Metal ion binding	Cd/Zn	Vogel-Mikuš (2013), Blande et al. (2017)
A. thaliana	HMA3	P0CW78	81.856	760	Vacuole membrane (Tonoplast)	ATP Binding; Metal ion binding	Cd Zn Pb Co Cu	Morel et al. (2009), Li et al. (2018), Pita-Barbosa et al. (2019)

A. halleri	HMA3	AJ556182	81.946	757	Membrane	ATP Binding; Metal binding	Cd/Zn	Becher et al. (2004), Zorrig et al. (2011), Leonhardt et al. (2011)
A. lyrata	HMA3 (Predicted Protein)	XM_002867320	81.772	757	Membrane	ATP Binding; Metal binding	Cd/Zn	Hu et al. (2011)
B. rapa	HMA3	XP_009137892	81.852	764	Membrane	ATP Binding; Metal ion binding	Cd/Zn	Wang et al. (2011), Yu et al. (2017), Pita-Barbosa et al. (2019), Wu et al. (2019)
B. napus	HMA3	XP_013752152	81.358	758	Membrane	ATP Binding	Cd/Zn	–
B. oleracea	HMA3	XP_013591300	81.390	758	Membrane	ATP Binding; Metal ion binding	Cd/Zn	Parkin et al. (2014)
N. caerulescens	HMA3	A0A1J3HSX9	81.484	759	Membrane	ATP Binding; Metal ion binding	Cd/Zn	Ueno et al. (2011), Leonhardt et al. (2011); Vogel-Mikuš (2013), Halimaa et al. (2014), Blande et al. (2017)
A. thaliana	HMA4	AT2G19110/O64474	127.209	1172	Membrane	ATP Binding; Metal ion binding	Zn Cd Co Cu	Verret et al. (2004) Mills et al. (2005), Wong and Cobbett (2009), Wong et al. (2009) Wu et al. (2015)
A. halleri	HMA4	ABB29495/Q2I7E8	124.873	1161	Membrane	ATP Binding; Metal ion binding	Cd/Zn	Hussain (2004), Courbot et al. (2007), Hanikenne et al. (2008), Kazemi-Dinan et al. (2014)
A. lyrata	HMA4 (Low quality protein)	XP_020869480	118.316	1099	–	Metal ion binding	Cd/Zn	–

(continued)

Table 5.1 (continued)

Organism	Gene name (HMA1–8)	Accession number	Molecular weight	Length of sequence (aa)	Location	Molecular function	Metal	References
B. rapa	HMA4	XP_009150707	129.583	1190	Membrane	Metal ion binding	Cd/ Zn	Wang et al. (2011), Yu et al. (2017), Wu et al. (2019)
B. juncea	HMA4	AFJ94635/ M1F4T6	137.956	1272	Membrane	ATP Binding; Metal ion binding	Cd/ Zn	Wang et al. (2019)
B. napus	HMA4	XP_022561353	152.774	1425	Membrane	Metal ion binding	Cd/ Zn	Wu et al. (2015) Li et al. (2018) Zhang et al. (2020)
B. oleracea	HMA4	XP_013629797	129.366	1195	Membrane	ATP Binding; Metal ion binding	Cd/ Zn	Parkin et al. (2014)
N. caerulescens	HMA4	JAU89865	129.024	1189	Membrane	ATP Binding; Metal ion binding	Zn Ni Cd	Courbot et al. (2007), Craciun et al. (2012), Halimaa et al. (2014), Blande et al. (2017)
A. thaliana	HMA5	OAP12074	108.336	995	Membrane	ATP Binding; Copper ion binding	Cu	Andrés-Colás et al. (2006), Kobayashi et al. (2008), Kimura et al. (2008)
B. rapa	HMA5	XP_009112946	108.422	999	–	Metal ion binding	Cu	Wu et al. (2019)
B. napus	HMA5	XP_013748077	108.422	999	–	Metal ion binding	Cu	-
B. oleracea	HMA5	XP_013606061	108.442	999	Membrane	ATP Binding; Copper ion binding	Cu	Parkin et al. (2014)
N. caerulescens	HMA5	JAU39366	112.776	1032	Membrane	ATP Binding; Copper ion binding	Cu	Blande et al. (2017)

A. thaliana	HMA6 (PAA1)	AT4G33520/ Q9SZC9	99.997	949	Chloroplast membrane	ATPase activity; Copper ion binding; P-type divalent/ monovalent copper transporter activity	Cu	Shikanai et al. (2003), Abdel-Ghany et al. (2005), Andrés-Colás et al. (2006), Seigneurin-Berny et al. (2006), Puig et al. (2007)
A. thaliana	HMA7 (RAN1)	NP_199292/ Q9S7J8	107.264	1001	Membrane/ Endosome/ Golgi apparatus	ATP Binding; Copper ion binding; P-type divalent/ monovalent copper transporter activity	Cu	Hirayama et al. (1999) Woeste and Kieber (2000), Shikanai et al. (2003), Abdel-Ghany et al. (2005), Williams and Mills (2005), Andrés-Colás et al. (2006), Seigneurin-Berny et al. (2006), Puig et al. (2007)
N. caerulescens	HMA7 (RAN1)	JAU79906	107.848	1011	Membrane	ATP Binding; Copper ion binding	Cu	Blande et al. (2017)
A. thaliana	HMA8 (PAA2)	NP_001031920/ B9DFX7	94.130	883	Chloroplast thylakoid membrane	ATP Binding; Copper ion binding; P-type divalent copper transporter activity	Cu	Shikanai et al. (2003), Abdel-Ghany et al. (2005), Andrés-Colás et al. (2006), Seigneurin-Berny et al. (2006), Puig et al. (2007)
N. caerulescens	HMA8 (PAA2)	JAU85510	94.446	886	Membrane	ATP Binding; Metal ion binding	Cu	Blande et al. (2017)

(*Glycine max*) (Fang et al. 2016), maize (*Zea mays*), sorghum (*Sorghum bicolor*) (Zhiguo et al. 2018), barley (*Hordeum vulgare*) (Mills et al. 2012), flax (*Linum usitatissimum*) (Khan et al. 2020), rape (*Brassica napus*) (Li et al. 2018), Chinese pear (*Pyrus bretschneideri*) (Manzoor et al. 2020), mulberry (*Morus alba*) (Fan et al. 2018), and *Medicago truncatula* (Ma et al. 2021) showed 8, 9, 12, 20, 11, 11, 9, 12, 31, 8, 8, and 9 HMA genes in their genomes, respectively.

Table 5.1 shows the molecular weight and amino acid sequence of metal transport ATPases in plant species in *Brassicaceae*. The function of HMA transporter proteins is closely related to their subcellular localization in the cell. In this connection, our bioinformatics analysis revealed that most of the transporters are located in the plasma membrane or chloroplast (see Table 5.1). HMA1 in *Arabidopsis* and all other species in *Brassicaceae* are located in chloroplast and involved in Cd, Zn, and Cu transport (Table 5.1). Our gene expression data with *B. nigra* and *B. juncea* showed that HMA1 is involved in Cu transport and belongs to Cu/Ag sub-group metal ATPases (Meraklı and Memon 2019). HMA2 and HMA4 transport Zn and Cd in the cell belonging to the Zn/Cd/Co/Pb sub-group ATPases (Table 5.1) (Axelsen and Palmgren 2001; Williams and Mills 2005). Genetic studies have shown that in *Arabidopsis*, HMA2 is homologous to HMA6 and contributes to Cd transport from roots to shoots (Hussain 2004). HMA2, HMA3, and HMA4 are closely related in sequence. HMA2 and HMA4 are located in the plasma membrane and function in long-distance transport from root to shoot, while HMA3 is localized in the tonoplast membrane and involved in the vacuolar transport of Zn and Cd (Hanikenne et al. 2008; Hussain 2004; Liu et al. 2017; Morel et al. 2009; Wong and Cobbett 2009) (see Table 5.1).

AtHMA5 is involved in Cu transport from root to shoot (Guex and Peitsch 1997; Hanikenne et al. 2008); MtHMA7, MtHMA8, and MtHMA9 are homologous to AtHMA5, and their expression is significantly high in roots compared to shoots. Our previous work showed that PAA1 (At HMA6) heavy metal ATPase expression is around 300-fold increased in *B. nigra* accumulator ecotype grown at 500 μM Cu compared to control (Memon and Zahirovic 2014). AtHMA6 (PAA1) is located in the chloroplast and transports Cu to the chloroplast matrix. AtHMA7 transports Cu to ethylene receptors and maintains Cu homeostasis in seedlings (Rhee et al. 2003; Franceschini et al. 2013; Pinto and Ferreira 2015). AtHMA8 (PAA2) transports Cu into the thylakoid lumen and is present in the thylakoid membrane (Guindon and Gascuel 2003; Hanikenne et al. 2008). Among 8 HMAs, AtHMA2 and AtHMA4 are of most significant interest because of their role in metal transport from roots to shoots. They function as putative transporters of divalent cations ($Zn^{2+,}$ Cd^{2+}, Pb^{2+}, Co^{2+}, and Cu^{2+}). (Hussain 2004; Ozturk et al. 2012; Iqbal et al. 2013).

HMA4, together with HMA5, is involved in Cd tolerance, especially in *A. halleri* (Alloway et al. 2012). HMA4 translocates metal from roots to shoots and functions in regulating Zn homeostasis in *A. thaliana* (Arnold et al. 2006; Benson et al. 2009; Benkert et al. 2011). Given the main tasks of HMA proteins in *A. thaliana,* we performed a 3D structure analysis. In addition, we predicted the subcellular localization of these proteins and their interaction with other transporters in different species in Brassicaceae. The primary approach is to generate the interactome of interacting proteins in the cell, specify the structural and functional differences between *B. rapa* and *A. halleri,* and compare this to *A. thaliana data.* A study on these protein–protein interactions is essential to understand the complexity of the role of HMA proteins in sub-cellular compartmentation and translocation.

5.5 Motif Composition of the HMA Proteins in Plant Species in *Brassicaceae*

Conserved motif analysis of the HMA proteins was carried out with HMAs 1–8 using Multiple EM for Motif Elicitation (MEME) online suite software toolkit (Bailey et al. 2006; Bailey et al. 2009) (see Fig. 5.2). This application helped to find out the conserved motifs in the members of the HMA transporter family. It will

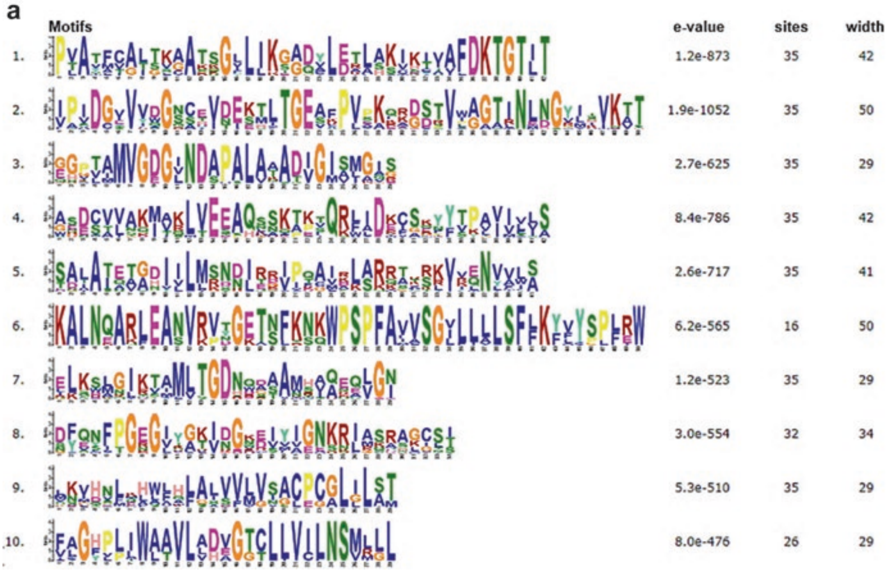


Fig. 5.2 Prediction of putative protein motifs for the P_{1B} ATPase family proteins from different plant species in *Brassicaceae* using the MEME. The different conserved motifs are shown with varying boxes of color, and the non-conserved sequences are depicted with gray lines. The differences in the motifs within these genes may influence their functions. This figure shows that *A. thaliana* HMA1, *A. lyrata* HMA1, *B. napus* HMA1, *B. rapa* HMA1, and *B. oleracea* HMA1 share all the same motifs with HMA5, HMA6, HMA7, and HMA8. (**a**) Conserved motifs observed are the MEME suite output for sequences from the P_{1B} ATPase family. The conserved ten motifs of HMA1–8 in different *Brassicaceae* spp. were detected using the MEME tool. The large letters indicate that the residue is more often expressed. (**b**) Sequence-specific MEME conserved motifs in the P_{1B} ATPase family. The two catalytic sequence motifs were boxed. (**c**) Distribution of the conserved motif of the P_{1B} ATPase family proteins from different plant species in *Brassicaceae*

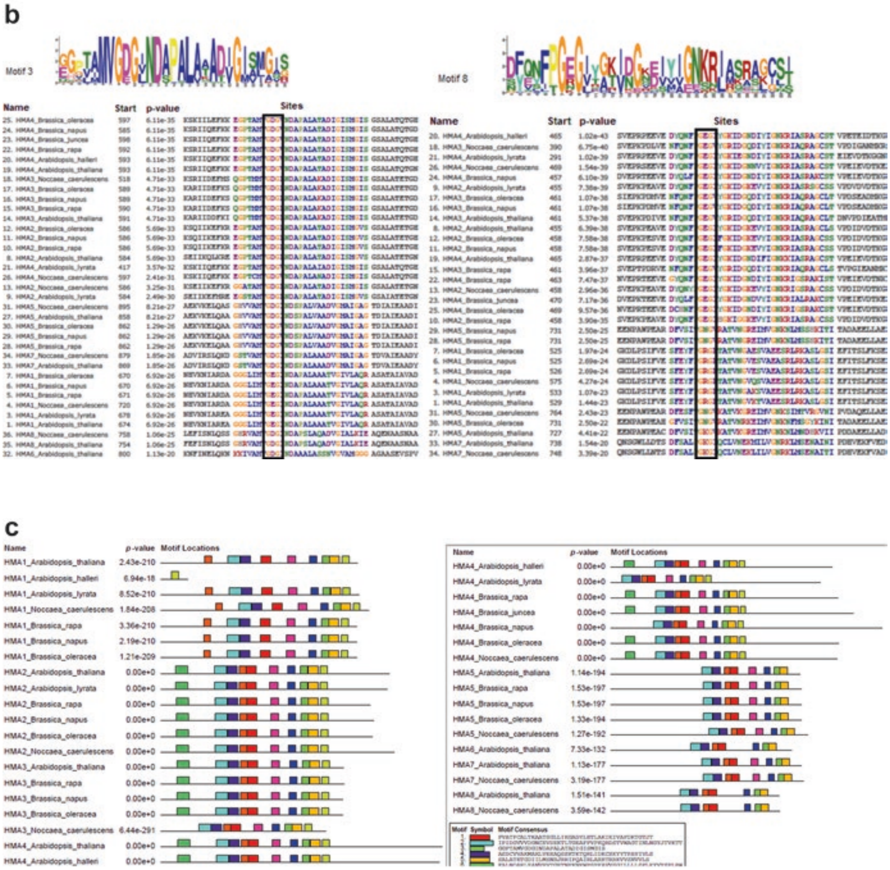


Fig. 5.2 (continued)

allow us to determine the functional relationship between these proteins and other interacting proteins. Using the MEME tool tree motif program, we searched ten most conserved motifs across the protein sequence (Fig. 5.2). Motifs 1 and 4 were 42 amino acid residues long, while motifs 2 and 6 were 50, motifs 3, 7, 9, and 10 were 29, motif 5 was 41, and motif 8 was 34 amino acids long (Fig. 5.2a). Most of the motifs in HMA1–8 proteins were related to each other. As shown in Fig. 5.2b, two motifs (3 and 8) were common in different *Brassicacea* members. Motif 3 (29 aa, *e* value = 2.7e-625) and motif 8 (34 aa, *e* value = 3.0–554) were common in all species in *Brassicaceae*, except AhHMA1 (partial) (Fig. 5.2b). On the other hand, the third and eighth motifs showed three large GDG/GEG (G = Glycine; D = Aspartic acid; E = Glutamic acid) letters shown in yellow and pink, respectively. The conserved glycine residues determined in the present work are possibly a heavy metal domain motif found in all HMA genes. The presence of long conserved residues in all aligned sequences and their relation with the P_{1B} ATPase family suggests the highly conserved structures of HMA1–8 homologs between species.

5.6 3D Structure Prediction and Validation of HMA Transporters

Using PyMol software, the 3D structure was generated and visualized. The confidence of the visualization was checked with respected Ramachandran plots (Van der Zaal et al. 1999). The results showed that there were 580 (88.8%) residues in the favored region for HMA1, 544 (81.3%) residues for HMA2, 409 (89.5%) residues for HMA3, and 544 (81.2%) for HMA4. A number of residues found in the outlier region are taken into account, further confirming the accuracy of the 3D structure prediction. The results are as follows: for HMA1, 25 (3.8%), for HMA2, 50 (7.5%), for HMA3, 6 (1.3%), and for HMA4, 51 (7.6%) residues were found in the outer region.

Analysis and prediction of the 3D structure of HMAs in plants are vital for a complete understanding of the function, interactions, possible ligands, conserved domains, their homologs, and many other functional properties.

It is known that the structure of one protein affects the function of the same protein, meaning that any alteration of the structure may result in the improper functioning of the proteins. 3D structure in *Arabidopsis* is done to analyze differences among all known HMAs in *Arabidopsis thaliana* thoroughly. It is known that HMAs of *A.thaliana* exist in RCSB PDB (Protein Data Bank) (Berman et al. 2000; Westbrook et al. 2003; Wheeler et al. 2005). Phyre2 server is used for 3D structure prediction. Phyre2 servers predict a protein sequence's three-dimensional structure using the principles and techniques of homology modeling (Kraemer 2009). Because the structure of a protein is more conserved in evolution than its amino acid sequence, a protein sequence of interest can be modeled with reasonable accuracy by this software.

The 3D structures of HMA proteins are predicted by the Phyre2 tool and are shown in Fig. 5.3. It is concluded that all HMAs (HMA1–HMA4) in *Arabidopsis* cells have shown similarities in their secondary structural elements, including the number of alpha helices, beta sheets, and loops. The 3D structure of HMA2 and HMA4 is remarkably very similar to each other, and both are localized in the plasma membrane.

In addition, for deep visualization of the proteins, Swiss-Pdb Viewer (DeepView) is performed (Guex and Peitsch 1997; Arnold et al. 2006; Bordoli et al. 2009). DeepView software is further used to show lectrostatic potential around these HMA transporter proteins and mapped to the molecular or protein surface. Understanding the electrostatic potential of molecules is important, because it can give much information in considering and hypothesizing the interaction among these transporter proteins and other interacting proteins (Guindon and Gascuel 2003; Biasini et al. 2014).

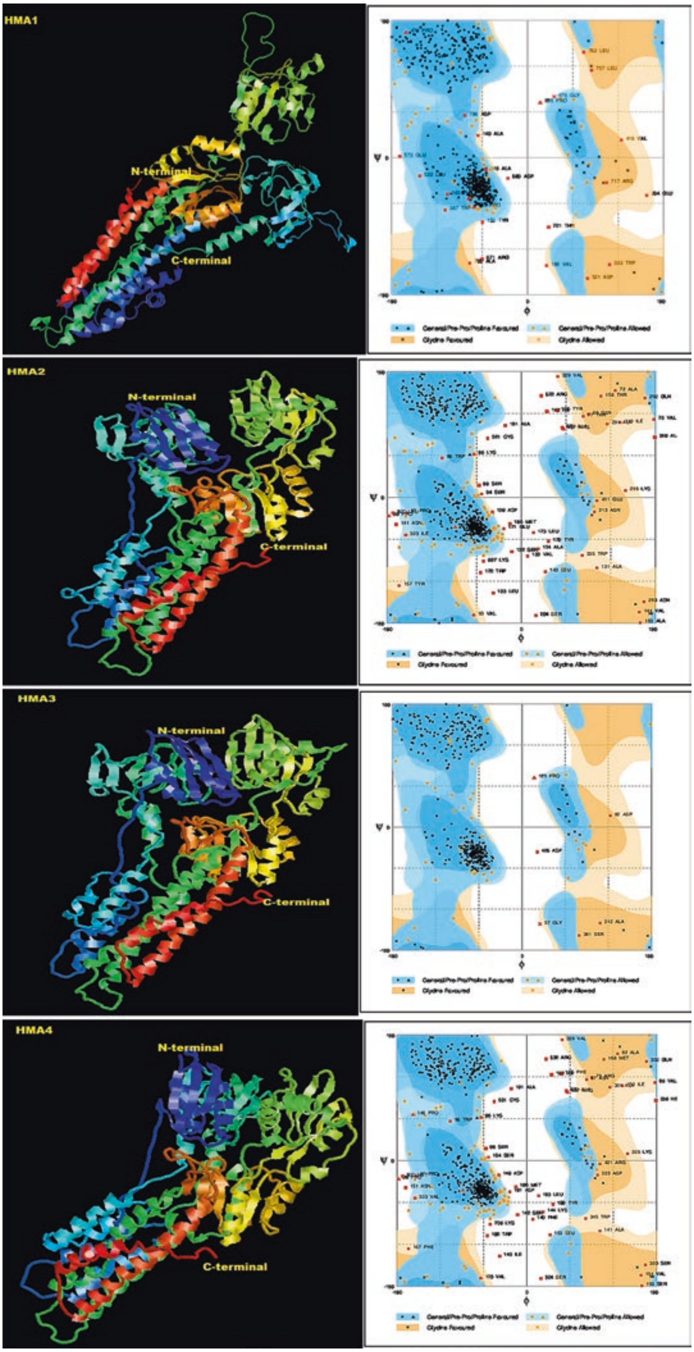


Fig. 5.3 Predicted 3D structures and respective Ramachandran plots of proteins HMA1, HMA2, HMA3, and HMA4 in *Arabidopsis thaliana.* Characteristic Cys residues are marked in magenta. Visualization of Ramachandran plots is done by RAMPAGE online tool, and PyMOL did a visualization of 3D pictures

The computations of the electrostatic field by DeepView showed that only charged residues are taken into consideration in the visualization of the protein. Coulomb computation method was used, which is derived from Coulomb's law measuring electrostatic interaction between electrically charged particles (Guex and Peitsch 1997; Guindon and Gascuel 2003; Franceschini et al. 2013).

As shown in Fig. 5.4, negative and positive charges vary among proteins in *Arabidopsis thaliana.* In HMA1 and HMA2 proteins, negative charge is dominant, whereas in HMA3 and HMA4, positive charge is dominant. HMA2 and HMA4 have similar visualization shapes of electrostatic potential. In other parts of the protein, respective white regions represent a neutral charge.

HMA2 and HMA4 are divalent cation transporters and are reported to play essential roles in the homeostasis of Zn/Cd in *Arabidopsis* and other plants (Hussain 2004). Recently, Escudero et al. (2022) inoculated *Arabidopsis thaliana* leaves with the necrotrophic fungus *Plectosphaerella cucumerina* BMM (PcBMM), and they observed a high accumulation of zinc and manganese at the infection sites in the leaves. Interestingly, zinc accumulation did not occur in a double mutant of HMA2 and HMA4, reducing the zinc translocation from roots to shoots. The results showed that the expression of *HMA2* and *HMA4* was up-regulated upon *Pc*BMM inoculation in wild plants, which makes the plants less susceptible to infection. It is because of the high translocation and accumulation of Zn in the leaves of wild plants.

On the contrary, *hma2hma4* mutants were more susceptible to *Pc*BMM infection because of little accumulation of metals in the leaves. This indicates that these

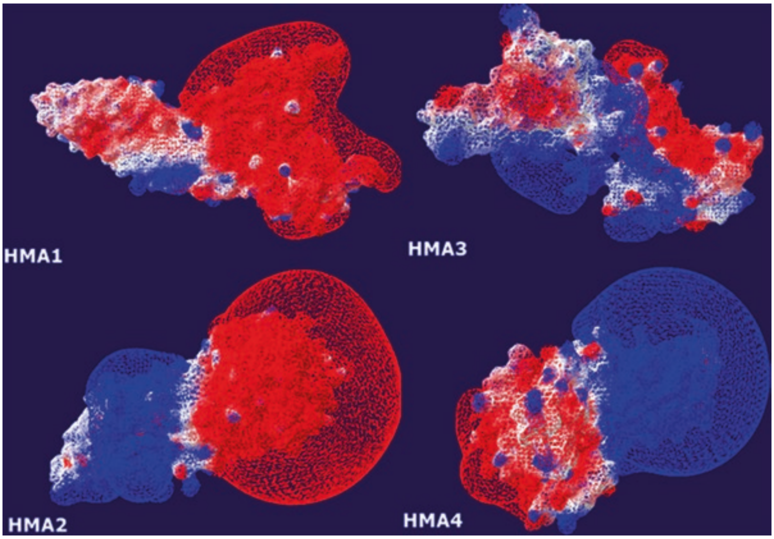


Fig. 5.4 HMA1, HMA2, HMA3, and HMA4 visualize electrostatic charges around the molecule and at the protein surface. Red color = negative charge, blue color = positive charge, white color = neutral charge (*Arabidopsis thaliana*)

transporters play an essential role in Zn translocation from roots to leaves of Arabidopsis and, in some way, play a role in plant immunity. Heavy metal ions may be an essential factor that induces chemical defenses against infective pathogens. The hormesis effect of metals on the growth, development, and biomass production of several crop plants has been previously reported (Morkunas et al. 2018). Hyperaccumulator plants possibly have developed a self-defense strategy against the natural enemy by accumulating metal in their tissues through the metal transporters.

5.7 Conclusions

The bioinformatics analysis of HMAs in Brassica species showed a considerable amount of similarities between each other. HMA1–8 sequences from *A. thaliana* were compared to its homologs in other species in Brassicaceae., for example, *B. juncea*, *B. rapa, B. napus, B. oleacea, A. lyrata, A. halleri,* and *N. caerulescens*. Phylogenetic analysis showed a very close relationship of BnHMA1 to BoHMA1; AtHMA1 to NcHMA8; AtHMA2 to AlHMA2; BrHMA2 to BnHMA2; BnHMA3 to BoHMA3; AtHMA4 to AhHMA4; BoHMA4 to NcHMA4; BjHMA4 to BrHMA4; and AlHMA4 to NcHMA3. HMA transporters are divided into the Cu/Ca/Zn/Cd/Co-ATPases group, the Zn/Cd/Pb/Co-ATPases group, and the Cu-ATPases group. HMA2 and HMA4 transporters are involved in metal transport from roots to shoots and belong in the Cu/Ca/Zn/Cd/Co-ATPases group. Conserved motif analysis of the HMA proteins was carried out with HMAs 1–8 using MEME (Multiple EM for Motif Elicitation) software toolkits. Among the ten most conserved motifs, motifs 1 and 4 were 42 amino acid residues long, while motifs 2 and 6 were 50, motifs 3, 7, 9, and 10 were 29, motif 5 was 41, and motif 8 was 34 amino acids long. Most of the motifs in HMA1–8 proteins were related to each other. In the 3D structural composition of proteins, we have concluded that all HMAs have shown similarities in their secondary structural elements, including the number of alpha helices, beta sheets, and loops.

Furthermore, electrostatic potential analysis of these proteins showed two groups of transporters, one with negative and the other one with positive electrostatic potential. This paper will help the researcher understand the role of these ATPases in detoxifying the toxic metals from the cells of accumulator plants. Further research on gene cloning, gene expression, and generating new super accumulator plants for phytoremediation is required to remediate polluted soils from toxic heavy metals efficiently.

Acknowledgements We appreciate the support given to Prof. Dr. Abdulrezzak Memon from BAP project (project No. 2017/TP042) and the grant for Plant Genetics and Agricultural Biotechnology program by the Council of Higher Education of Turkey (YÖK). The Ph.D. scholarship (100/2000) by the Council of Higher Educational of Turkey (YÖK) and the financial support by TÜBİTAK under the 2211-A-Ph.D. program given to Ms. Nuriye Meraklı is appreciated.

References

Abdel-Ghany SE, Müller-Moulé P, Niyogi KK, Pilon M, Shikanai T (2005) Two P-type ATPases are required for copper delivery in *Arabidopsis thaliana* chloroplasts. Plant Cell 17(4):1233–1251. https://doi.org/10.1105/tpc.104.030452

Alloway B, Centeno J, Finkelman R, Fuge R, Lindh U, Smedley P, Selinus O (2012) Essentials of medical geology. Springer, Dordrecht

Andrés-Colás N, Sancenón V, Rodríguez-Navarro S, Mayo S, Thiele DJ, Ecker JR, Puig S, Peñarrubia L (2006) The *Arabidopsis* heavy metal P-type ATPase HMA5 interacts with metallochaperones and functions in copper detoxification of roots. Plant J: Cell Mol Biol 45(2):225–236. https://doi.org/10.1111/j.1365-313X.2005.02601.x

Anjum NA, Ahmad I, Pereira ME, Duarte AC, Umar S, Khan NA (2012) The plant family *Brassicaceae*:an introduction. In: Anjum NA, Ahmad I, Pereira ME, Duarte AC, Umar S, Khan NA (eds) The plant family *Brassicaceae*: contribution towards phytoremediation, environmental pollution series, vol no. 21. Springer, Dordrecht, pp 1–33

Arnold K, Bordoli L, Kopp J, Schwede T (2006) The SWISS-MODEL workspace: a web-based environment for protein structure homology modelling. Bioinformatics (Oxford, England) 22(2):195–201. https://doi.org/10.1093/bioinformatics/bti770

Axelsen KB, Palmgren MG (2001) Inventory of the superfamily of P-type ion pumps in *Arabidopsis*. Plant Physiol 126(2):696–706

Bailey TL, Williams N, Misleh C, Li WW (2006) Meme: discovering and analyzing DNA and protein sequence motifs. Nucleic Acids Res 34:W369–W373

Bailey TL, Boden M, Buske FA, Frith M, Grant CE, Clementi L, Ren J, Li WW, Noble WS (2009) MEME SUITE:tools for motif discovery and searching. Nucl Acids Res 37(Web Server issue):W202–W208. https://doi.org/10.1093/nar/gkp335

Baker A, Whiting SN (2002) In search of the Holy Grail-a further step in understanding metal hyperaccumulation? New Phytol 155(1):1–4

Becher M, Talke IN, Krall L, Krämer U (2004) Cross-species microarray transcript profiling reveals high constitutive expression of metal homeostasis genes in shoots of the zinc hyperaccumulator *Arabidopsis halleri*. Plant J: Cell Mol Biol 37(2):251–268. https://doi.org/10.1046/j.1365-313x.2003.01959.x

Benkert P, Biasini M, Schwede T (2011) Toward the estimation of the absolute quality of individual protein structure models. Bioinformatics 27(3):343–350

Benson DA, Karsch-Mizrachi I, Lipman DJ, Ostell J, Sayers EW (2009) GenBank. Nucl Acids Res 37(Database issue):D26–D31. https://doi.org/10.1093/nar/gkn723

Berman HM, Westbrook J, Feng Z, Gilliland G, Bhat TN, Weissig H, Shindyalov IN, Bourne PE (2000) The protein data bank. Nucleic Acids Res 28(1):235–242

Biasini M, Bienert S, Waterhouse A, Arnold K, Studer G, Schmidt T, Kiefer F, Cassarino TG, Bertoni M, Bordoli L, Schwede T (2014) SWISS-MODEL: modelling protein tertiary and quaternary structure using evolutionary information. Nucleic Acids Res 42:W252

Blande D, Halimaa P, Tervahauta AI, Aarts MG, Kärenlampi SO (2017) De novo transcriptome assemblies of four accessions of the metal hyperaccumulator plant *Noccaea caerulescens*. Sci Data 4(1):1–9

Bordoli L, Kiefer F, Arnold K, Benkert P, Battey J, Schwede T (2009) Protein structure homology modeling using SWISS-MODEL workspace. Nat Protoc 4(1):1–13

Bull PC, Cox DW (1994) Wilson disease and Menkes disease: new handles on heavy-metal transport. Trends Genet 10(7):246–252

Chaney RL, Angle JS, Broadhurst CL, Peters CA, Tappero RV, Sparks DL (2007) Improved understand in hyperaccumulation yields commercial phytoextraction and phytomining technologies. J Environ Qual 36(5):1429–1443

Claus J, Bohmann A, Chavarría-Krauser A (2013) Zinc uptake and radial transport in roots of *Arabidopsis thaliana*: a modelling approach to understand accumulation. Ann Bot 112(2):369–380

Cobbett CS, Hussain D, Haydon MJ (2003) Structural and functional relationships between type 1B heavy metal-transporting P-type ATPases in Arabidopsis. New Phytol 159(2):315–321

Colangelo EP, Guerinot ML (2006) Put the metal to the petal: metal uptake and transport throughout plants. Curr Opin Plant Biol 9(3):322–330. https://doi.org/10.1016/j.pbi.2006.03.015

Courbot M, Willems G, Motte P, Arvidsson S, Roosens N, Saumitou-Laprade P, Verbruggen N (2007) A major quantitative trait locus for cadmium tolerance in *Arabidopsis halleri* colocalizes with HMA4, a gene encoding a heavy metal ATPase. Plant Physiol 144(2):1052–1065

Craciun A, Meyer C, Chen J, Roosens N, De Groodt R, Hilson P, Verbruggen N (2012) Variation in HMA4 gene copy number and expression among *Noccaea caerulescens* populations presenting different levels of Cd tolerance and accumulation. J Exp Bot 63(11):4179–4189

Dehkordi EA, Alemzadeh A, Ebrahimie E, Agagolzadeh P, Ebrahimi M (2010) Bioinformatics study on P_{1B}-ATPase; an important hyperaccumulator heavy metal transporter in Phytoremediation. New Biotechnol 27:S22

Ducic T, Polle A (2005) Transport and detoxification of manganese and copper in plants. Braz J Plant Physiol 17(1):103–112

Eren E, Arguello JM (2004) *Arabidopsis* HMA2, a divalent heavy metal-transporting P_{IB}-type ATPase, is involved in cytoplasmic Zn^{2+} homeostasis. Plant Physiol 136(3):3712–3723

Escudero V, Ferreira Sánchez D, Abreu I, Sopeña-Torres S, Makarovsky-Saavedra N, Bernal M, Jordá L (2022) *Arabidopsis thaliana* Zn^{2+-} efflux ATPases HMA2 and HMA4 are required for resistance to the necrotrophic fungus *Plectosphaerella cucumerina* BMM. J Exp Bot 73(1):339–350

Fan W, Liu C, Cao B, Qin M, Long D, Xiang Z, Zhao A (2018) Genome-wide identification and characterization of four gene families putatively involved in cadmium uptake, translocation and sequestration in mulberry. Front Plant Sci 9. https://doi.org/10.3389/fpls.2018.00879

Fang X, Wang L, Deng X, Wang P, Ma Q, Nian H, Wang Y, Yang C (2016) Genome-wide characterization of soybean P_{1B}-ATPases gene family provides functional implications in cadmium responses. BMC Genomics 17(1):1–15. https://doi.org/10.1186/s12864-016-2730-2

Franceschini A, Szklarczyk D, Frankild S, Kuhn M, Simonovic M, Roth A, Lin J, Minguez P, Bork P, von Mering C, Jensen LJ (2013) STRING v91: protein-protein interaction networks, with increased coverage and integration. Nucl Acids Res 41(Database issue):D808–D815. https://doi.org/10.1093/nar/gks1094

Guex N, Peitsch MC (1997) SWISS-MODEL and the Swiss-Pdb viewer: an environment for comparative protein modelling. Electrophoresis 18(15):2714–2723. https://doi.org/10.1002/elps.1150181505

Guindon S, Gascuel O (2003) A simple, fast, and accurate algorithm to estimate large phylogenies by maximum likelihood. Syst Biol 52(5):696–704

Halimaa P, Lin YF, Ahonen VH, Blande D, Clemens S, Gyenesei A, Tervahauta AI (2014) Gene expression differences between *Noccaea caerulescens* ecotypes help to identify candidate genes for metal phytoremediation. Environ Sci Technol 48(6):3344–3353

Hall J (2002) Cellular mechanisms for heavy metal detoxification and tolerance. J Exp Bot 53(366):1–11

Hall JL, Williams LE (2003) Transition metal transporters in plants. J Exp Bot 54:2601–2613

Hanikenne M, Talke IN, Haydon MJ, Lanz C, Nolte A, Motte P, Kroymann J, Weigel D, Krämer U (2008) Evolution of metal hyperaccumulation required cis-regulatory changes and triplication of HMA4. Nature 453(7193):391–395. https://doi.org/10.1038/nature06877

Hermand V, Julio E, Dorlhac de Borne F, Punshon T, Ricachenevsky FK, Bellec A, Gosti F, Berthomieu P (2014) Inactivation of two newly identified tobacco heavy metal ATPases leads to reduced Zn and cd accumulation in shoots and reduced pollen germination. Metallomics: Integr Biometal Sci 6:1427–1440. https://doi.org/10.1039/c4mt00071d

Higuchi M, Ozaki H, Matsui M, Sonoike K (2009) A T-DNA insertion mutant of AtHMA1 gene encoding a Cu transporting ATPase in Arabidopsis thaliana has a defect in the water-water cycle of photosynthesis. J Photochem Photobiol B Biol 94(3):205–213. https://doi.org/10.1016/j.jphotobiol.2008.12.002

Hirayama T, Kieber JJ, Hirayama N, Kogan M, Guzman P, Nourizadeh S, Alonso JM, Dailey WP, Dancis A, Ecker JR (1999) RESPONSIVE-TO-ANTAGONIST1, a Menkes/Wilson disease- related copper transporter, is required for ethylene signaling in Arabidopsis. Cell 97(3):383–393. https://doi.org/10.1016/s0092-8674(00)80747-3

Hu TT, Pattyn P, Bakker EG, Cao J, Cheng JF, Clark RM, Fahlgren N, Fawcett JA, Grimwood J, Gundlach H, Haberer G, Hollister JD, Ossowski S, Ottilar RP, Salamov AA, Schneeberger K, Spannagl M, Wang X, Yang L, Nasrallah ME et al (2011) *The Arabidopsis lyrata* genome sequence and the basis of rapid genome size change. Nat Genet 43(5):476–481. https://doi.org/10.1038/ng.807

Hussain D (2004) P-type ATPase heavy metal transporters with roles in essential zinc homeostasis in *Arabidopsis*. Plant Cell Online 16(5):1327–1339

Iqbal M, Nawaz I, Hassan Z, Hakvoort HW, Bliek M, Aarts MG, Schat H (2013) Expression of HMA4 cDNAs of the zinc hyperaccumulator *Noccaea caerulescens* from endogenous NcHMA4 promoters does not complement the zinc-deficiency phenotype of the *Arabidopsis thaliana* hma2hma4 double mutant. Front Plant Sci 4:404

Kazemi-Dinan A, Thomaschky S, Stein RJ, Krämer U, Müller C (2014) Zinc and cadmium hyperaccumulation act as deterrents towards specialist herbivores and impede the performance of a generalist herbivore. New Phytol 202(2):628–639. https://doi.org/10.1111/nph.12663

Khan N, You FM, Datla R, Ravichandran S, Jia B, Cloutier S (2020) Genome-wide identification of ATP binding cassette (ABC) transporter and heavy metal associated (HMA) gene families in flax (*Linum usitatissimum* L.). BMC Genomics 21(1). https://doi.org/10.1186/s12864-020-07121-9

Kim YY, Choi H, Segami S, Cho HT, Martinoia E, Maeshima M, Lee Y (2009) AtHMA1 contributes to the detoxification of excess Zn(II) in Arabidopsis. Plant J Cell Mol Biol 58(5):737–753. https://doi.org/10.1111/j.1365-313X.2009.03818.x

Kimura K, Southron-Francis JL, Iuchi S, Furuzawa A, Taylor GJ, Kobayashi Y, ... Kuroda K (2008) Amino acid polymorphisms in strictly conserved domains of a P-type ATPase HMA5 are involved in the mechanism of copper tolerance variation in *Arabidopsis*

Kobayashi Y, Kuroda K, Kimura K, Southron-Francis JL, Furuzawa A, Kimura K, Luchi S, Kobayashi M, Taylor GJ, Koyama H (2008) Amino acid polymorphisms in strictly conserved domains of a P-type ATPase HMA5 are involved in the mechanism of copper tolerance variation in Arabidopsis. Plant Physiol 148(2):969–980. https://doi.org/10.1104/pp.108.119933

Koch MA, German D (2013) Taxonomy and systematics are key to biological information: *Arabidopsis*, Eutrema (Thellungiella), *Noccaea* and Schrenkiella (*Brassicaceae*) as examples. Front Plant Sci 4:267

Kraemer U (2009) The dilemma of controlling heavy metal accumulation in plants. New Phytol 181(1):3–5

Leonhardt N, Cun P, Richaud P, Vavasseur A (2011) Zn/Cd/Co/Pb P_{1B}-ATPases in plants, physiological roles and biological interest. In: Metal toxicity in plants: perception, signaling and remediation. Springer, Berlin, Heidelberg, pp 227–248. https://doi.org/10.1007/978-3-642-22081-4_11

Li D, Xu X, Hu X, Liu Q, Wang Z, Zhang H, Wang H, Wei M, Wang H, Liu H, Li C (2015) Genome-wide analysis and heavy metal-induced expression profiling of the HMA gene family in *Populus trichocarpa*. Front Plant Sci 6:1149. https://doi.org/10.3389/fpls.2015.01149

Li N, Xiao H, Sun J, Wang S, Wang J, Chang P, Zhou X, Lei B, Lu K, Luo F, Shi X, Li J (2018) Genome-wide analysis and expression profiling of the HMA gene family in *Brassica napus* under Cd stress. Plant Soil 426(1–2):365–381. https://doi.org/10.1007/s11104-018-3637-2

Liu H, Zhao H, Wu L, Liu A, Zhao FJ, Xu W (2017) Heavy metal ATPase 3 (HMA3) confers cadmium hypertolerance on the cadmium/zinc hyperaccumulator *Sedum plumbizincicola*. New Phytol 215(2):687–698. https://doi.org/10.1111/nph.14622

Ma Y, Wei N, Wang Q, Liu Z, Liu W (2021) Genome-wide identification and characterization of the heavy metal ATPase (HMA) gene family in *Medicago truncatula* under copper stress. Int J Biol Macromol 19:893–902

Manzoor MA, Cheng X, Li G, Su X, Abdullah M, Cai Y (2020) Gene structure, evolution and expression analysis of the P-ATPase gene family in Chinese pear (*Pyrus bretschneideri*). Comput Biol Chem 107346. https://doi.org/10.1016/j.compbiolchem.2020.107346

Mayer K, Schüller C, Wambutt R, Murphy G, Volckaert G, Pohl T, Düsterhöft A, Stiekema W, Entian KD, Terryn N, Harris B, Ansorge W, Brandt P, Grivell L, Rieger M, Weichselgartner M, de Simone V, Obermaier B, Mache R, Müller M et al (1999) Sequence and analysis of chromosome 4 of the plant *Arabidopsis thaliana*. Nature 402(6763):769–777. https://doi.org/10.1038/47134

Memon AR (2016) Metal hyper-accumulators: mechanism of hyperaccumulation and metal tolerance. Phytoremediation: management of environmental contaminants, vol 3. Springer, pp 239–268

Memon AR (2020) Heavy metal–induced gene expression in plants. In: Naeem M, Ansari A, Gill S (eds) Contaminants in agriculture. Springer, Cham. https://doi.org/10.1007/978-3-030-41552-5_7

Memon A, Schröder P (2009) Implications of metal accumulation mechanisms to phytoremediation. Environ Sci Pollut Res 16:162–175

Memon AR, Yatazawa M (1988) Genotypic differences in absorption and accumulation microelements in temperate forest vegetation of Japan. In: Ozturk MA (ed) Plants and pollutants developed and developing countries, pp 294–304

Memon AR, Zahirovic E (2014) Genomics and transcriptomics analysis of Cu accumulator plant *Brassica nigra* L. J Appl Biol Sci 8:1–8

Memon AR, Aktoprakligıl D, Özdemir A, Vertii A (2001) Heavy metal accumulation and detoxification mechanisms in plants. Turkish J Bot 25:111–121

Memon A, Kusur F, Memon M (2021) Metal hyperaccumulator plants and their role in phytoremediation. In: Prasad R (ed) Phytoremediation for environmental sustainability. Springer, Singapore. https://doi.org/10.1007/978-981-16-5621-7_1

Meraklı N, Memon AR (2019) Farklı bakır (Cu) seviyelerinde yetistirilen *Brassica nigra* ve *Brassica juncea*'da HMA1, P_{1B} ATPaz'nın anlatım. International Congress of Medical Sciences and Biotechnology, Medickal Yayıncılık Bilimsel Eserler dizisi, Kongre Kitap, ISBN-978-605-7607-42-3, p 381–388

Meraklı N, Bulduk İ, Memon A (2022) Identification of genes regulated in response to Cu exposure in *Brassica nigra* L. Trakya University J Nat Sci 0-0. https://doi.org/10.23902/trkjnat.978842

Meyer CL, Verbruggen N (2012) The use of the model species *Arabidopsis halleri* towards phytoextraction of cadmium polluted soils. New Biotechnol 30:9–14

Mills R, Francini A, Ferreira da Rocha P, Baccarini P, Aylett M, Krijger G, Williams L (2005) The plant P_{1B}-type ATPase AtHMA4 transports Zn and Cd and plays a role in detoxification of transition metals supplied at elevated levels. FEBS Lett 579:783–791

Mills RF, Peaston KA, Runions J, Williams LE (2012) HvHMA2, a P_{1B}-ATPase from barley, is highly conserved among cereals and functions in Zn and Cd transport. PLoS One 7(8):e42640. https://doi.org/10.1371/journal.pone.0042640

Morel M, Crouzet J, Gravot A, Auroy P, Leonhardt N, Vavasseur A, Richaud P (2009) AtHMA3, a P_{1B}-ATPase allowing Cd/Zn/Co/Pb vacuolar storage in *Arabidopsis*. Plant Physiol 149(2):894–904. https://doi.org/10.1104/pp.108.130294

Moreno I, Norambuena L, Maturana D, Toro M, Vergara C, Orellana A, Zurita-Silva A, Ordenes VR (2008) AtHMA1 is a thapsigargin-sensitive $Ca^{2+/}$heavy metal pump. J Biol Chem 283:9633–9641

Morkunas I, Wozniak A, Mai VC, Rucinska-Sobkowiak R, Jeandet P (2018) The role of heavy metals in plant response to biotic stress. Molecules 23(2320):1–30. https://doi.org/10.3390/molecules23092320

Olsen LI, Hansen TH, Larue C, Østerberg JT, Hoffmann RD, Liesche J, Krämer U, Surblé S, Cadarsi S, Samson VA, Grolimund D, Husted S, Palmgren M (2016) Mother-plant-mediated pumping of zinc into the developing seed. Nat Plants 2(5):16036. https://doi.org/10.1038/nplants.2016.36

Ozturk M, Memon AR, Gucel S, Sakcali MS (2012) *Brassicas* in Turkey and their possible role in the phytoremediation of degraded habitats. In: Anjuman NA et al (eds) The plant family *Brassicaceae*: contribution towards phytoremediation, vol 21. Springer, pp 265–288. ISBN 978-94-007-3912-3

Parkin IA, Koh C, Tang H, Robinson SJ, Kagale S, Clarke WE et al (2014) Transcriptome and methylome profiling reveals relics of genome dominance in the mesopolyploid *Brassica oleracea*. Genome Biol 15(6):1–18

Pinto E, Ferreira I (2015) Cation transporters/channels in plants: tools for nutrient biofortification. J Plant Physiol 179:64–82

Pita-Barbosa A, Ricachenevsky FK, Wilson M, Dottorini T, Salt DE (2019) Transcriptional plasticity buffers genetic variation in zinc homeostasis. Sci Rep 9(1):1–11. https://doi.org/10.1038/s41598-019-55736-0

Puig S, Andrés-Colás N, García-Molına A, Peñarrubıa L (2007) Copper and iron homeostasis in *Arabidopsis*: responses to metal deficiencies, interactions and biotechnological applications. Plant Cell Environ 30:271–290

Rascio N, Navari-Izzo F (2011) Heavy metal hyperaccumulating plants: how and why do they do it? And what makes them so interesting? Plant Sci 180:169–181

Rhee SY, Beavis W, Berardini TZ, Chen G, Dixon D, Doyle A, Garcia-Hernandez M, Huala E, Lander G, Montoya M, Miller N, Mueller LA, Mundodi S, Reiser L, Tacklind J, Weems DC, Wu Y, Xu I, Yoo D, Yoon J, Zhang P (2003) The *Arabidopsis* Information Resource (TAIR): a model organism database providing a centralized, curated gateway to *Arabidopsis* biology, research materials and community. Nucleic Acids Res 31(1):224–228

Salt DE, Blaylock M, Kumar NPBA, Dushenkov V, Ensley BD, Chet I et al (1995) Phytoremediation: a novel strategy for the removal of toxic metals from the environment using plants. Nat Biotechnol 13:468–474

Salt DE, Smith RD, Raskin I (1998) Phytoremediation. Annu Rev Plant Physiol Plant Mol Biology 49:643–668

Seigneurin-Berny D, Gravot A, Auroy P, Mazard C, Kraut A, Finazzi G, Grunwald D, Rappaport F, Vavasseur A, Joyard J, Richaud P, Rolland N (2006) HMA1, a new Cu-ATPase of the chloroplast envelope, is essential for growth under adverse light conditions. J Biol Chem 281(5):2882–2892. https://doi.org/10.1074/jbc.M508333200

Shikanai T, Müller-Moulé P, Munekage Y, Niyogi KK, Pilon M (2003) PAA1, a P-type ATPase of *Arabidopsis*, functions in copper transport in chloroplasts. Plant Cell 15(6):1333–1346. https://doi.org/10.1105/tpc.011817

Smith AT, Smith KP, Rosenzweig AC (2014) Diversity of the metal-transporting P_{1B}-type ATPases. J Biol Inorganic Chem: JBIC: a publication of the Society of Biological Inorganic Chemistry 19(6):947–960. https://doi.org/10.1007/s00775-014-1129-2

Sytar O, Ghosh S, Malinska H, Zivcak M, Brestic M (2021) Physiological and molecular mechanisms of metal accumulation in hyperaccumulator plants. Physiol Plant 173(1):148–166

Takahashi R, Bashir K, Ishimaru Y, Nishizawa N, Nakanishi H (2012) The role of heavy-metal ATPases, HMAs, in zinc and cadmium transport in rice. Plant Signal Behav 7(12):1605–1607. https://doi.org/10.4161/psb.22454

Ueno D, Milner MJ, Yamaji N, Yokosho K, Koyama E, Zambrano MC, Kaskie M, Ebbs S, Kochian LV, Ma JF (2011) Elevated expression of TcHMA3 plays a role in the extreme Cd tolerance in a Cd-hyperaccumulating ecotype of *Thlaspi cearulescens*. Plant J 66(5):852–862. https://doi.org/10.1111/j.1365-313X.2011.04548.x

Van der Ent A, Baker AJ, Reeves RD, Pollard AJ, Schat H (2013) Hyperaccumulators of metal and metalloid trace elements: facts and fiction. Plant and Soil 362(1–2):319–334

Van der Zaal BJ, Neuteboom LW, Pinas JE, Chardonnens AN, Schat H, Verkleij JA, Hooykaas PJ (1999) Overexpression of a novel *Arabidopsis* gene related to putative zinc-transporter genes from animals can lead to enhanced zinc resistance and accumulation. Plant Physiol 119(3):1047–1056

Verbruggen N, Hermans C, Schat H (2009) Mechanisms to cope with arsenic or cadmium excess in plants. Curr Opin Plant Biol 12:364–372

Verret F, Gravot A, Auroy P, Leonhardt N, David P, Nussaume L, Vavasseur A, Richaud P (2004) Overexpression of AtHMA4 enhances root-to-shoot translocation of zinc and cadmium and plant metal tolerance. FEBS Lett 576(3):306–312. https://doi.org/10.1016/j.febslet.2004.09.023

Vogel-Mikuš K (2013) *Thlaspi caerulescens* and/or related species: progress and future prospects recent advances towards improved phytoremediation of heavy metal pollution 89

Wang X, Wang H, Wang J, Sun R, Wu J, Liu S, Bai Y, Mun JH, Bancroft I, Cheng F, Huang S, Li X, Hua W, Freeling M, Pires JC, Paterson AH, Chalhoub B, Wang B, Hayward A et al (2011) The genome of the mesopolyploid crop species *Brassica rapa*. Nat Genetic 43(10):1035–1040. https://doi.org/10.1038/ng.919

Wang J, Liang S, Xiang W, Dai H, Duan Y, Kang F, Chai T (2019) A repeat region from the *Brassica juncea* HMA4 gene BjHMA4R is specifically involved in Cd^{2+} binding in the cytosol under low heavy metal concentrations. BMC Plant Biol 19(1):89. https://doi.org/10.1186/s12870-019-1674-5

Westbrook J, Feng Z, Chen L, Yang H, Berman HM (2003) The Protein Data Bank and structural genomics. Nucleic Acids Res 31:489–491

Wheeler DL, Barrett T, Benson DA, Bryant SH, Canese K, Church DM, DiCuccio M, Edgar R, Federhen S, Helmberg W, Kenton DL, Khovayko O, Lipman DJ, Madden TL, Maglott DR, Ostell J, Pontius JU, Pruitt KD, Schuler GD, Schriml LM et al (2005) Database resources of the national center for biotechnology information. Nucleic Acids Res 33(Database issue):D39–D45. https://doi.org/10.1093/nar/gki062

Williams LE, Mills RF (2005) P_{1B}-ATPases–an ancient family of transition metal pumps with diverse functions in plants. Trends Plant Sci 10(10):491–502

Woeste KE, Kieber JJ (2000) A strong loss-of-function mutation in RAN1 results in constitutive activation of the ethylene response pathway as well as a rosette-lethal phenotype. Plant Cell 12(3):443–455

Wong C, Cobbett CS (2009) HMA P-type ATPases are the major mechanism for root-to-shoot Cd translocation in *Arabidopsis thaliana*. New Phytol 181(1):71–78

Wong CKE, Jarvis RS, Sherson SM, Cobbett CS (2009) Functional analysis of the heavy metal binding domains of the Zn/Cd-transporting ATPase, HMA2, in *Arabidopsis thaliana*. New Phytol 181(1):79–88. https://doi.org/10.1111/j.1469-8137.2008.02637.x

Wu Z, Zhao X, Sun X, Tan Q, Tang Y, Nie Z, Hu C (2015) Xylem transport and gene expression play decisive roles in cadmium accumulation in shoots of two oilseed rape cultivars (*Brassica napus*). Chemosphere 119:1217–1223. https://doi.org/10.1016/j.chemosphere.2014.09.099

Wu Y, Li X, Chen D, Han X, Li B, Yang Y, Yang Y (2019) Comparative expression analysis of heavy metal ATPase subfamily genes between Cd-tolerant and Cd-sensitive turnip landraces. Plant Diversity 41(4):275–283

Yu R, Li D, Du X, Xia S, Liu C, Shi G (2017) Comparative transcriptome analysis reveals key cadmium transport-related genes in roots of two pak choi (*Brassica rapa* L. ssp. chinensis) cultivars. BMC Genomics 18(1):587. https://doi.org/10.1186/s12864-017-3973-2

Zhang L, Cai X, Wu J, Liu M, Grob S, Cheng F, Liang J, Cai C, Liu Z, Liu B, Wang F, Li S, Liu F, Li X, Cheng L, Yang W, Li MH, Grossniklaus U, Zheng H, Wang X (2018) Improved *Brassica* *rapa* reference genome by single-molecule sequencing and chromosome conformation capture technologies. Horticult Res 5(1):50. https://doi.org/10.1038/s41438-018-0071-9

Zhang F, Xiao X, Wu X (2020) Physiological and molecular mechanism of cadmium (Cd) tolerance at initial growth stage in rapeseed (*Brassica napus* L.). Ecotoxicol Environ Saf 197(110613). https://doi.org/10.1016/j.ecoenv.2020.110613

Zhiguo E, Tingting LI, Chen C, Lei WANG (2018) Genome-wide survey and expression analysis of P_{1B}-ATPases in rice, maize and sorghum. Rice Sci 25(4):208–217

Zorrig W, Abdelly C, Berthomieu P (2011) The phylogenetic tree gathering the plant Zn/Cd/Pb/Co P_{1B}-ATPases appears to be structured according to the botanical families. C R Biol 334(12):863–871. https://doi.org/10.1016/j.crvi.2011.09.004

Chapter 6
Bioformulations for Sustainable Phytoremediation of Heavy Metal-Polluted Soil

Sana Ashraf, Sajid Rashid Ahmad, Qasim Ali, Muhammad Bilal Shakoor, Sobia Ashraf, Humaira Nawaz, Hina Chaudhry, and Zahra Majid

Abstract Industrialization (industrial waste, paints, sewage discharge, and mining activities), agricultural practices (agricultural runoff, insecticides, and pesticides), and natural sources (soil erosion and weathering) are the main sources of heavy metal contamination of the environment and pose serious threat to the human health. Therefore, removal of heavy metals from the environment is very important to protect the surroundings we live. The traditional physio-chemical methods to phase out toxic metals from soil are not economical and environmentally sound. Indigenous and genetically engineered microorganisms can be used for the bioremediation of the hazardous metal-polluted sites for the stabilization of the ecosystem. Bacterial consortium can also be advantageous for effective bioremediation of toxic metal-contaminated sites. Furthermore, heavy-metal hyperaccumulator (HMH) plants have great potential to concentrate on heavy metals' 100–1000-fold higher in their above-ground tissues in contrast to non-HMHs, thus can be good option to remove the contaminants from the environment.

Keywords Bioformulations · Phytoremediation · Heavy metal · Microbial consortia · Urbanization · Agro-chemicals

---

S. Ashraf (✉) · S. R. Ahmad · M. B. Shakoor · H. Nawaz · Z. Majid
College of Earth and Environmental Sciences, Quaid-e-Azam Campus, University of the Punjab Lahore, Punjab Lahore, Pakistan

Q. Ali
Department of Soil Science, The Islamia University of Bahalwalpur, Bahalwalpur, Pakistan

S. Ashraf
Department of Environmental Sciences & Engineering, Government College University Faisalabad, Faisalabad, Pakistan

H. Chaudhry
Department of Environmental Sciences, Lahore College for Women University, Lahore, Pakistan

L. Newman et al. (eds.), *Phytoremediation*, https://doi.org/10.1007/978-3-031-17988-4_6

6.1 Introduction

Heavy metals are highly poisonous, recalcitrant, and persistent in the ecosystem. Heavy metals have relatively higher atomic number and density, and cause environmental and health consequences (Ma et al. 2011a; Alloway 2012; Bolisetty et al. 2019). Toxic metals can cause mental retardation and cardiovascular, liver, and kidney diseases as well as disturb the normal functioning of the brain. Heavy metals can also cause endocrine disruption, hormonal changes, and psychological problems (Sah et al. 2019). There are different symptoms of toxicity in human health (Järup 2003; Wasi et al. 2013). Toxic heavy metals are mostly ingested, inhaled, and dermally absorbed by humans (Khan et al. 2013; Martin and Dowling 2013; Tongesayi et al. 2013). Their agricultural sources include agricultural runoff, insecticides, pesticides, etc. The industrial sources include industrial waste, paints, sewage discharge, and mining activities. Heavy metals also enter the ecosystem through soil erosion and weathering and should be removed from the environment (Rajkumar et al. 2009; Lum et al. 2014; Bai et al. 2019; Ali et al. 2019).

6.2 Bioremediation of Heavy Metal-Polluted Soils

The traditional physio-chemical methods to phase out toxic metals from soil are not economical and environmentally sound (Maximous et al. 2010; Ma et al. 2011b). However, biological process is very effective to extract heavy metals (Kenneth et al. 2019). In order to stabilise the environment through bioremediation of hazardous metalsmetal-polluted places, native and genetically modified microorganisms should be utilised. These microorganisms can lower the toxicity of heavy metals. Bioremediation will be effective if heavy metal tolerant microbes are utilized (Gupta et al. 2016; Kang et al. 2016). Bacterial consortium can be advantageous for effective bioremediation of toxic metal-contaminated sites. Phytoremediation is a practice that employs fast-growing plants to move hazardous metals from soil (Salt et al. 1998; Liu et al. 2005; Clemens 2006). When plant material is harvested, metals are eliminated from the hazardous sites. There are some specialized plants called heavy-metal hyperaccumulators (HMHs), as they have potential to concentrate heavy metals 100–1000-fold higher in their aboveground tissues in contrast to non-HMHs (Rascio and Navari-Izzo 2011).

6.3 Phytoremediation of Heavy Metal-Polluted Soils

Phytoremediation is an environmentally friendly as well as economical method to rehabilitate toxic metal-polluted sites. In phytoremediation, both plants and rhizospheric microbes eliminate heavy metals from soil (Ali et al. 2013; Dixit et al. 2015; Jan and Parray 2016). The heavy metal removal potential through phytoremediation at any hazardous site depends upon the contamination volume and the plant's efficiency to remove hazardous substances from soil (Tak et al. 2013). In phytoremediation, both hyperaccumulator and non-hyperaccumulator plants are used (Abbaszadeh-Dahaji et al. 2016; Choudhary et al. 2017). Phytoremediation technique comprises the following methods as shown in Fig. 6.1.

6.3.1 Phytoextraction/Phytoaccumulation

Hyperaccumulator plants take up and accumulate heavy metals at high level (Jabeen et al. 2009; Rascio and Navari-Izzo 2011). Based on the process of hyperaccumulation, phytoextraction comprises the movement and uptake of pollutants present in the soil (Jutsz and Gnida 2015). Phytoextraction is a potent process to separate heavy metals from soil. However, there are some problems with this process like the availability and solubility of target metal contaminants (Ma et al. 2011a, b). Rhizobacteria are capable of increasing the phytoremediation process. It can increase the process of solubilization of zinc and phosphorus. It can also change soil pH, release enzymes, and chelate heavy metals (Glick 2010; Rajkumar et al. 2012). Utilizing post-phytoremediation procedures, metals can be extracted from harvested plant material, eliminating the requirement for harmful metals to be mined through phytomining (Anderson et al. 1999; Robinson et al. 1999; Alford et al. 2010; Sheoran et al. 2011).

6.3.2 Phytostimulation

Phytostimulation is the disintegration of organic pollutants by enhanced microbial activity through root exudates rhizosphere. Low concentration of ethylene increases root lengths, while high levels prevent DNA synthesis and cell division. Ethylene

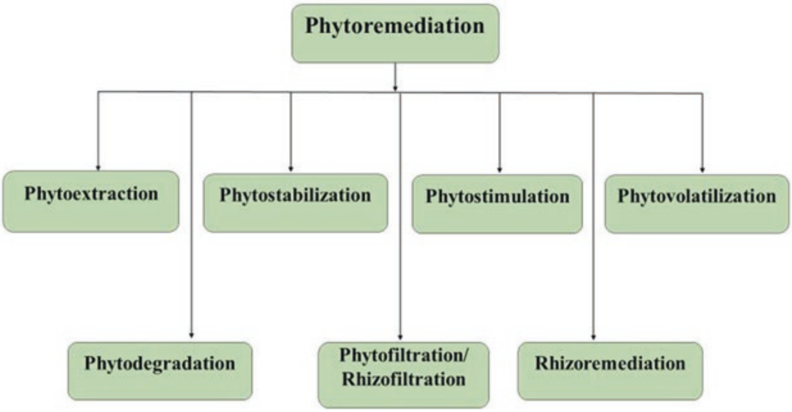


Fig. 6.1 Types of phytoremediation

level in plants can be decreased by 1-aminocyclopropane-1-carboxylase deaminase enzyme to lower the environmental stress in growing plants (Donot et al. 2012; Gaiero et al. 2013). This enzyme is produced by plant growth promoting rhizobacteria (PGPR) that are associated with plant root exudates for getting energy and carbon to degrade pollutants (Tak et al. 2013).

6.3.3 Phytostabilization

In this technique, plant roots are used to extract toxicants from soil and hold within the rhizosphere and prevent toxicants from dispersion in the soil (Lone et al. 2008). The dissolved volume of hazardous metals in soil is lowered by precipitation in rhizosphere (Freitas et al. 2013; Abbaszadeh-Dahaji et al. 2016; Arora et al. 2016; Choudhary and Varma 2016). The concentration of metals available for uptake in soil determines the mobility of metals to plant body and efficiency of phytostabilization (Ma et al. 2011b; Rajkumar et al. 2012; Abbaszadeh-Dahaji et al. 2016). For this technique, plants should have widespread root network and less translocation factor (Islam et al. 2013). The phytostabilization efficacy can be increased by the adding biochar, organic matter and compost by altering the soil pH that will enhance plant productivity and immobilize heavy metals (Tak et al. 2013).

6.3.4 Phytovolatilization

Phytovolatilization is a process in which plants are used to eliminate soil pollutants that are easily converted into vapors and are discharged into the atmosphere (Ali et al. 2013; Rahman et al. 2016). Tobacco plant has the ability to intake CH_3Hg from Hg-contaminated sites and to convert Hg into volatile form to release into atmosphere through leaves (Mukhopadhyay and Maiti 2010; Rayu et al. 2012). By converting pollutants into volatile forms, plants carry out their metabolic processes. The contaminants are converted into volatile form by plant metabolic activity and rhizobacteria (Tak et al. 2013).

6.3.5 Phytodegradation

Phytodegradation disintegrates the organic pollutants either into less or non-toxic compounds by the action of plant enzymes like nitroreductases and dehalogenases (Favas et al. 2014). Optimum temperature and pH are required for complete breakdown of pollutants. The breakdown of organic toxicants in soil can also be augmented by microbes in the rhizosphere, because rhizosphere contains high level of root exudates and consequently high microbial population to degrade contaminants.

However, this method is limited only for organic toxicants, as heavy metals are not biodegradable (Babalola 2010; Mukhopadhyay and Maiti 2010; Ali et al. 2013; Ogunmayowa 2015; Khanam 2016).

6.3.6 Phytofiltration/Rhizofiltration

In phytofiltration, plant roots are exercised to remove contaminants from water (Mesjasz-Przybyłowicz et al. 2004; Dixit et al. 2015; Rahman et al. 2016). The phytofiltration process consists of three forms; first is rhizofiltration that involves the application of plant roots, second is blastofiltration that consists of application of seedlings, and third is caulofiltration that involves the application of evacuated plant shoots. In rhizofiltration, hazardous compounds are removed from groundwater through filtration by plant roots. The land plants are more effective for rhizofiltration than aquatic plants (López-Chuken 2012). Hyperaccumulators plants are appropriate for rhizofiltration. Bioaugmentation of PGPR in polluted site lessens metal toxicity in plants by lowering accessibility of metals in soil (Tak et al. 2013). However, this technology has some limitations that include decrease in remediation potential with high level of toxicants in contaminated site and their intake by test plants (Ma et al. 2011a, b).

6.3.7 Rhizoremediation

The rhizoremediation is the removal of toxicants by microbes present in the rhizosphere (Kuiper et al. 2004; Chaudhry et al. 2005; Zhuang et al. 2007; Segura et al. 2009). The rhizospheric microbes enhance the degradation mechanism by yielding hydrolytic enzymes (Brazil et al. 1995; Daane et al. 2001; Mejare and Bulow 2001; Prasad 2011). For efficient rhizoremediation process, there should be an association between plants and rhizospheric microbes. Root exudates stimulate growth of microorganisms in rhizosphere and consequently enhance rhizoremediation and plant growth by performing different PGP activities like N_2 fixation, phosphorus dissolution, phytohormones, and siderophore production and defense against plant diseases (Kuiper et al. 2004; Newman and Reynolds 2004; Dzantor 2007; Lee et al. 2012). The ACC deaminase-generating bacteria promote plant root growth under hazardous sites (Belimov et al. 2001; Idris et al. 2004; Kuiper et al. 2004; Arshad et al. 2007). Ectomycorrhizal fungi keep safe plant roots from toxicants by coating roots with mycelial sheath (Cairney 2000; Wenzel 2009). The PGPR assists their host plants to survive under heavy metal-stressed soil (Tordoff et al. 2000). The dissolution and accessibility of toxicants in soil depend upon soil pH, clay and organic matter fraction, redox potential, and mineral content. The minerals and organic matter in soil adsorb toxicants and reduce their accessibility (Semple et al. 2003; Mohan et al. 2006). Plant–microbial associations enhance the accessibility of these adsorbed toxicants (Erickson 1997; Ferro et al. 1994). Likewise, plants and rhizospheric microbes secrete biosurfactants and improve the solubility of entrapped toxicants (Wenzel 2009).

In rhizospheric, saprotrophic fungi are very functional in the remediation process as compared to other microbial communities. These fungi form a fungal cover around roots and defend roots from toxicants and also degrade those toxicants (Hassan et al. 2010). Mycorrhizal fungi also have potency to cumulate toxic metals (Gonzales-Chavez et al. 2004; Kuiper et al. 2004; Carnejo et al. 2008). Soil microorganisms also secrete biosurfactants that boost the removal or breakdown of organic toxicants by enhancing their bioavailability. Organic acids exist in anionic forms and chelate metal cations and consequently reduce their mobility and harmful effects on plants and microbes (Ryan et al. 2001; Ling et al. 2015). Likewise, phenolic compounds secreted from plant roots are a carbon pool for microbial growth. To oxidize the phenolic compounds, microorganisms secrete enzymes to co-metabolize the pesticides having the same structures (Chaudhry et al. 2005; Rohrbachen and St-Arnaud 2016). Mechanisms of plant–microbial–metal associations in the rhizosphere include metal detoxification, solubilization, immobilization, distribution, and plant uptake.

6.4 Microorganisms to Enhance Phytoremediation of Polluted Soil

6.4.1 Enhanced Metal Availability in Soil for Phytoextraction

Use of microorganisms in phytoextraction can minimize the groundwater leaching of heavy metals by solubilizing and concentrating heavy metals in the rhizosphere, where maximum microbial activity takes place. Moreover, chelate-producing microorganisms in soil give rise to metal-solubilizing compounds in the rhizosphere for plant uptake.

6.4.2 Improving Plant Uptake of Heavy Metals to Augment Phytoextraction

Enhancing plant growth is another way to stimulate phytoextraction. Plant growth promotion increases plant biomass for more absorption of toxic metals (Robinson et al. 1997). Soil can be bioaugmented with microorganisms to boost plant growth and phytoextraction of heavy metals like *Pseudomonas fluorescens* and *P. tolaasii* inoculations improved canola biomass and consequently Cd-phytoextraction by

72% and 107%, respectively (Dell'Amico et al. 2008). Microorganisms improve plant development by generating plant growth promoting (PGP) compounds like cytokines, gibberellins and indole-3-acetic acid (IAA) and by enhancing accessibility of plant nutrients through solubilizing inorganic phosphate and nitrogen fixation. Microbial siderophores enhance plant development by dissolving ferric iron and also chelate and mobilize heavy metals (Hernlem et al. 1996; Neilands 1995). Phosphate-solubilizing microorganisms produce organic acids in rhizosphere to enhance availability of phosphorus for plant growth but they also increase solubilization of heavy metals through chelation and altering soil pH (Li et al. 2010; Kim et al. 2013). The following processes are associated with microbial remediation:

- Sequestration of toxicants by cell wall components or within cell wall.
- Adjustment of biochemical pathways to restrict metal absorption.
- Transformation of hazardous metals into non-toxic by enzymes (Jan et al. 2014).

6.5 Concept of Plant Growth Promotor Bioformulations

Bioformulations are microbial formulations that are more beneficial than synthetic chemicals as microbes directly interact with pathogens to resist plant infections and to improve plant growth (Rodrigo et al. 2011). Bioformulations consist of single or multi-strains. Multi-strains bioformulations help to advance plant growth under stress conditions. Bioformulations are active products comprising single or multiple valuable strains and are cost effective. Bioformulation includes aids to preserve applied beneficial strains and to transfer them to their targets. Microbial-based bioformulation can be slight or whole substitute for inorganic fertilization and pesticides (Validov et al. 2009; Arora et al. 2010). Bioformulation encompasses an active element, a carrier medium, and an additive. An active element is a living object (microbe or spore) and its viability throughout storing time is the basic requirement for bioformulation preparation (Auld et al. 2003). A carrier medium should be inert to support and establish living organism in or around the plant. Different carrier media like alginate and polyacrylamide beads, cellulose, diatomaceous earth, fine clay, peat, polymers, talc, vermiculite, and xanthan gum improve life-span of the bioformulation. Additives like gums, methyl cellulose, silica gel, and starch save bioformulations from unfavorable environmental circumstances and boost physiochemical and nutritious features of bioformulations (Schisler et al. 2004; Hynes and Boyetchko 2006). Carrier medium can be grouped into three classes:

- Soils (clays, coal, inorganic soil, and peat).
- Waste material of plants.
- Inert materials like alginate beads, crushed rock phosphate, and vermiculite (Bashan 1998).

6.6 Biofertilizers as Bioformulations

Biofertilizers consist of beneficial microorganisms and can increase crop growth by transforming nutrients from unavailable to available form. These microorganisms are grown in laboratory, mixed with proper carrier medium and then applied to fields. They enhance soil health and reduce environmental pollution by lowering the use of chemicals (Tripti 2012). Biofertilizers for plant growth are applied at global level. In bioformulations, different rhizobial species are being used active ingredients. Application of rhizobial inoculants as biofertilizers rather N fertilizers is economical and sustainable substitute (Mia et al. 2007; Mishra and Arora 2016).

6.7 Plant Growth Promoting Microbes

The plant growth promoting microbes (PGPM) are present in soil especially rhizosphere to encourage soil health and plant growth through plant–microbe interaction (Antoun and Prevos 2005; Spaepen et al. 2009). In rhizosphere, there is intense microbial activity primarily by native bacteria as well as fungi (Nelson 2004). The PGPM can be grouped as plant growth-promoting rhizobacteria and fungi. In rhizosphere, there is a mutual link between PGPR and plant roots (Kloepper and Schroth 1978). The PGPR are extensively being applied for plant growth, as they solubilize inorganic compounds, degrade organic compounds, and secrete biologically active materials like antibiotics, chelators, and phytohormones (Kapulnik and Okon 2002; Reddy et al. 2014).

6.7.1 Plant Growth Promoting Rhizobacteria (PGPR)

A vast array of PGPR has been recognized as plant growth promotor species (Beneduzi et al. 2012; Ahemad and Kibret 2014). The PGPR improve plant development directly by N-fixation, phosphorus dissolution, siderophore and ACC deaminase production, iron sequestration, and synthesis of phytohormones (Hirel et al. 2011; Glick 2012; Sayyed et al. 2013; Sharma et al. 2013; Maheshwari et al. 2015). The PGPR indirectly boost plant growth by defeating infectious agents (Fernando et al. 2005; Fatima et al. 2009; Mishra and Arora 2012). The other ways that indirectly contribute toward plant growth by PGPR include competition for niche, generation of inhibitory allelochemicals, and instigation of systemic resistance in plants against stress (Compant et al. 2005).

6.7.1.1 Role of PGPR to Boost Plant Growth Under Abiotic Stress

The rhizospheric bacteria are being utilized for phytoremediation of hazardous sites, as they can tolerate environmental pollutants. Pros and cons of PGPR-induced phytoremediation are presented in Table 6.1. Rhizospheric bacteria enhance nutrients availability for plant development, secrete plant hormones as indole 3-acetic acid, suppress plant pathogens, and remediate heavy metal-contaminated soil (Ahemad and Kibret 2014; Nehra and Choudhary 2015). The PGPR could be intracellular or extracellular (Martínez-Viveros et al. 2010; Ramadan et al. 2016). The PGPB produce hydrogen cyanide (HCN) (antimicrobial compound) for biological control of plant root ailments (Ramette et al. 2003). The valuable PGPR also activate a plant-mediated ISR response to fight pathogens (Ramos et al. 2008). The ISR seems like pathogen-instigated resistance in which non-infected parts of already diseased plants develop more resistance against pathogens (Pieterse et al. 2001). The antagonistic functions of PGPR also produce hydrolytic enzymes to breakdown hyphae of disease-causing fungi (Maksimov et al. 2011). Actinomycete strains act as biocontrol factors against disease-causing fungi (Sreevidya et al. 2016). Actinomycetes help plants through production of phytohormones, antibiotics, and fungal cell wall deteriorating enzymes (Solans et al. 2011).

6.7.2 *Plant Growth Promoting Fungi (PGPF)*

The PGP characteristics of rhizospheric fungi have also been studied (Salas-Marina 2011; Murali et al. 2012). The PGPF like arbuscular mycorrhizal fungi (AMF), *Aspergillus*, *Fusarium*, *Penicillium*, *Phoma,* and *Trichoderma* have potential to stimulate plant development and to overcome the diseases. The AMF enhance plant

Table 6.1 Pros and cons of PGPR-assisted phytoremediation

Pros	Cons
PGPR-aided phytoremediation is an economic approach	PGPR-aided phytoremediation is slow process as compared to physio-chemical techniques
PGPR activate plant development and up take of toxicants by dissolving nutrients and heavy metals	At times, PGPR are heavy metal specific
PGPR are added in rhizosphere to enhance phytoremediation and no maintenance is required	PGPR-aided phytoremediation is limited to contaminated soil as deep as plant roots grow
PGPR-assisted phytoremediation converts toxic compounds into simpler nontoxic form	Post-phytoremediation treatment of plants containing toxic metals is a main issue
Environmentally sound technique	Still transgenic PGPR and plants are not acknowledged worldwide

growth by promoting phosphorus uptake (Smith et al. 2010). The PGPF boost plant growth by secreting plant hormones, breakdown of organic matter, dissolution of soil nutrients, and plant protection under unfavorable environmental conditions (Magdoff and Weil 2004; Khan et al. 2010, 2012). The PGPF also indirectly promote plant growth through predation, mycoparasitism, antibiosis, and niche exclusion, (Benhamou et al. 2002; Bent 2006).

6.8 Techniques for Improving the Manufacturing of Bioformulations

Bioinoculants are microbe-based soil amendments for plant growth promotion. They contain active cells of efficient N-fixing, HCN (hydrogen cyanide) and siderophore yielding microbes. The plant–microbe interaction promotes plant growth by boosting accessibility of nutrients (Imam et al. 2017). Bioinoculants are also employed for seed coating, bioremediation, and induction of systematic acquired resistance (Ma 2019). Many microbial species as *Azospirillum, Bacillus,* mycorrhiza, *Pseudomonas, Rhizobium*, *Trichoderma,* and yeast have been tested as bioinoculants for promoting plants growth (Tahir et al. 2017). Plants get benefits from microorganisms by different means as:

- PGPR that function as bioinoculants.
- Microorganisms secreted phytohormones that directly enhance plant growth.
- Suppressing phytopathogens and also protecting plants from heavy metals during phytoremediation (Tang et al. 2020).

Bioformulations are processed through different approaches and harmful substances are destroyed by microbial activity (Gopi et al. 2019). Different types of bioformulations are shown in Fig. 6.2.

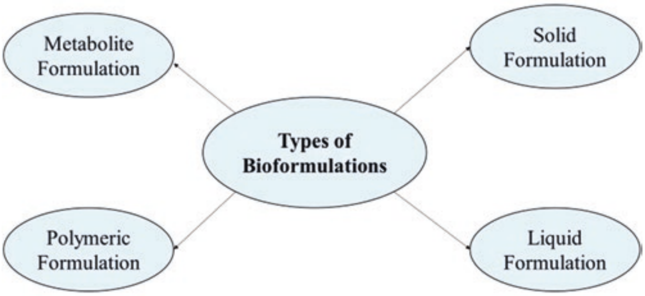


Fig. 6.2 Types of bioformulations

6.8.1 Solid Formulation

In the solid preparation, the desired isolated microbial species is combined with a solid carrier like peat, powder, and granules to provide protecting and nourishing environment to the microbes. Peat must be nontoxic, smoothly sterilized and with excessive water-holding capacity (Ceglie et al. 2015). First, peat is dried, then pass across 250 μm sieve, and finally blend with proper strain. Peat is incubated at a definite temperature in the curing process for the growth of microorganisms. For ectomycorrhizal and arbuscular mycorrhizal fungi, specifically, peat is utilized (Aini et al. 2019). Ectomycorrhiza grow quickly on glucose medium and produce sporophores that are applied in the fields for plant growth promotion. Pure mycelia culture is mixed with glucose and salt medium and 10% peat and 15% vermiculite as a carrier material. Chelating process is increased during this formulation by producing fulvic acid. Before sowing, seed coating is performed with inoculated peat by the assistance of cement mixers and mechanical tumbling machines. Due to different composition and varieties of peat, hazardous substances are secreted from peat in sterilization process that can disturb microbial viability and growth (Malusa et al. 2012).

Hence, granules are being utilized in place of peat, as they are beneficial as compared to peat. Calcite, marble, and silica-based granules are coated with beneficial microbes. Granules are less dusty and easy to store, handle, and transport. Few studies have shown that use of granular inoculants does not result in improved N-fixation. However, some studies have proved that granule-based bioformulation is better than liquid and peat inoculants in terms of N-fixation, nodule number, and total biomass. The granular inoculants have more nitrogen fixation and nodule formation and hence promote plant growth under stressed conditions. Biochar could also be used as a carrier material for bioformulation. Biochar is environment friendly and nontoxic waxy material that helps in the persistence of bioinoculant and plant growth promotion. Biochar has low water content and can be stored without sterilization (Zaidi et al. 2017).

6.8.2 Liquid Formulation

The liquid bioformulation contains those beneficial microbes that have potential to solubilize, fix, or mobilize important plant minerals (Bahadur et al. 2016). Potassium and phosphorus solubilizing microorganisms, nitrogen fixing microbes, and many others are being implemented in preparation of liquid bioformulation (Surendra and Baby 2016). The liquid bioformulation is a modern and advantageous method as compared to carrier-based formulation. The carrier-based formulations have short shelf life (2–3 months) and cannot be retained through all stages of crop growth.

Hence, the liquid formulation is being applied that provides prolong survival rate to applied microbes throughout the crop cycle. Liquid formulation has high temperature and stress tolerance as compared to carrier-based bioinoculants. For the preparation of this formulation, proper sterilization is performed to control contamination, but in carrier-based formulation, bulk sterilization cannot be achieved. Liquid formulation enhances the shelf life of strain up to 19–25 months by retaining high moisture content and protectants for unfavorable conditions (Chandra et al. 2018). The *Azospirillum* with other phosphate-solubilizing strains (*Pseudomonas*, *Bacillus*, and *Penicillium*) is being used for liquid formulation. The storage of 108 cells/mL until 8–10 month duration can be achieved by amending *Azospirillum* with polyvinylpyrrolidone (PVP), glycerol, and trehalose in N-free bromothymol blue meat broth. Because of high water holding ability, PVP defend microorganisms under stressed conditions.

6.8.3 Metabolite Formulation

Metabolite formulations contain microbial metabolites that provide bioregulators and nutrients to plants. For metabolite formulation, *Mesorhizobium*, *Pseudomonas*, *Rhizobium,* and *Trichoderma* strains are used (Tewari and Arora 2016). Flavonoids molecules along with rhizobia can enhance nitrogen fixation under unfavourable conditions. Rhizobium species linked with leguminous host plants discharge lipo-chitooligosachharide molecules to assist in symbiosis in rhizobial deficient soils. Like Rhizobial species, mycorrhizal fungi also secrete Myc factors that assist in symbiosis and stimulate signal transduction pathway (Maillet et al. 2011). Exopolysaccharides (EPSs) discharged by PGPR like *Pseudomonas* and *Rhizobia* promote biofilm formation, root colonization, and nodulation under stressed conditions (Wang et al. 2019). Exopolysaccharides based bioformulation protects microbial strains from unfavorable environmental conditions and toxic substances. Enhanced IAA production by supplementation with tryptophan precursor can enhance grain production, plant weight, and root hair development. Both PGPR and l-methionine (precursor of ethylene) can be applied to enhance plant growth. Amino acids, molasses, and starch wastewater have been used as useful amendments to prepare metabolite formulations. These amendments can enhance the survival rate of beneficial strains under unfavorable environmental conditions (Timmusk et al. 2014). The phosphate solubilizing bacteria secrete biosurfactants possessing antimicrobial properties against plant pathogens (Arora and Mishra 2016). The *Pseudomonas* and *Bacillus* spp. have also studied for antibiotic production and anti-phytopathogenic activities to boost plant growth. The key drawbacks of this bioformulation are high price and generation at large scale. In the future, consortium of different PGPR along with additive and carrier should be considered for metabolite formulation.

6.8.4 Polymeric Formulation

The alginate beads and different bacteria like *Azotobacter* and *Pseudomonas* are utilized for this formulation. The alginate is nontoxic, biodegradable, and liberates slowly in the soil. The development of alginate beads is a complex process (De-Bashan et al. 2012). Alginate beads are anionic copolymer which consist of d-mannuronic acid and l-guluronic acid that are extracted from *Macrocystis pyrifera* (brown algae) and *Sargassum sinicola* (macroalga) (Yabur et al. 2007; Singh et al. 2011). Microbeads and macrobeads are two types of alginate beads that can store 109–110 CFU/g. Many techniques have been established for polymeric formulation by encapsulation of latent cell in the gel matrix. Gel matrix has potential for enhancing the shelf life of bacterial strain under stressed conditions. During encapsulation, essential nutrients like skimmed milk are added that promote growth in the presence of glycerol under aerobic and anaerobic conditions (Schoebitz and Belchi 2016). It has been estimated that chitin-filled beads have more permeability as compared to starch-filled and glycerol–alginate beads can survive better in the presence of UV radiation (Zohar-Perez et al. 2002). Growth of *Sinorhizobium meliloti* can be enhanced utilizing alginate and soy oil to 108 CFU/mL after 10 weeks of storage time (Malusa et al. 2012).

6.9 Role of Plant–Microbial–Metal Associations in Phytoremediation

Plant–microbial–metal associations perform a substantial character in the running of metal cycle and phytoremediation of contaminated environment. Specific plant–microbe–metal associations can enhance efficiency of phytoremediation process. The plant–microbe associations contribute in detoxification, solubilization/immobi lization, and plant uptake of heavy metals for successful remediation of polluted soil (Ma et al. 2011a). The effect of bacterial and fungal activities on dissolution and stabilization of metals for bioremediation of toxic metal-polluted soil has been extensively studied Sessitsch et al. 2013; Ahemad and Kibret 2014). Heavy metal resilient plant growth promoting microorganisms are involved in metal bioaccumulation, bioleaching, and bioexclusion processes. The decreased soil pH, chelation, and protonation processes cause dissolution of metals, while alkalinization, complexation, and precipitation processes reduce metal bioavailability through immobilization.

6.9.1 Metal Detoxification

In microbe-assisted phytoremediation, specific heavy metal tolerant plant and microbes should be used. Once plants are grown under heavy metal-contaminated sites, the metal contaminants activate the physiological and molecular systems of plants to adapt stressed environment. Plants tolerate heavy metals via different processes which include biosorption and bioaccumulation, complexation by peptide ligands within cells, and sequestration of metal–siderophore complexes in root apoplasm or soils (Miransari 2011). The processes taken in microbial metal resistance include:

- Biosorption and in-solubilization of metals.
- Active efflux pumping of metals from cell through transport structure.
- Sequestration of metals in internal cell segments (mostly cell vacuole).
- Discharge of metal chelates into outer cell spaces.
- Enzymatic redox reaction by converting metals into less or non-toxic form.

6.9.2 Biosorption and Bioaccumulation

Biosorption is the surface assimilation of metal ions to a biological matrix by physical (electrostatic forces) and chemical associations (complexation, or chelation). At neutral pH, the cell wall of microbes comprises anionic functional groups like carboxyl, phosphonate, amine, and hydroxyl that deliver attachment sites for binding of cationic HMs (Vijayaraghavan and Yun 2008; Fomina and Gadd 2014). Gram-positive microbes possess high biosorption potential because of their thick peptidoglycan layer that possesses biosorption sites (Van Hullebusch et al. 2003). Biosorption involves exclusion of heavy metals by the means of passive binding from contaminated media; hence, the process is not metabolically dependent. Different species of microbes have been used for adsorption (surface assimilation) of HMs (Ayangbenro and Babalola 2017; Ilyas et al. 2017). Bioaccumulation is a metabolically active method in which microbes take up toxic metals into their inside cell spaces by importer complexes that form a translocation path across the lipid bilayer. In the intracellular spaces, toxic metals could be sequestered by proteins and peptide ligands. Metabolically active bioaccumulation process needs the host cell to be alive (Malik 2004; Mishra and Malik 2013). In-situ bioremediation of heavy metal-polluted sites, the prevention of secondary pollution, and cost effectiveness are benefits of biosorption and bioaccumulation (Abdi and Kazemi 2015).

6.9.3 Bioleaching

Iron- and sulfur-oxidizing bacteria and some other bacterial and fungal species like *Acetobacter*, *Acidophilum*, *Arthrobacter, Pseudomonas, Penicillium*, *Aspergillus, Fusarium,* and *Trichoderma* have capability for leaching of toxic metals from soil, sediments, and sludge and hence alleviate metal phytotoxicity directly or indirectly by different metabolic processes like adsorption, complexation, dissolution, oxidation, and reduction (Pathak et al. 2009). Acidophilic sulfur oxidizing bacteria *Acidithiobacillus thiooxidans* create acidic conditions to bioleach heavy metals (Kumar and Nagendran 2009). Bioleaching potential depends on type of bacterial species and acidophilic bacteria have more bioleaching ability as compared to neutrophilic bacteria.

6.9.4 Metal Mobilization

Metals become insoluble and consequently unavailable for plant uptake because they bind to soil particles or precipitate. The availability of toxic metals in the soil determines how effective phytoextraction is (Ma et al. 2013). For this purpose, metal-solubilizing microbes can be applied to influence the metal speciation and dissolution in soil by decreasing soil pH, protonation, and chelation processes (Rajkumar et al. 2012; Sessitsch et al. 2013). The soil pH is the main characteristic that affects the dissolution of hazardous metals in the soil. Toxic metals become insoluble at higher pH (Richards et al. 2000). The soil pH is mostly impacted by plant and microbial actions. Plant roots secrete exudates in the rhizosphere that can decrease the soil pH by two units in comparison with bulk soil and consequently enhance the dissolution and accessibility of hazardous metals in soil solution for translocation in plants (Alford et al. 2010; Kim et al. 2010; Sheoran et al. 2011). Chen et al. (2014) estimated that inoculation of endophytic bacteria enhanced the excretion of root exudates from *S. alfredii* and consequently improved the Cd bioavailability and plant uptake. Soil microbial population can also reduce pH in rhizosphere zone by transporting protons to exchange toxic metal ions at binding places (Rajkumar et al. 2012).

Root exudates contain organic acids like malate, citrate, acetate, and oxalate (Berkelaar and Hale 2003). Mucha et al. (2005) reported that both malonate and oxalate secreted by *Juncus maritimus* complex heavy metals and enhanced their solubility and bioavailability in soil. However, organic acids secreted by microbes have more influence on enhancing metal solubility than root exudates (Amir and Pineau 2003). The organic acids secreted by plants and microbes are required for different rhizospheric processes like nutrient acquirement, mineral weathering, and detoxification and solubilization of heavy metal in soil (Rajkumar et al. 2012). Organic chelator compounds secreted by plants and microbes have capacity to take metallic ions from sorption places and heavy metal-containing minerals (Gadd 2004).

Natal organic chelators are recognized as biosurfactants, metal-binding composites, metallophores, organic acid anions, and siderophores (Sessitsch et al. 2013). The metal chelation in soil by addition of metal-binding peptides can reduce toxic effects of dissolved metal ions on plants, boost metal sequestration, xylem loading, and uptake by plant (Cai and Ma 2003). Phytochelatins (PCs), the heavy metal binding peptides, are produced from the tripeptide glutathione and also by an enzymatic process activated by PC's synthase (Solanki and Dhankhar 2011). Heavy metal stress instigates the formulation of PCs in plants that help plants to uptake and accumulate heavy metals (Pal and Rai 2010). Microorganisms produce siderophores that have more affinity for metals than PSs, and thus, microbes can be utilized to improve solubility of heavy metals in soil for translocation into plants. In recent times, Yuan et al. (2014) verified that inoculation of endophytic bacteria improved the Cd solubility in metal-spiked soil by liberating siderophores and consequently improved Cd translocation and accumulation by *Amaranthus hypochondriacus* and *A. mangostanus*.

6.9.5 Metal Immobilization

Microorganisms can also decrease the metal solubility and bioavailability through precipitation, complexation, and alkalinization processes. Sulfate-reducing bacteria (SRB) precipitate heavy metals and diminish their mobility in soil. Hence, SRB can be useful for phytostabilization of hazardous metal-polluted sites (Blazquez et al. 2016). In heavy metal-contaminated soil, plant-associated microorganisms excrete EPSs for biosorption of hazardous metals and lessen the accessibility of hazardous metals for plant uptake (Hou et al. 2013). The processes associated with metal biosorption on EPSs are adsorption, complexation by negatively charged functional groups, ion exchange, and precipitation (Zhang et al. 2006). Some arbuscular mycorrhizal fungi (AMF) and bacteria like SRB and cyanobacteria absorb metals by alkalinization in the rhizosphere and reduce the metal solubility in soil (Büdel et al. 2004). The AMF induce the alkalinizing reaction by releasing hydroxyl ions and diminish metal bioavailability in the rhizosphere. In short, AMF serve as metal binding agents to decrease metal dissolution and availability in soil and hence promote plant growth under metal-polluted sites (Gohre and Paszkowski 2006).

6.10 Plant Mechanisms for Metal Detoxification

High volume of heavy metals in soil prevents plant development by hindering normal metabolic functions via formation of reactive oxygen species (ROS). Heavy metal toxicity prevents enzymatic activity that affects the framework of the cytoplasmic membrane and function of photosynthesis and respiration processes (Gupta et al. 2015; Ali et al. 2013; Emamverdian et al. 2015; Krumova et al. 2016; Hossain et al. 2012). The first line of protection from heavy metals in plants involves physical blocks like morphological structures that include hard cuticle, biologically active tissues such as trichomes and cell walls and also mycorrhizal symbiosis that function as biophysical blocks when plants are exposed to heavy metals (Emamverdian et al. 2015). If heavy metals cross these blocks and enter plant cells, then antioxidant defense system becomes active to lessen the damaging consequences of heavy metals. Plants naturally have antioxidant defense system to remove the toxicity of ROS via production of enzymatic antioxidants like catalase, glutathione reductase, and superoxide dismutase and non-enzymatic antioxidants like alkaloids, ascorbate, glutathione, and tocopherols (Skórzynska-Polit et al. 2010; Rastgoo et al. 2011; Sharma et al. 2012).

6.11 Conclusions

Single or multi-strain bioformulations help to advance plant growth under environmental stress conditions and also to remediate heavy metal-polluted soil. Combining microbial bioremediation and phytoremediation is an effectual and environment-friendly method to retrieve heavy metal-polluted soil by employing inherent biological mechanisms of microorganisms and plants. Beneficial microorganisms like endophytes or rhizosphere bacteria and fungi may lessen metal phytotoxicity and enhance plant growth indirectly by instigating defense system to fight pathogens and directly by dissolution of minerals. These beneficial microorganisms can also influence metal accessibility in soil by different processes like acidification, chelation, complexation, precipitation, and redox reactions.

References

Abbaszadeh-Dahaji P, Omidvari M, Ghorbanpour M (2016) Increasing phytoremediation efficiency of heavy metal-contaminated soil using PGPR for sustainable agriculture. In: Choudhary DK, Varma A, Tuteja N (eds) Plant microbe interaction: an approach to sustainable agriculture. Springer, New Delhi, pp 187–204

Abdi O, Kazemi M (2015) A review study of biosorption of heavy metals and comparison between different biosorbents. J Mater Environ Sci 6:1386–1399

Ahemad M, Kibret M (2014) Mechanisms and applications of plant growth promoting rhizobacteria: current perspective. J King Saudi Univ Sci 26:1–20

Aini N, Yamika WSD, Ulum B (2019) Effect of nutrient concentration PGPR and AMF on plant growth, yield, and nutrient uptake of hydroponic lettuce. Int J Agric Biol 21(1):175–183

Alford ÉR, Pilon-Smits EAH, Paschke MW (2010) Metallophytes-a view from the rhizosphere. Plant Soil 337:33–50

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

Ali F, Jilani G, Fahim R, Bai L, Wang C, Tian L, Jiang H (2019) Functional and structural roles of wiry and sturdy rooted emerged macrophytes root functional traits in the abatement of nutrients and metals. J Environ Manag 249:109330

Alloway BJ (2012) Heavy metals in soils: trace metals and metalloids in soils and their bioavailability, 22 Vol. Springer Science & Business Media

Amir H, Pineau R (2003) Release of Ni and Co by microbial activity in New Caledonian ultramafic soils. Can J Microbiol 49:288–293

Anderson CWN, Brooks RR, Chiarucci A, LaCoste CJ, Leblanc M, Robinson BH, Simcock R, Stewart RB (1999) Phytomining for nickel, thallium and gold. J Geochem Explor 67:407–415

Antoun H, Prevos D (2005) Ecology of plant growth promoting rhizobacteria. In: Siddiqui ZA (ed) PGPR: biocontrol and biofertilization. Springer, Dordrecht, pp 1–38

Arora NK, Mishra J (2016) Prospecting the roles of metabolites and additives in future bioformulations for sustainable agriculture. Appl Soil Ecol 107:405–407

Arora NK, Khare E, Maheshwari DK (2010) Plant growth promoting rhizobacteria: constraints in bioformulation, commercialization, and future strategies. In: Plant growth and health promoting bacteria. Springer, Berlin, Heidelberg, pp 97–116

Arora K, Sharma S, Monti A (2016) Bio-remediation of Pb and Cd polluted soils by switchgrass: a case study in India. Int J Phytoremediation 18:704–709

Arshad M, Saleem M, Hussain S (2007) Perspectives of bacterial ACC deaminase in phytoremediation. Trends Biotechnol 25:356–362

Auld BA, Hetherington SD, Smith HE (2003) Advances in bioherbicide formulation. Weed Biol Manag 3:61–67

Ayangbenro AS, Babalola OO (2017) A new strategy for heavy metal polluted environments: a review of microbial biosorbents. Int J Environ Res Public Health 14:94

Babalola OO (2010) Beneficial bacteria of agricultural importance. Biotechol Lett 32:1559–1570

Bahadur I, Maurya BR, Kumar A, Meena VS, Raghuwanshi R (2016) Towards the soil sustainability and potassium-solubilizing microorganisms. In: Meena VS, Maurya BR, Verma JP, Meena RS (eds) Potassium solubilizing microorganisms for sustainable agriculture. Springer, New Delhi, pp 255–266

Bai J, Zhao Q, Wang W, Wang X, Jia J, Cui B, Liu X (2019) Arsenic and heavy metals pollution along a salinity gradient in drained coastal wetland soils: depth distributions, sources and toxic risks. Ecol Indic 96:91–98

Bashan Y (1998) Inoculants of plant growth-promoting bacteria for use in agriculture. Biotechnol Adv 16(4):729–770

Belimov AA, Safronova VI, Sergeyeva TA, Egorova TN, Matveyeva VA, Tsyganov VE (2001) Characterization of plant growth-prompting rhizobacteria isolated from polluted soils and containing 1-aminocyclopropane-1-carboxylate deaminase. Can J Microbiol 47:642–652

Beneduzi A, Ambrosini A, Passaglia LMP (2012) Plant growth-promoting rhizobacteria (PGPR): their potential as antagonists and biocontrol agents. Genet Mol Biol 35:1044–1051

Benhamou N, Garand C, Goulet A (2002) Ability of nonpathogenic *Fusarium oxysporum* strain Fo47 to induce resistance against *Pythium ultimum* infection in cucumber. Appl Environ Microbiol 68:4044–4060

Bent E (2006) Induced systemic resistance mediated by plant growth-promoting rhizobacteria (PGPR) and fungi (PGPF). In: Tuzun S, Bent E (eds) Multigenic and induced systemic resistance in plants. Springer, Boston, pp 225–258

Berkelaar E, Hale BA (2003) Accumulation of cadmium by durum wheat roots: bases for citrate-mediated exceptions to the free ion model. Environ Toxicol Chem 22:1155–1161

Blazquez E, Gabriel D, Antonio Baeza J, Guisasola A (2016) Treatment of high-strength sulfate wastewater using an autotrophic biocathode in view of elemental sulfur recovery. Water Res 105:395–405

Bolisetty S, Peydayesh M, Mezzenga R (2019) Sustainable technologies for water purification from heavy metals: review and analysis. Chem Soc Rev 48(2):463–487

Brazil GM, Kenefick L, Callanan M, Haro A, Lorenzo VD, Dowling DN, Gara FO (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

Büdel B, Weber B, Kuhl M, Pfanz H, Sultemeyer D, Wessels D (2004) Reshaping of sandstone surfaces by cryptoendolithic cyanobacteria: bioalkalization causes chemical weathering in arid landscapes. Geobiology 2:261–268

Cai Y, Ma LQ (2003, January) Metal tolerance, accumulation, and detoxification in plants with emphasis on arsenic in terrestrial plants. In: ACS Symposium Series, American Chemical Society 835, Washington, DC, pp. 95–114

Cairney JWG (2000) Evolution of mycorrhiza systems. Naturwissenschaften 87:467–475

Carnejo P, Meier S, Borie G, Rillig MC, Borie F (2008) Glomalin-related soil protein in a Mediterranean ecosystem affected by a copper smelter and its contribution to Cu and Zn sequestration. Sci Total Environ 406:154–160

Ceglie FG, Bustamante MA, Amara MB, Tittarelli F (2015) The challenge of peat substitution in organic seedling production: optimization of growing media formulation through mixture design and response surface analysis. PLoS One 10(6):1–14

Chandra D, Barh A, Sharma IP (2018) Plant growth promoting bacteria: a gateway to sustainable agriculture. Microb Biotechnol Environ Monit Cleanup 2018:318–338

Chaudhry Q, Blom-Zandstra M, Gupta S, Joner EJ (2005) Utilising the synergy between plants and rhizosphere microorganisms to enhance breakdown of organic pollutants in the environment. Environ Sci Pollut Res 12(1):34–48

Chen B, Zhang Y, Rafiq MT, Khan KY, Pan F, Yang X (2014) Improvement of cadmium uptake and accumulation in *Sedum alfredii* by endophytic bacteria Sphingomonas SaMR12: effects on plant growth androot exudates. Chemosphere 117:367–373

Choudhary DK, Varma A (2016) Microbial-mediated induced systemic resistance in plants. Springer, New York

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. Biochimie 88:1707–1719

Compant S, Duffy B, Nowak J, Clement C, Barka EA (2005) Use of plant growth-promoting bacteria for biocontrol of plant diseases: principles, mechanisms of action, and future prospects. Appl Environ Microbiol 71:4951–4959

Daane LL, Harjono I, Zylstra GJ, Haggblom MM (2001) Isolation and characterization of polycyclic aromatic hydrocarbon– degrading bacteria associated with the rhizosphere of salt marsh plants. Appl Environ Microbiol 67:2683–2691

De-Bashan LE, Hernandez JP, Bashan Y (2012) The potential contribution of plant growth-promoting bacteria to reduce environmental degradation-a comprehensive evaluation. Appl Soil Ecol 61:171–189

Dell'Amico E, Cavalca L, Andreoni V (2008) Improvement of Brassica napus growth under cadmium stress by cadmium-resistant rhizobacteria. Soil Biol Biochem 40:74–84

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

Donot F, Fontana A, Baccou J, Schorr-Galindo S (2012) Microbial exopolysaccharides: Main examples of synthesis, excretion, genetics and extraction. Carbohydr Polym 87:951–962

Dzantor EK (2007) Phytoremediation: the state of rhizosphere "engineering" for accelerated rhizodegradation of xenobiotic contaminants. J Chem Technol Biotechnol 82:228–232

Emamverdian A, Ding Y, Mokhberdoran F, Xie Y (2015) Heavy metal stress and some mechanisms of plant defense response. Sci World J 2015:756120

Erickson LE (1997) An overview of research on the beneficial effects of vegetation in contaminated soil. Ann N Y Acad Sci 829:30–35

Fatima Z, Saleemi M, Zia M, Sultan T, Aslam M, Rehman RU, Chaudhary MF (2009) Antifungal activity of plant growth-promoting rhizobacteria isolates against *Rhizoctonia solani* in wheat. Afr J Biotechnol 8:219–225

Favas PJC, Pratas J, Varun M, Souza RD, Paul MS (2014) Phytoremediation of soils contaminated with metals and metalloids at mining areas: potential of native flora. In: Maria C, Hernandez S (eds) Environmental risk assessment of soil contamination. In Tech, Shanghai, pp 485–517

Fernando WGD, Ramarathnam R, Krishnamoorthy AS, Savchuk SC (2005) Identification and use of potential bacterial organic antifungal volatiles in biocontrol. Soil Biol Biochem 37:955–964

Ferro AM, Sims RC, Bugbee B (1994) Hycrest crested wheatgrass accelerates the degradation of pentachlorophenol in soil. J Environ Qual 23:272–279

Fomina M, Gadd GM (2014) Biosorption: current perspectives on concept, definition and application. Bioresour Technol 160:3–14

Freitas EV, Nascimento CW, Souza A, Silva FB (2013) Citric acid-assisted phytoextraction of lead: a field experiment. Chemosphere 92:213–217

Gadd GM (2004) Microbial influence on metal mobility and application for bioremediation. Geoderma 122:109–119

Gaiero JR, McCall CA, Thompson KA, Day NJ, Best AS, Dunfield KE (2013) Inside the root microbiome: bacterial root endophytes and plant growth promotion. Am J Bot 100:1738–1750

Glick BR (2010) Using soil bacteria to facilitate phytoremediation. Biotechnol Adv 28(3):367–374

Glick BR (2012) Plant growth-promoting bacteria: mechanisms and applications. Scientifica 2012:15

Gohre V, Paszkowski U (2006) Contribution of the arbuscular mycorrhizal symbiosis to heavy metal phytoremediation. Planta 223:1115–1122

Gonzales-Chavez MC, Carrillo-Gonzales R, Wright SF, Nichols KA (2004) The role of glomalin, a protein produced by arbuscular mycorrhizal fungi, in sequestering potentially toxic elements. Environ Pollut 130:317–323

Gopi GK, Meenakumari KS, Nysanth NS, Subha P (2019) An optimized standard liquid carrier formulation for extended shelf-lifeof plant growth promoting bacteria. Rhizosphere 11:100–160

Gupta VK, Nayak A, Agarwal S (2015) Bioadsorbents for remediation of heavy metals: current status and their future prospects. Environ Eng Res 20:1–18

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

Hassan S, St-Arnaud M, Labreque M, Hijri M (2010) Phytoremediation: biotechnological procedures involving plants and arbuscular mycorrhizal fungi. In: Devarajan Thangadurai CAB, Hijri M (eds) Mycorrhizal biotechnology. CRC Press, New York, p 152

Hernlem BJ, Vane LM, Sayles GD (1996) Stability constants for complexes of the siderophore desferrioxamine B with selected heavy metal cations. Inorg Chim Acta 244:179–184

Hirel B, Tétu T, Lea PJ, Dubois F (2011) Improving nitrogen use efficiency in crops for sustainable agriculture. Sustainability 3(12):1452–1485

Hossain MA, Piyatida P, da Silva JAT, Fujita M (2012) Molecular mechanism of heavy metal toxicity and tolerance in plants: central role of glutathione in detoxification of reactive oxygen species and methylglyoxal and in heavy metal chelation. J Bot 2012:872875

Hou W, Ma Z, Sun L, Han M, Lu J, Li Z (2013) Extracellular polymeric substances from copper-tolerance *Sinorhizobium meliloti* immobilize Cu^{2+}. J Hazard Mater 261:614–620

Idris R, Trifonova R, Puschenreiter M, Wenzel WW, Sessitsch A (2004) Bacterial communities associated with flowering plants of the Ni hyperaccumulator *Thlaspi goesingense*. Appl Environ Microbiol 70:2667–2677

Ilyas S, Kim MS, Lee JC, Jabeen A, Bhatti HN (2017) Bio-reclamation of strategic and energy critical metals from secondary resources. Metals 7:1–17

Imam J, Shukla P, Prasad Mandal N, Variar M (2017) Microbial interactions in plants: perspectives and applications of pro-teomics. Curr Protein Pept Sci 18(9):956–965

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

Jabeen R, Ahmad A, Iqbal M (2009) Phytoremediation of heavy metals: physiological and molecular mechanisms. Bot Rev 75:339–364

Jan S, Parray JA (2016) Approaches to heavy metal tolerance in plants. Springer, Singapore

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

Järup L (2003) Hazards of heavy metal contamination. Br Med Bull 68:167–182

Jutsz AM, Gnida A (2015) Mechanisms of stress avoidance and tolerance by plants used in phytoremediation of heavy metals. Arch Environ Prot 41:104–114

Kang CH, Kwon YJ, So JS (2016) Bioremediation of heavy metals by using bacterial mixtures. Ecol Eng 89:64–69

Kapulnik Y, Okon Y (2002) Plant growth promotion by rhizosphere bacteria. In: Waisel Y, Eshel A, Kafkafi U (eds) Plant roots: the hidden half. Marcel Dekker, New York, pp 869–885

Kenneth OC, Nwadibe EC, Kalu AU, Unah UV (2019) Plant growth promoting rhizobacteria (PGPR): a novel agent for sustainable food production. Am J Agric Biol Sci 14:35–54

Khan MS, Zaidi A, Ahemad M, Oves M, Wani PA (2010) Plant growth promotion by phosphate solubilizing fungi – current perspective. Arch Agron Soil Sci 56:73–98

Khan AL, Hamayun M, Radhakrishnan R (2012) Mutualistic association of *Paecilomyces formosus* LHL10 offers thermotolerance to *Cucumis sativus*. Antonie Van Leeuwenhoek 101(2):267–279

Khan S, Shahnaz M, Jehan N (2013) Drinking water quality and human health risk in Charsadda district. Pakistan J Clean Prod 60:93–101

Khanam A (2016) Phytoremediation: a green bio-engineering technology for cleanup the environmental contaminants. Int J Recent Sci Res 7:9925–9928

Kim S, Lim H, Lee I (2010) Enhanced heavy metal phytoextraction by Echinochloa crus-galli using root exudates. J Biosci Bioeng 109:47–50

Kim JO, Lee YW, Chung J (2013) The role of organic acids in the mobilization of heavy metals from soil. KSCE J Civ Eng 17:1596–1602

Kloepper JW, Schroth MN (1978) Association of in vitro antibiosis with inducibility of increased plant growth by Pseudomonas spp. (Abstr). Phytopathol News 12:136

Krumova E, Kostadinova N, Miteva-Staleva J, Gryshko V, Angelova M (2016) Cellular response to Cu-and Zn-induced oxidative stress in aspergillus fumigatus isolated from polluted soils in Bulgaria. Clean Soil Air Water 44:657–666

Kuiper I, Lagendijk EL, Bloemberg GV, Lugtenberg BJ (2004) Rhizoremediation: a beneficial plant-microbe interaction. Mol Plant-Microbe Interact 17:6–15

Kumar N, Nagendran R (2009) Fractionation behavior of heavy metals in soil during bioleaching with *Acidithiobacillus thiooxidans*. J Hazard Mater 169:1119–1126

Lee S, Ka JO, Gyu SH (2012) Growth promotion of Xanthium italicum by application of rhizobacterial isolates of *Bacillus aryabhattai* in microcosm soil. J Microbiol 50:45–49

Li WC, Ye ZH, Wong MH (2010) Metal mobilization and production of short-chain organic acids by rhizosphere bacteria associated with a Cd/Zn hyperaccumulating plant, Sedum alfredii. Plant Soil 326:453–467

Ling W, Sun R, Gao X, Xu R, Li H (2015) Low-molecular-weight organic acids enhance desorption of polycyclic aromatic hydrocarbons from soil. Eur J Soil Sci 66:339–347

Liu H, Probst A, Liao B (2005) Metal contamination of soils and crops affected by the Chenzhou lead/zinc mine spill (Hunan, China). Sci Total Environ 339:153–166

Lone MI, He ZL, Stoffella PJ, Yang XE (2008) Phytoremediation of heavy metal polluted soils and water: progresses and perspectives. J Zhejiang Univ Sci B 9:210–220

López-Chuken UJ (2012) Hydroponics and environmental clean-up. In: Toshiki A (ed) Hydroponics-A standard methodology for plant biological researches. InTech, Shanghai, p 181

Lum AF, Ngwa ESA, Chikoye D (2014) Phytoremediation potential of weeds in heavy metal contaminated soils of the Bassa industrial zone of Douala. Cameroon Int J Phytoremediation 16:302–319

Ma Y (2019) Seed coating with benefcial microorganisms for preci-sion agriculture. Biotechnol Adv 37(7):107423

Ma Y, Rajkumar M, Luo Y, Freitas H (2011a) Inoculation of endophytic bacteria on host and non-host plants – effects on plant growth and Ni uptake. J Hazard Mater 195:230–237

Ma Y, Prasad MNV, Rajkumar M, Freitas H (2011b) Plant growth promoting rhizobacteria and endophytes accelerate phytoremediation of metalliferous soils. Biotechnol Adv 29:248–258

Ma Y, Rajkumar M, Luo Y, Freitas H (2013) Phytoextraction of heavy metal polluted soils using sedum plumbizincicola inoculated with metal mobilizing Phyllobacterium myrsinacearum RC6b. Chemosphere 93:1386–1392

Magdoff F, Weil RR (2004) Soil organic matter in sustainable agriculture, 412 Vol. CRC Press, Boca Raton

Maheshwari DK, Dheeman S, Agarwal M (2015) Phytohormone-producing PGPR for sustainable agriculture. In: Maheshwari DK (ed) Bacterial metabolites in sustainable agroecosystem. Springer, Cham, pp 159–182

Maillet F, Poinsot V, André O (2011) Fungal lipochitooligo-saccharide symbiotic signals in arbuscular mycorrhiza. Nature 469(7328):58

Maksimov IV, Abizgildina RR, Pusenkova LI (2011) Plant growth promoting rhizobacteria as alternative to chemical crop protectors from pathogens. Appl Biochem Microbiol 47:333–345

Malik A (2004) Metal bioremediation through growing cells. Environ Int 30:261–278

Malusa E, Sas-Paszt L, Ciesielska J (2012) Technologies for benefcial microorganisms inocula used as biofertilizers. Sci World J 2012:1–12

Martin R, Dowling K (2013) Trace metal contamination of mineral spring water in an historical mining area in regional Victoria. Australia J Asian Earth Sci 77:262–267

Martínez-Viveros O, Jorquera M, Crowley D, Gajardo G, Mora M (2010) Mechanisms and practical considerations involved in plant growth promotion by rhizobacteria. J Soil Sci Plant Nutr 10:29–319

Maximous NN, Nakhla GF, Wan WK (2010) Removal of heavy metals from wastewater by adsorption and membrane processes: a comparative study. Eng Technol 4(4):532–537

Mejare M, Bulow L (2001) Metal-binding proteins and peptides in bioremediation and phytoremediation of heavy metals. Trends Biotechnol 19:67–73

Mesjasz-Przybyłowicz J, Nakonieczny M, Migula P, Augustyniak M, Tarnawska M, Reimold W, Koeberl C, Przybyłowiczand W, Głowacka E (2004) Uptake of cadmium, lead nickel and zinc from soil and water solutions by the nickel hyperaccumulator Berkheya coddii. Acta Biol Crac Ser Bot 46:75–85

Mia MAB, Shamsuddin ZH, Zakaria W (2007) Associative nitrogen fixation by Azospirillum and bacillus spp. in bananas. Infomusa 16(1–2):11–15

Miransari M (2011) Hyperaccumulators, arbuscular mycorrhizal fungi and stress of heavy metals. Biotechnol Adv 29(6):645–653

Mishra S, Arora NK (2012) Evaluation of rhizospheric Pseudomonas and Bacillus as biocontrol tool for *Xanthomonas campestris* pv campestris. World J Microbiol Biotechnol 28(2):693–702

Mishra J, Arora NK (2016) Bioformulations for plant growth promotion and combating phytopathogens: a sustainable approach. In: Arora NK, Mehnaz S, Balestrini R (eds) Bioformulations: for sustainable agriculture. Springer, New Delhi, pp 3–33

Mishra A, Malik A (2013) Recent advances in microbial metal bioaccumulation. Crit Rev Environ Sci Technol 43:1162–1222

Mohan SV, Kisa T, Ohkuma T, Kanaly RA, Shimizu Y (2006) Bioremediation technologies for treatment of PAH contaminated soil and strategies to enhance process efficiency. Rev Environ Sci Biotechnol 5:347–374

Mucha AP, Marisa C, Almeida R, Bordalo AA, Teresa M, Vasconcelos SD (2005) Exudation of organic acids by a marsh plant and implications on trace metal availability in the rhizosphere of estuarine sediments. Estuar Coast Shelf Sci 65:191–198

Mukhopadhyay S, Maiti SK (2010) Phytoremediation of metal mine waste. Appl Ecol Environ Res 8:207–222

Murali M, Amruthesh KN, Sudisha J, Niranjana SR, Shetty HS (2012) Screening for plant growth promoting fungi and their ability for growth promotion and induction of resistance in pearl millet against downy mildew disease. J Phytology 4(5):30–36

Nehra V, Choudhary MA (2015) 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

Neilands JB (1995) Siderophores: Structure and function of microbial iron transport compounds. J Biol Chem 270(45):26723–26726

Nelson LM (2004) Plant growth promoting rhizobacteria (PGPR): prospects for new inoculants. Crop Manag 3(1):1–7

Newman LA, Reynolds CM (2004) Phytodegradation of organic compounds. Curr Opin Biotechnol 15:225–230

Ogunmayowa OT (2015) Coupling Bio/phytoremediation with switchgrass to biofuel feedstock production in mixed-contaminant soils, Ph.D. Thesis. Tennessee State University, Nashville

Pal R, Rai JPN (2010) Phytochelatins: peptides involved in heavy metal detoxification. Appl Biochem Biotechnol 160:945–963

Pathak A, Dastidar MG, Sreekrishnan TR (2009) Bioleaching of heavy metals from sewage sludge: a review. J Environ Manag 90:2343–2353

Pieterse CMJ, Ton J, Van Loon LC (2001) Cross-talk between plant defence signalling pathways:boost or burden? AgBiotechNet 3:1–8

Prasad MNV (2011) A state of the art report on bioremediation, its applications to contami-nated sites in India. Ministry of Environment and Forests, Government of India, New Delhi

Rahman MA, Reichman SM, Filippis LD, Sany SBT, Hasegawa H (2016) Phytoremediation of toxic metals in soils and wetlands: concepts and applications. In: Hasegawa H, Rahman MM, Rahman I (eds) Environmental remediation technologies for metal-contaminated soils. Springer, Tokyo, pp 161–195

Rajkumar M, Prasad MNV, Freitas H (2009) Biotechnological applications of serpentine soil bacteria for phytoremediation of trace metals. Crit Rev Biotechnol 29:120–130

Rajkumar M, Sandhya S, Prasad MNV, Freitas H (2012) Perspectives of plant-associated microbes in heavy metal phytoremediation. Biotechnol Adv 30:1562–1574

Ramadan EM, AbdelHafez AA, Hassan EA, Saber FM (2016) Plant growth promoting rhizobacteria and their potential for biocontrol of phytopathogens. Afr J Microbiol Res 10:486–504

Ramette A, Frapolli M, Défago G, Moënne-Loccoz Y (2003) Phylogeny of HCN synthase- encoding hcnBC genes in biocontrol fluorescent Pseudomonads and its relation-ship with host plant species and HCN synthesis ability. Mol Plant Microbe Interact 16:525–535

Ramos SB, Barriuso MJ, Pereyra de la Iglesia MT, Domenech J, Gutierrez MFT (2008) Systemic disease protection elicited by plant growth promoting rhizobacteria strains: relationship between metabolic responses, systemic disease protection, and biotic elicitors. Phytopathology 98(4):451–457

Rascio N, Navari-Izzo F (2011) Heavy metal hyperaccumulating plants: how and why do they do it? And what makes them so interesting? Plant Sci 180:169–181

Rastgoo L, Alemzadeh A, Afsharifar A (2011) Isolation of two novel isoforms encoding zinc and copper-transporting P1b-atpase from gouan (*Aeluropus littoralis*). Plant Omics J 4:377–383

Rayu S, Karpouzas DG, Singh BK (2012) Emerging technologies in bioremediation: constraints and opportunities. Biodegradation 23:917–926

Reddy MS, Rodolfo II, Patricio SF, William DD, William DB, Riyaz S, Sudini H, Vijay KKK, Armanda A, Gopalkrishnan S (2014) Recent advances in biofertilizers and biofungicides (PGPR) for sustainable agriculture. Cambridge Scholars Publishing, Newcastle Upon Tyne, p 540

Richards BK, Steenhuis TS, Peverly JH, McBride MB (2000) Effect of sludge-processing mode, soil texture and soil pH on metal mobility in undisturbed soil columns under accelerated loading. Environ Pollut 109(2):327–346

Robinson BH, Chiarucci A, Brooks RR (1997) The nickel hyperaccumulator plant Alyssum bertolonii as a potential agent for phytoremediation and phytomining of nickel. J Geochem Explor 59:75–86

Robinson BH, Brooks RR, Gregg PEH (1999) The nickel phytoextraction potential of some ultramafic soils as determined by sequential extraction. Geoderma 87:293–304

Rodrigo R, González J, Paoletto F (2011) The role of oxidative stress in the pathophysiology of hypertension. Hypertens Res 34(4):431–440

Rohrbachen F, St-Arnaud M (2016) Root exudation: the ecological driver of hydrocarbon rhizoremediation. Agronomy 6(19):1–27

Ryan PR, Delhaize E, Jones DL (2001) Function and mechanism of organic anion exudation from plant roots. Ann Rev Plant Physiol Plant Mol Biol 52:527–560

Sah D, Verma PK, Kandikonda MK, Lakhani A (2019) Pollution characteristics, human health risk through multiple exposure pathways, and source apportionment of heavy metals in PM10 at Indo-Gangetic site. Urban Clim 27:149–162

Salas-Marina MA (2011) The plant growth-promoting fungus Aspergillus ustus promotes growth and induces resistance against different lifestyle pathogens in Arabidopsis thaliana. J Microbiol Biotechnol 21:686–696

Salt DE, Smith RD, Raskin I (1998) Phytoremediation. Annu Rev Plant Physiol Plant Mol Biol 49:643–668

Sayyed RZ, Chincholkar SB, Reddy MS, Gangurde NS, Patel PR (2013) Siderophore producing PGPR for crop nutrition and phytopathogen suppression. In: Maheshwari KD (ed) Bacteria in agrobiology: disease management. Springer, Berlin, pp 449–471

Schisler DA, Slininger PJ, Behle RW, Jackson MA (2004) Formulation of Bacillus spp. for biological control of plant diseases. Phytopathology 94:1267–1271

Schoebitz M, Belchi MDL (2016) Encapsulation techniques for plant growth-promoting rhizobacteria. In: Arora NK, Mehnaz S, Balestrini R (eds) Bioformulations for sustainable agriculture. Springer, New Delhi, pp 251–265

Segura A, Rodríguez-Conde S, Ramos C, Ramos JL (2009) Bacterial responses and interactions with plants during rhizoremediation. Microb Biotechnol 2:452–464

Semple KT, Morriss AWJ, Paton GI (2003) Bioavailability of hydrophobic contaminants in soils: fundamental concepts and techniques for analysis. Eur J Soil Sci 54:809–818

Sessitsch A, Kuffner M, Kidd P, Vangronsveld J, Wenzel WW, Fallmann K (2013) The role of plant-associated bacteria in the mobilization and phytoextraction of trace elements in contaminated soils. Soil Biol Biochem 60:182–194

Sharma P, Jha AB, Dubey RS, Pessarakli M (2012) Reactive oxygen species, oxidative damage, and antioxidative defense mechanism in plants under stressful conditions. J Bot 2012:1

Sharma SB, Sayyed RZ, Trivedi MH, Gobi TA (2013) Phosphate solubilizing microbes: sustainable approach for managing phosphorus deficiency in agricultural soils. Springerplus 2(1):14

Sheoran V, Sheoran AS, Poonia P (2011) Role of hyperaccumulators in phytoextraction of metals from contaminated mining sites: a review. Crit Rev Environ Sci Technol 41:168–214

Singh JS, Pandey VC, Singh DP (2011) Efficient soil microorganisms: a new dimension for sustainable agriculture and environmental development. Agric Ecosyst Environ 140(3–4):339–353

Skórzynska-Polit E, Azkiewicz M, Krupa Z (2010) Lipid peroxidation and antioxidative response in *Arabidopsis thaliana* exposed to cadmium and copper. Acta Physiol Plant 32:169

Smith EE, Facelli E, Pope S, Smith FA (2010) Plant performance in stressful environments. Interpreting new and established knowledge of the roles of arbuscular mycorrhizas. Plant Soil 326:3–20

Solanki R, Dhankhar R (2011) Biochemical changes and adaptive strategies of plants under heavy metal stress. Biologia 66:195–204

Solans M, Vobis G, Cassán F, Luna V, Wall VG (2011) Production of phytohormones by root- associated saprophytic actinomycetes isolated from the actinorhizal plant *Ochetophila trinervis*. World J Microbiol Biotechnol 27:2195–2202

Spaepen S, Vanderleyden J, Okon Y (2009) Plant growth-promoting actions of rhizobacteria. Adv Bot Res 51:283–320

Sreevidya M, Gopalakrishnan S, Kudapa H, Varshney RK (2016) Exploring plant growth promotion actinomycetes from vermicompost and rhizosphere soil for yield enhancement in chickpea. Braz J Microbiol 47(1):85–95

Surendra KA, Baby A (2016) Enhanced shelf life of Azospirillum and PSB (Phosphate solubilizing Bacteria) through addition of chemical additives in liquid formulations. Int J Sci Environ Technol 5(4):2023–2029

Tahir HAS, Gu Q, Wu H, Niu Y, Huo R, Gao X (2017) Bacillus vola-tiles adversely affect the physiology and ultra-structure of *Ralstonia solanacearum* and induce systemic resistance in tobacco against bacterial wilt. Sci Rep 7:40481

Tak HI, Ahmad F, Babalola OO (2013) Advances in the application of plant growth-promoting rhizobacteria in phytoremediation of heavy metals. In: Whitacre DM (ed) Reviews of environmental contamination and toxicology. Springer, New York, pp 33–52

Tang Y, Kang H, Qin Z, Zhang K, Zhong Y, Li H, Mo L (2020) Significance of manganese resistant Bacillus cereus strain WSE01as a bioinoculant for promotion of plant growth and manganese accumulation in *Myriophyllum verticillatum*. Sci Total Environ 707:135867

Tewari S, Arora NK (2016) Exopolysaccharides based bioformulation from Pseudomonas aeruginosa combating saline stress. Recent Trends PGPR Res Sustain Crop Prod 2016:93

Timmusk S, El-Daim IAA, Copolovici L (2014) Drought tolerance of wheat improved by rhizosphere bacteria from harsh environments: enhanced biomass production and reduced emissions of stress volatiles. PLoS One 9(5):96086

Tongesayi T, Fedick P, Lechner L (2013) Daily bioaccessible levels of selected essential but toxic heavy metals from the consumption of non-dietary food sources. Food Chem Toxicol 62:142–147

Tordoff GM, Baker AJM, Willis AJ (2000) Current approaches to the revegetation and reclamation of metalliferous mine wastes. Chemosphere 41:219–228

Tripti VK (2012) Anshumali. Phosphate solubilizing activity of some bacterial strains isolated from chemical pesticide exposed agriculture soil. Int J Eng Res Dev 3(9):1–6

Validov SZ, Kamilova F, Lugtenberg BJ (2009) Pseudomonas putida strain PCL1760 controls tomato foot and root rot in stonewool under industrial conditions in a certified greenhouse. Biol Control 48(1):6–11

Van Hullebusch ED, Zandvoort MH, Lens PN (2003) Metal immobilisation by biofilms: mechanisms and analytical tools. Rev Environ Sci Biotechnol 2:9–33

Vijayaraghavan K, Yun YS (2008) Bacterial biosorbents and biosorption. Biotechnol Adv 26:266–291

Wang Y, Ren W, Li Y (2019) Nontargeted metabolomic analysis to unravel the impact of di (2-ethylhexyl) phthalate stress on root exudates of alfalfa (*Medicago sativa*). Sci Total Environ 646:212–219

Wasi S, Tabrez S, Ahmad M (2013) Toxicological effects of major environmental pollutants: an overview. Environ Monit Assess 185:2585–2593

Wenzel WW (2009) Rhizosphere processes and management in plant-assisted bioremediation (phytoremediation) of soils. Plant Soil 321:385–408

Yabur R, Bashan Y, Hernández-Carmona G (2007) Alginate from the macroalgae *Sargassum sinicola* as a novel source for microbial immobilization material in wastewater treatment and plant growth promotion. J Appl Phycol 19(1):43–53

Yuan M, He HD, Xiao L, Zhong T, Liu H, Li SB (2014) Enhancement of Cd phytoextraction by two Amaranthus species with endophytic Rahnella sp. JN27. Chemosphere 103:99–104

Zaidi A, Khan MS, Saif S (2017) Role of nitrogen-fxing plant growth-promoting rhizobacteria in sustainable production of vegetables. Current perspective. In: Zaidi A, Khan MS (eds) Microbial strategies for vegetable production. Springer, Cham, pp 49–79

Zhang D, Wang J, Pan X (2006) Cadmium sorption by EPSs produced by anaerobic sludge under sulfate-reducing conditions. J Hazard Mater 138(3):589–593

Zhuang X, Chen J, Shim H, Bai Z (2007) New advances in plant growth-promoting rhizobacteria for bioremediation. Environ Int 33:406–413

Zohar-Perez C, Ritte E, Chernin L (2002) Preservation of chitinolytic *Pantoaeag glomerans* in a viable form by cellular dried alginate-based carriers. Biotechnol Prog 18(6):1133–1140

Part II

Planning and Engineering Applications to Phytoremediation

Chapter 7
Application of Electroremediation Coupled with Phytoremediation Techniques for the Removal of Trace Metals in Sewage Sludge

A. Ram Sailesh, Shaik Riyazuddin, K. Suresh Kumar,
Anindita Chakraborthy, and Srinivas Namuduri

Abstract The amount of waste production has increased due to various anthropogenic activities. To treat these wastes, industries and regulatory bodies employ treatment plants. These treatment plants produce a secondary waste known as 'sewage sludge,' which is rich in nutrient content, organic compounds, and metals. The concentration of metals depends upon the type and activities performed. This sludge can be used as a fertilizer. However, due to the concentration of metals, bioaccumulation and biomagnification problems arise. There is a need to employ remediation technologies to convert toxic metals to non-toxic forms. Several physical, chemical, and biological techniques are available, which are cost-inclusive and are suitable only to a certain types of waste substrates. Electroremediation serves as a low-cost and effective technique in the remediation of contaminated soils and sewage sludge. Phytoremediation can be applied to these remediated substrates for the removal/reduction of metal concentrations. Application of electric charge alters the characteristics of waste (pH, availability of metals, etc.). This supports the physiology and microflora of the plants at rhizosphere, which substantially helps in the removal of metals by phytoremediation. Thus, there is a need to apply combined techniques like electroremediation coupled with phytoremediation to overcome the challenges of single remediation technique.

Keywords Electroremediation · Phytoremediation · Coupled technique · Trace metals · Sewage sludge

---

A. R. Sailesh · S. Riyazuddin · K. S. Kumar · S. Namuduri (✉)
Department of Environmental Science, School of Science, GITAM (Deemed to be University), Visakhapatnam, India
e-mail: snamudur@gitam.edu

A. Chakraborthy
UGC DAE, Consortium for Scientific Research, Kolkata Centre, Kolkata, India

L. Newman et al. (eds.), *Phytoremediation*, https://doi.org/10.1007/978-3-031-17988-4_7

7.1 Introduction

Economic and population growth is responsible for an exponential increase in anthropogenic activities. One of the outcomes of population growth is the generation and disposal of waste, including sewage sludge (Azizi et al. 2013). Soil contamination is one of the significant environmental problems and is gaining importance across the world. Various anthropogenic activities, including mining ores, industrial operations, agricultural activities, and application of agrochemicals, are the primary cause to buildup heavy metals in soil (Shah and Daverey 2020; Zhao et al. 2015; Jabeen et al. 2009).

Organic compounds, inorganic compounds, and toxic metals like chromium, cadmium, nickel, and copper are responsible for the increased contamination of soils and have resulted in the disturbance of self-purification capacity of soil and the environment causing land and soil pollution (Lotfy and Mostafa 2014; Cameselle et al. 2013; Reimann and Garrett 2005). Industries employ treatment systems to minimize the impacts of their produced wastes on the environment. These processes produce a secondary waste known as sewage sludge which is to be appropriately disposed to reduce the effects of these sludges on water bodies and soils, as they interfere with the food chain and interrupt the ecological balance of the ecosystem (Zhang et al. 2014; Chen et al. 2012).

Several remediation techniques like stabilization, soil washing, solidification, vitrification, electroremediation, phytoremediation, and bioremediation are employed to remediate contaminated soils. However, most of these processes can be applied only to certain types of soil contaminants or contaminated sites. The treatment process becomes difficult if these sites contain different contaminants, and only a few technologies have been proven in the effective remediation of sites to prevent cross-contamination (Sharma and Reddy 2004). During the treatment, soil washing, solidification, and stabilization use improper chemicals to soils with low permeability. Sometimes, it may also change the properties and texture of the soil, which cannot be used for agricultural purposes. Processes such as stabilization and vitrification may immobilize the metals in the soil, leaving them undisturbed. However, these may pose the risk of mobilization or contamination in future use. Most of the methods are cost inclusive and require a lot of energy and greater treatment time. (Cameselle et al. 2013).

Phytoremediation is a plant-based approach and economically viable remediation techniques for polluted soils. This is a low-cost method applicable for contaminated soils without modifying the actual soil properties or texture before and after the treatment. Phytoremediation poses some limitations during field studies and application. Due to this reason, coupled techniques are gaining importance. Phytoremediation can be combined with a treatment called ‘electroremediation,’ which uses low voltage direct current in removal of heavy metals from contaminated media such as soils. The coupled technique is applied to overcome the challenges of a single remediation technique. Electro-phytoremediation is combined to overcome the limitations that occur in phytoremediation (Cameselle et al. 2013).

7.2 Sewage Sludge and Its Characteristics

Biological or industrial wastewater treatment releases a by-product called sewage sludge, which is semisolid, insoluble, and has a high moisture content (up to 95%). Depending upon the process of wastewater treatment, generation of sludge, the characteristics, and composition of sewage sludge change (Tytła et al. 2016; Karvelas et al. 2003). Sewage sludge is rich in organic compounds (PAHs, PCBs, and POP's), organic matter, and macro- and micronutrients (nitrogen and phosphorous). It is also rich in microorganisms and trace metals (Ozcan et al. 2013; Singh and Agrawal 2008).

The presence of organic matter and nutrients helps recycle nitrogen, phosphorous, and other nutrients by plants as fertilizer for agricultural purposes (Haynes et al. 2009; Fernández et al. 2009). On the other hand, metals that arise from industrial waste discharges pose a risk of bioaccumulation and biomagnification to higher trophic levels. If sludge disposal is improperly managed, the effect would be higher (Huang and Yuan 2016; Hung et al. 2015; Yang et al. 2014; Zennegg et al. 2013). The quantities of sewage sludge produced by different countries are represented in Table 7.1. Several technologies can transform the concentration of toxic metals to lesser toxic forms which can reduce the impact on the environment (Leng et al. 2014; Li et al. 2015; Rizzardini and Goi 2014; Fernández et al. 2009).

7.3 Potentiality of Land Application of Sewage Sludge

The low-cost alternative of sewage sludge disposal is a challenging problem, as the disposal requires proper management and should also be cost-effective. The most common disposal methods include incineration, landfilling, land application, and building materials usage. As sanitary landfill is gradual and cost-inclusive, land application is preferred as an alternative to landfilling. The presence of higher organic matter content and plant nutrients in sewage sludge helps in enriching the

Table 7.1 Production rate of sewage sludge in different nations

S. No.	Country	Quantity (In Mt Dm/year)	References
1.	Europe	13.5	EurObserv'ER Report (2016)
2.	Germany	1.821	EurObserv'ER Report (2016)
3.	Poland	0.568	EurObserv'ER Report (2016)
4.	China	6.25	Yang et al. (2015)
5.	U.S.A	12.56	Seiple et al. (2017)
6.	Russian federation	2.5	Pakhnenko (2007)
7.	Japan	2.4	Hong et al. (2009)
8.	India	13.99	Kaur et al. (2012)

Million tons of dry matter per year (mtDM/year) properties of soil that includes specific gravity and water retention in soil and also promotes the recycling of nutrients, thus facilitating in the growth of plant (Zhang et al. 2017). A study on adding composted sewage sludge to the soil in a 10–20% ratio helped improve soil nutrient supply (Cheng et al. 2007). Potassium and phosphorous are released early, while nitrogen is released slowly in composted sewage sludge, thus providing a long-term supply of nutrient sources.

7.4 Consequences of Sewage Sludge Application on Land

After the addition of sewage sludge into the soil, the characteristics of soil such as redox potential, pH, microorganisms, and organic matter help in the dispersal of heavy metals into the soil by four mechanisms: namely, ion exchange, sorption, complexation, and precipitation (Zhang et al. 2017; Fang et al. 2016). Heavy metals derive from both natural and anthropogenic sources. Activities like natural soil erosion, weathering of parent rock, and geologic activities are some of the natural sources of adding heavy metals into the soil surface (Mishra et al. 2008; Alorro et al. 2008). Industrial and other human activities include anthropogenic sources (Cameselle et al. 2013). Metals are persistent in nature and not easily biodegradable (Han and Singer 2007; Clemente et al. 2005). When sewage sludge containing heavy metals is applied to soil for longer periods, it may lead to the accumulation of metals on the soil surface and eventually transferred into the food chain, causing various effects to environment and life of various species (Liu and Sun 2013; Nedjimi 2009). The total concentration of heavy metals helps determine the level of contamination and speciation, which determines the toxicity, mobility, and bioavailability (Zhang et al. 2017). Top soil is more prone to the accumulation of heavy metals from the hydrosphere and atmosphere, which includes arsenic and lead (Salazar and Pignata 2014).

7.5 Soil Remediation Techniques

The concentration of heavy metals has increased in recent years due to enhanced urban and industrial activities like water discharges, crop production, and exploring of mining ores. Most of the metals are toxic in nature, which cannot be degraded easily and enter the food chain causing damaging effects on human health (Han and Singer 2007; Han et al. 2002, 2003; Mulligan et al. 2001). To reduce the effect of these heavy metals on environment and human health, there is a need to remediate the contaminated soils. Application of chelator to contaminated soil enhances precipitation or absorption of heavy metals into the soil solution. These metals could not be absorbed by plants, resulting in the excess contamination of soil and groundwater (Zhou et al. 2007; Romkens et al. 2002; Huang et al. 1997).

There is a need to develop new technologies that increase the uptake of heavy metals. Remediation methods like precipitation, ion exchange, chemical washing, incineration, chemical leaching, heat treatment, phytoremediation, and electroremediation can be applied to contaminated soils. Some methods are cost inclusive and efficient in remediation of heavy metals and can only be used to remediate particular types of contaminants or soils due to their persistence, lower degradation, and alteration of soil properties such as pH and fertility (Jomova and Valko 2011; Shiyab et al. 2009; Chen et al. 2009; Nedjimi and Daoud 2009; Thewys and Kuppens 2008; Su et al. 2005, 2007, 2008; Han and Singer 2007; Han et al. 2004a, b). Chemical treatment helps in the binding or stabilization of metals in soil and is considered as an economical technique (Zhang et al. 2017). The heavy metals removed by applying either of the above techniques must be disposed of properly with care to avoid further contamination (He et al. 2015).

Some of the techniques for remediation of heavy metals are discussed below:

7.5.1 Heat Treatment

A physical method in which sewage sludge is subjected to treatment at high temperatures, i.e., 300–400 °C which facilitates the removal of some heavy metals through evaporation, while other metals can be obtained in ash or in evaporated water in condensed form (Shi et al. 2013; Li et al. 2012; Zorpas et al. 2001).

7.5.2 Ion Exchange Treatment

A chemical process in which potential ions or metals are replaced by non-pollutant ions (Dabrowski et al. 2004). Liquid substrates are used in the process. Quaternary phosphonium and ammonium-based reagents are used in a study conducted by Fuerhacker et al. 2012.

7.5.3 Use of Chelating Agents

Chelators or chelating agents are organic compounds with metal ions. Ethylenediaminetetraacetic acid and nitrilotriacetic acid are used as chelators in the extraction of metals in the substrate (Deng et al. 2009).

7.5.4 Use of Basic Compounds

Heavy metals are usually precipitated at acidic pH, which is increased with basic compounds, such as 'Lime.' An increase in the pH of the substrate enhances the precipitation of metals which reduces the exchangeable metal concentration.

7.5.5 Use of Aluminosilicate Materials

Chemical passivating agents such as fly ash, bentonite, and zolite are used in sewage sludge as aluminosilicate materials to stabilize the metals. The mineral composition of these materials is similar to that of soil. For this reason, even with more prolonged usage, there would be no significant effect on the soil (Zhang et al. 2017).

7.5.6 Composting

Sewage sludge is enriched with nutrients, microorganisms, and organic carbon. Composting can be defined as a process in which the microorganisms degrade the biological components into humus, which can be used as a soil conditioner (Kalderis et al. 2010). This process helps reduce waste up to 50% and the heat generated during the process the pathogens present (Neklyudov et al. 2008; Bustamante et al. 2008). During the degradation process, heavy metals present in it are certainly absorbed by the plants when this waste is used as a fertilizer. This results in bioaccumulation of metals in various trophic levels (Rihani et al. 2010). Bulking agents are materials used to enhance the properties of the substrate. These include moisture content, pH, porosity, and C/N ratio. This also affects the composting rate and helps in the dilution of heavy metals (Zhang et al. 2017).

7.5.7 Biosurfactant Application

The application of biosurfactants is a biological method in which substrates are used. Surfactants are amphiphilic compounds with hydrophilic and hydrophobic ends. Biosurfactants are also produced by micro-organisms that interact with poorly soluble contaminants and toxic metals, forming functional amine, hydroxyl, and carbonyl groups. This process helps in the removal of metals (Franzetti et al. 2014; Lawniczak et al. 2013).

7.5.8 Bioleaching

The metabolic activities of microbes can alter the mobility of ions and change the form of metals. This process is termed ‘bioleaching.’ This technique can be applied to different substances such as river sediments, sewage sludge, and contaminated soils without altering the properties of the material used. It is an efficient, economical, and simple technique with promising results in the removal of metals (Mishra and Rhee 2014; Fang et al. 2011; Pathak et al. 2009; Fang and Zhou 2007; Picardal and Cooper 2005).

7.5.9 Phytoremediation

It is one of the prominent biological techniques, where green plants are applied to remediate contaminants from the soil. It is also considered as one of the sustainable, cost-effective, efficient and reliable and technique when compared with mechanical approaches and can also be applied to large areas. Plants control nutrients' availability, reduce soil erosion, increase the moisture content, and stabilize the soil by regulating the microclimate, rhizosphere interactions, and local biogeochemistry (McCutcheon and Schnoor 2004). The transpiration of plants helps in the migration of metals and water (Schnoor et al. 1995). Plants with a higher capacity of metals are called hyperaccumulators (Cho-Ruk et al. 2006). Translocation, bioaccumulation, and the abilities of plants help in the extraction of metals from soil surfaces (Negri et al. 1996). There are several kinds of plants used in phytoremediation of different wastes that include contaminated waters, polluted soils, sewage sludge, etc., (Table 7.2).

Table 7.2 Plant species used in the process of phytoremediation of heavy metals

S. No.	Plant species	Common name	Hyper accumulation of heavy metals	References
1.	*Ricinus communis*	Castor	Cd, Co, Ni, Pb, Cu, As, Fe, Zn	Palanivel et al. (2020), Yashim et al. (2016)
2.	*Eichhornia crassipes*	Common water hyacinth	Zn, Cr, Cu, Pb, Ag, Cd	Odjegba and Fasidi (2007), Lytle et al. (1996), Muramoto and Oki (1983)
3.	*Zea mays*	Corn	Cd, Pb, Zn	Chiwetalu et al. (2020), Meers et al. (2010)
4.	*Brassica juncea*	Mustard	Se, Pb, Zn, Cd	Roychowdhury et al. (2017), Singh and Fulekar (2012)
5.	*Jatropha curcas*	Physic nut	Cd, Cu, Ni, Pb, Cr, Zn	Chang et al. (2014)
6.	*Medicago sativa*	Alfalfa	Pb, Cd, Zn, Ni	Wang et al. (2015), Barbafieri (2000)
7.	*Helianthus annus*	Sunflower	Cd, Ni, Pb, Cu, As, Fe, Zn,	Chauhan and Mathur (2020), Mahardika et al. (2018), Subhashini and Swamy (2013)
8.	*Pteris vittata*	Chinese Brake Fern	Hg, As, Cu, Cr, Cd	Su et al. (2008), Xiyuan et al. (2008), Koller et al. (2008)
9.	*Berkheya coddii*		Ni, Pd, Pt	Slatter (2013), Nemutandani et al. (2006)

7.5.10 Electroremediation

Electroremediation is a technique in which electrodes are immersed at a suitable depth in a contaminated medium and provided with low electric charge to induce the migration and transport of contaminants toward their respective electrodes (based on the charge of ions) by electro-osmosis and electromigration (Cameselle and Reddy 2012). The addition of chemical substrates causes a change in pH, speciation, and dissolution of contaminants, leading to redox reactions and acid/base reactions (Reddy and Cameselle 2009).

7.6 Scope of Electroremediation

Electroremediation serves as an alternative to physical and chemical methods, widely used in the last decade. The removal of contaminants is enabled by the mineralization and mobilization under electric charge (Elicker et al. 2014). This method can be applied to contaminated soils, sewage, and wastewater (Ebbers et al. 2015; Niroumand et al. 2012; Wang et al. 2005). The advantage of this treatment is its short period of exposure and recovery of metals (Elicker et al. 2014).

Electroremediation works on three principles such as electromigration, electro-osmosis, and electrophoresis:

(a) Electromigration is a mechanism in which the applied electric charge influences the migration of ions (cations toward cathode and anions toward anode).
(b) Electro-osmosis is a mechanism in which the difference in electric potential, the transport of fluids occurs through capillaries in sludge or soils (Niroumand et al. 2012).
(c) Electrophoresis is a mechanism in which the external electric potential helps in the migration of charged particles and ions (Niroumand et al. 2012).

7.7 Scope of Coupled Technique at Laboratory Scale

Metals and metalloids present in sewage sludge or contaminated soils are present in various forms, which include organically bound metals, oxide bound metals, exchangeable form, carbonate bound metals, and solid/liquid phases (Han et al. 2012; Han and Singer 2007; Han and Banin 1997; Tessier et al. 1979). In electroremediation, due to the passage of current, electrolytic decomposition takes place at electrodes. This controls the pH of the substrate and helps in the migration of metals toward respective ionic phases, i.e., cathode or anode, which enhances the remediation potential. In phytoremediation, the leaves, stems, roots, and other plant parts absorb and store metals enhanced through electroremediation (Reddy and Cameselle 2009; Raskin and Ensley 2000).

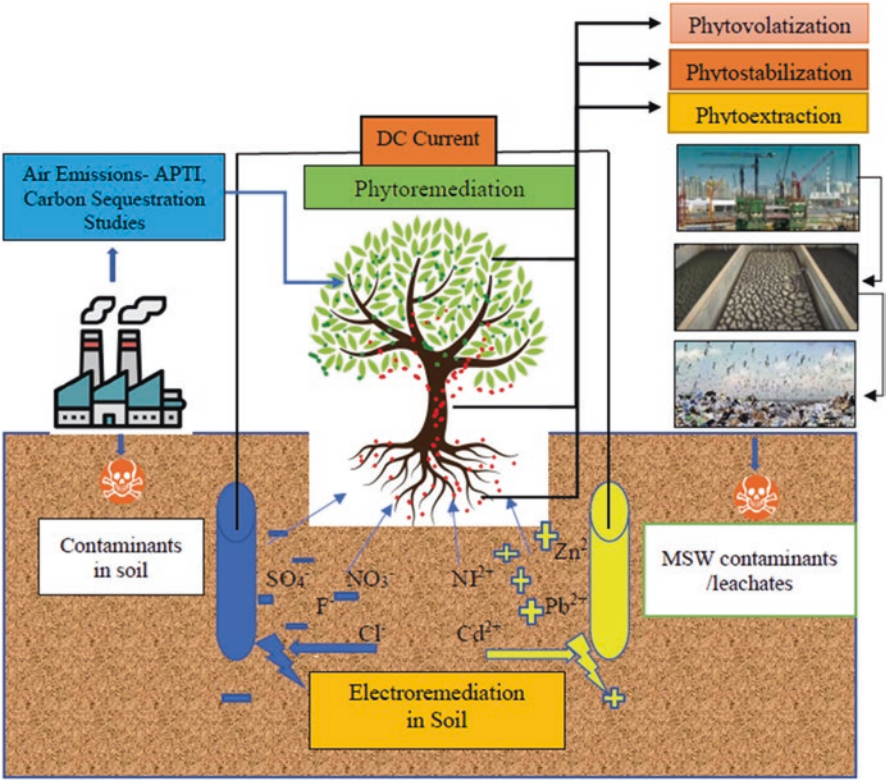


Fig. 7.1 Representation of the process of electroremediation coupled with phytoremediation

The combined technique of electroremediation with phytoremediation involves the process of stabilizing the conditions to solubilize metals by electro-osmosis, electrophoresis, and electromigration (Cameselle and Reddy 2012). When used in plants, this treated substrate's translocation ability enhances the metals to accumulate into plant parts (Lotfy and Mostafa 2014; Cui et al. 2007). Continuous application of voltage enhances the pH of sludge or soil. The prevalence of change in pH conditions due to electroremediation helps transform metals into bioavailable forms (Fig. 7.1). Thus, supporting the release of H^+ ions by roots of plant helps in the mobility of metals around the rhizosphere (Cameselle et al. 2013; Han and Singer 2007; Thangavel and Subbhuraam 2004; Barber 1995). Hyperaccumulators are plants with rapid growth used in phytoremediation to remove contaminants and in combined electro-phytoremediation techniques (Bedmar et al. 2009).

7.8 Advantages

Several studies have researched the application of electroremediation in the removal of contaminants like hydrophobic organic contaminants, heavy metals, and inorganic contaminants. Some works focused on removing both organic pollutants and heavy metals. Combined techniques of electroremediation coupled with bioremediation, thermal desorption, and phytoremediation have gained importance in recent times. This coupled technique is developed to overcome the disadvantages of a single remediation technique (Reddy and Cameselle 2009).

7.9 Limitations

Factors that may limit the application of electroremediation are as follows:

- Moisture content: the effectiveness of electroremediation is higher when the moisture content is above 14%. If the moisture content is below 10%, there is a decline in the effectiveness of the process.
- The presence of materials that induce electrical conductivity is a constraint. Geologic deposits and ore deposits show high electrical conductivity making the efficiency of the process low.
- Electrodes may sometimes corrode and introduce these residues into the soil mass. Thus, inert materials such as carbon, graphite, or stainless-steel electrodes must be used.
- Sometimes, reactions such as oxidation/reduction that induce the formation of undesirable reactions may form undesirable by-products (e.g., hydrogen sulphide gas and chlorine gas).

Although the coupled technique of electro-phytoremediation has a higher potential in the restoration of soils, only limited research studies are conducted on applying this technique. Laboratory studies use artificially contaminated soils, while it differs from actual field contaminated soils. This makes the application difficult in field applications than in the laboratory. The operating conditions and the results in laboratory studies concluded that the combination of both techniques, i.e., phytoremediation coupled with electroremediation has provided promising results, when applied to field studies with limited variables and testing conditions.

7.10 Conclusions

Environmental remediation is a promising treatment aspect to promote green economy and to redevelop the contaminated sites. Among the remediation techniques, electroremediation helps to mitigate organic and inorganic contamination in an economical way (Hassan et al. 2018). Phytoremediation also helps in efficient removal of heavy metals from contaminated soils. Promising results were observed when these both techniques were applied as a combination. However, when both these techniques are applied to field studies, much emphasis is needed in the understanding the optimization and the influence of electric field on the role of degradation of organics at rhizosphere, which plays a critical role in knowing the concept of electro-phytoremediation.

Acknowledgements The authors are thankful to UGC–DAE Consortium for Scientific Research for providing financial assistance during the project period.

References

Alorro RD, Mitani S, Hiroyoshi N, Ito M, Tsunekawa M (2008) Recovery of heavy metals from M.S.W. molten fly ash by carrier-in-pulp method: Fe powder as carrier. Miner Eng 21(15):1094–1101

Azizi AB, Lim MP, Noor ZM, Abdullah N (2013) Vermiremoval of heavy metal in sewage sludge by utilising *Lumbricus rubellus*. Ecotoxicol Environ Saf 90:13–20

Barber SA (1995) Soil nutrient bioavailability: a mechanistic approach. Wiley

Bedmar ML, Pérez-Sanz A, Martínez-Iñigo MJ, Benito AP (2009) Influence of coupled electrokinetic–phytoremediation on soil remediation. In: Electrochemical remediation technologies for polluted soils, sediments and groundwater. Wiley Hoboken

Barbafieri M (2000) The importance of nickel phytoavailable chemical species characterization in soil for phytoremediation applicability. Int J Phytoremediation 2(2):105–115

Bustamante MA, Paredes C, Marhuenda-Egea FC, Pérez-Espinosa A, Bernal MP, Moral R (2008) Co-composting of distillery wastes with animal manures: carbon and nitrogen transformations in the evaluation of compost stability. Chemosphere 72(4):551–557

Cameselle C, Chirakkara RA, Reddy KR (2013) Electrokinetic-enhanced phytoremediation of soils: status and opportunities. Chemosphere 93(4):626–636

Cameselle C, Reddy KR (2012) Development and enhancement of electro-osmotic flow for the removal of contaminants from soils. Electrochim Acta 86:10–22

Chang FC, Ko CH, Tsai MJ, Wang YN, Chung CY (2014) Phytoremediation of heavy metal contaminated soil by Jatropha curcas. Ecotoxicology 23(10):1969–1978

Chauhan P, Mathur J (2020) Phytoremediation efficiency of Helianthus annuus L. for reclamation of heavy metals-contaminated industrial soil. Environ Sci Pollut Res 27(24):29954–29966

Chen H, Yan SH, Ye ZL, Meng HJ, Zhu YG (2012) Utilization of urban sewage sludge: Chinese perspectives. Environ Sci Pollut Res 19(5):1454–1463

Chen J, Shiyab S, Han FX, Monts DL, Waggoner CA, Yang Z, Su Y (2009) Bioaccumulation and physiological effects of mercury in Pteris vittata and Nephrolepis exaltata. Ecotoxicology 18(1):110–121

Cheng H, Xu W, Liu J, Zhao Q, He Y, Chen G (2007) Application of composted sewage sludge (CSS) as a soil amendment for turfgrass growth. Ecol Eng 29(1):96–104

Chiwetalu UJ, Mbajiorgu CC, Ogbuagu NJ (2020) Remedial ability of maize (zea-mays) on lead contamination under potted condition and non-potted field soil condition. J Bioresourc Bioprod 5(1):51–59

Cho-Ruk K, Kurukote J, Supprung P, Vetayasuporn S (2006) Perennial plants in the phytoremediation of lead-contaminated soils. Biotechnology 5(1):1–4

Clemente R, Walker DJ, Bernal MP (2005) Uptake of heavy metals and As by Brassica juncea grown in a contaminated soil in Aznalcóllar (Spain): the effect of soil amendments. Environ Pollut 138(1):46–58

Cui S, Zhou Q, Chao L (2007) Potential hyperaccumulation of Pb, Zn, Cu and Cd in endurant plants distributed in an old smeltery, northeast China. Environ Geol 51(6):1043–1048

Dabrowski A, Hubicki Z, Podkościelny P, Robens E (2004) Selective removal of the heavy metal ions from waters and industrial wastewaters by ion-exchange method. Chemosphere 56(2):91–106

Deng J, Feng X, Qiu X (2009) Extraction of heavy metal from sewage sludge using ultrasound-assisted nitric acid. Chem Eng J 152(1):177–182

Ebbers B, Ottosen LM, Jensen PE (2015) Electrodialytic treatment of municipal wastewater and sludge for the removal of heavy metals and recovery of phosphorus. Electrochim Acta 181:90–99

Elicker C, Sanches Filho PJ, Castagno KR (2014) Electroremediation of heavy metals in sewage sludge. Braz J Chem Eng 31:365–371

Fang W, Wei Y, Liu J (2016) Comparative characterization of sewage sludge compost and soil: heavy metal leaching characteristics. J Hazard Mater 5:303–310

Fang D, Zhou LX (2007) Enhanced Cr bioleaching efficiency from tannery sludge with coinoculation of Acidithiobacillus thiooxidans TS6 and Brettanomyces B65 in an air-lift reactor. Chemosphere 69(2):303–310

Fang D, Zhang R, Zhou L, Li J (2011) A combination of bioleaching and bioprecipitation for deep removal of contaminating metals from dredged sediment. J Hazard Mater 192(1):226–233

Fernández JM, Plaza C, García-Gil JC, Polo A (2009) Biochemical properties and barley yield in a semiarid Mediterranean soil amended with two kinds of sewage sludge. Appl Soil Ecol 42(1):18–24

Franzetti A, Gandolfi I, Fracchia L, Van Hamme J, Gkorezis P, Marchant R, Banat IM (2014) Biosurfactant use in heavy metal removal from industrial effluents and contaminated sites. Biosurfactants: Prod Utiliz—Proc Technol Econom 159:361

Fuerhacker M, Haile TM, Kogelnig D, Stojanovic A, Keppler B (2012) Application of ionic liquids for the removal of heavy metals from wastewater and activated sludge. Water Sci Technol 65(10):1765–1773

Han FX, Singer A (2007) Solution chemistry of trace elements in arid zone soils. In: Biogeochemistry of trace elements in arid environments. Springer, Dordrecht. p 69–105

Han F, Banin A (1997) Long-term transformations and redistribution of potentially toxic heavy metals in arid-zone soils incubated: I. Under saturated conditions. Water Air Soil Pollut 95(1):399–423

Han FX, Banin A, Su Y, Monts DL, Plodinec JM, Kingery WL, Triplett GE (2002) Industrial age anthropogenic inputs of heavy metals into the pedosphere. Naturwissenschaften 89(11):497–504

Han FX, Sridhar BM, Monts DL, Su Y (2004a) Phytoavailability and toxicity of trivalent and hexavalent chromium to Brassica juncea. New Phytol 162(2):489–499

Han FX, Su Y, Sridhar BM, Monts DL (2004b) Distribution, transformation and bioavailability of trivalent and hexavalent chromium in contaminated soil. Plant Soil 265(1):243–252

Han FX, Su Y, Monts DL, Plodinec MJ, Banin A, Triplett GE (2003) Assessment of global industrial-age anthropogenic arsenic contamination. Naturwissenschaften 90(9):395–401

Han FX, Su Y, Shi Z, Xia Y, Tian W, Philips V, Monts DL, Gu M, Liang Y (2012) Mercury distribution and speciation in floodplain soils and uptake into native earthworms (Diplocardia spp.). Geoderma 170:261–268

Hassan I, Mohamedelhassan E, Yanful EK, Yuan ZC (2018) Enhancement of bioremediation and phytoremediation using electrokinetics. Adv Bioremed Phytoremed 169:169–189

Haynes RJ, Murtaza G, Naidu R (2009) Inorganic and organic constituents and contaminants of biosolids: implications for land application. Adv Agron 104:165–267

He JH, Zhang YQ, Cheng G (2015) Research progress in technologies of heavy metals from urban sewage sludge. Appl Chem Indust 44(8):1541–1545

Hong J, Hong J, Otaki M, Jolliet O (2009) Environmental and economic life cycle assessment for sewage sludge treatment processes in Japan. Waste Manag 29(2):696–703

Huang JW, Chen J, Berti WR, Cunningham SD (1997) Phytoremediation of lead-contaminated soils: role of synthetic chelates in lead phytoextraction. Environ Sci Technol 31(3):800–805

Huang HJ, Yuan XZ (2016) The migration and transformation behaviors of heavy metals during the hydrothermal treatment of sewage sludge. Bioresour Technol 200:991–998

Hung CV, Cam BD, Mai PT, Dzung BQ (2015) Heavy metals and polycyclic aromatic hydrocarbons in municipal sewage sludge from a river in highly urbanized metropolitan area in Hanoi, Vietnam: levels, accumulation pattern and assessment of land application. Environ Geochem Health 37(1):133–146

Jabeen R, Ahmad A, Iqbal M (2009) Phytoremediation of heavy metals: physiological and molecular mechanisms. Bot Rev 75(4):339–364

Jomova K, Valko M (2011) Advances in metal-induced oxidative stress and human disease. Toxicology 283(2–3):65–87

Kalderis D, Aivalioti M, Gidarakos E (2010) Options for sustainable sewage sludge management in small wastewater treatment plants on islands: the case of Crete. Desalination 260(1–3):211–217

Karvelas M, Katsoyiannis A, Samara C (2003) Occurrence and fate of heavy metals in the wastewater treatment process. Chemosphere 53(10):1201–1210

Kaur R, Wani SP, Singh AK, Lal K. Wastewater production, treatment and use in India. In: National Report presented at the 2nd regional workshop on Safe Use of Wastewater in Agriculture 2012 May 16. p 1–13

Koller CE, Patrick JW, Rose RJ, Offler CE, MacFarlane GR (2008) Arsenic and heavy metal accumulation by Pteris vittata L. and P. umbrosa R. Br Bull Environ Contaminat Toxicol 80(2):128–133

Lawniczak Ł, Marecik R, Chrzanowski Ł (2013) Contributions of biosurfactants to natural or induced bioremediation. Appl Microbiol Biotechnol 97(6):2327–2339

Li J, Luo G, Gao J, Yuan S, Du J, Wang Z (2015) Quantitative evaluation of potential ecological risk of heavy metals in sewage sludge from three wastewater treatment plants in the main urban area of Wuxi. China Chem Ecol 31(3):235–251

Li L, Xu ZR, Zhang C, Bao J, Dai X (2012) Quantitative evaluation of heavy metals in solid residues from sub-and super-critical water gasification of sewage sludge. Bioresour Technol 121:169–175

Liu JY, Sun SY (2013) Total concentrations and different fractions of heavy metals in sewage sludge from Guangzhou, China. Trans Nonferrous Metals Soc China 23(8):2397–2407

Leng L, Yuan X, Huang H, Jiang H, Chen X, Zeng G (2014) The migration and transformation behavior of heavy metals during the liquefaction process of sewage sludge. Bioresour Technol 167:144–150

Lotfy SM, Mostafa AZ (2014) Phytoremediation of contaminated soil with cobalt and chromium. J Geochem Explor 144:367–373

Lytle CM, Zayed A, Terry N, Lytle FW (1996) Phytoconversion of Cr (VI) to Cr (III) by water hyacinth: a case for phytoremediation. In: Annual Combined Meeting of the Ecological Society of America on Ecologists/Biologists as Problem Solvers, Providence, RI

Mahardika G, Rinanti A, Fachrul MF (2018) Phytoremediation of heavy metal copper (Cu2+) by sunflower (Helianthus annuus l.). In: IOP conference series: earth and environmental science, Vol. 106, No. 1. IOP Publishing. p 012120

McCutcheon SC, Schnoor JL (2004) Phytoremediation: transformation and control of contaminants. Wiley

Meers E, Van Slycken S, Adriaensen K, Ruttens A, Vangronsveld J, Du Laing G, Tack FMG (2010) The use of bio-energy crops (Zea mays) for ‘phytoattenuation’of heavy metals on moderately contaminated soils: a field experiment. Chemosphere 78(1):35–41

Mishra D, Rhee YH (2014) Microbial leaching of metals from solid industrial wastes. J Microbiol 52(1):1–7

Mishra VK, Upadhyaya AR, Pandey SK, Tripathi BD (2008) Heavy metal pollution induced due to coal mining effluent on surrounding aquatic ecosystem and its management through naturally occurring aquatic macrophytes. Bioresour Technol 99(5):930–936

Mulligan CN, Yong RN, Gibbs BF (2001) Remediation technologies for metal-contaminated soils and groundwater: an evaluation. Eng Geol 60(1–4):193–207

Muramoto S, Oki Y (1983) Removal of some heavy metals from polluted water by water hyacinth (Eichhornia crassipes). Bull Environ Contam Toxicol 30(1):170–177

Nemutandani T, Dutertre D, Chimuka L, Cukrowska E, Tutu H (2006) The potential of Berkheya coddii for phytoextraction of nickel, platinum, and palladium contaminated sites. Toxicol Environ Chem 88(2):175–185

Niroumand H, Nazir R, Kassim KA (2012) The performance of electrochemical remediation technologies in soil mechanics. Int J Electrochem Sci 7(6):5708–5715

Nedjimi B (2009) Can calcium protect Atriplex halimus subsp. schweinfurthii against cadmium toxicity? Acta Botanica Gallica 156(3):391–397

Nedjimi B, Daoud Y (2009) Ameliorative effect of CaCl2 on growth, membrane permeability and nutrient uptake in Atriplex halimus subsp. schweinfurthii grown at high (NaCl) salinity. Desalination 249(1):163–166

Negri MC, Hinchman RR, Gatliff EG (1996) Phytoremediation: using green plants to clean up contaminate soil, groundwater, and wastewater. Argonne National Lab., I.L. (United States)

Neklyudov AD, Fedotov GN, Ivankin AN (2008) Intensification of composting processes by aerobic microorganisms: a review. Appl Biochem Microbiol 44(1):6–18

Odjegba VJ, Fasidi IO (2007) Phytoremediation of heavy metals by Eichhornia crassipes. Environmentalist 27(3):349–355

Ozcan S, Tor A, Aydin ME (2013) Investigation on the levels of heavy metals, polycyclic aromatic hydrocarbons, and polychlorinated biphenyls in sewage sludge samples and ecotoxicological testing. Clean–Soil Air Water 41(4):411–418

Pakhnenko E (2007) Sewage sludge and other non-traditional organic fertilizers; BINOM. Laboratoriya znaniy, Moscow

Palanivel TM, Pracejus B, Victor R (2020) Phytoremediation potential of castor (Ricinus communis L.) in the soils of the abandoned copper mine in Northern Oman: implications for arid regions. Environ Sci Pollut Res 27(14):17359–17369

Pathak A, Dastidar MG, Sreekrishnan TR (2009) Bioleaching of heavy metals from sewage sludge: a review. J Environ Manag 90(8):2343–2353

Picardal F, Cooper DC (2005) Microbially mediated changes in the mobility of contaminant metals in soils and sediments. Heavy metal contamination of soil: problems and remedies, pp 43–88

Raskin I, Ensley BD (2000) Phytoremediation of toxic metals. Wiley

Reddy KR, Cameselle C (2009) Electrochemical remediation technologies for polluted soils, sediments and groundwater. Wiley

Reimann C, Garrett RG (2005) Geochemical background—concept and reality. Sci Total Environ 350(1–3):12–27

Rihani M, Malamis D, Bihaoui B, Etahiri S, Loizidou M, Assobhei O (2010) In-vessel treatment of urban primary sludge by aerobic composting. Bioresour Technol 101(15):5988–5995

Rizzardini CB, Goi D (2014) Sustainability of domestic sewage sludge disposal. Sustainability. 6(5):2424–2434

Romkens P, Bouwman L, Japenga J, Draaisma C (2002) Potentials and drawbacks of chelate-enhanced phytoremediation of soils. Environ Pollut 116(1):109–121

Roychowdhury R, Roy M, Zaman S, Mitra A (2017) Bioaccumulation of heavy metals in Brassica juncea: an indicator species for phytoremediation. Int J Innov Res Multidiscipl Field 3(9):92–95

Salazar MJ, Pignata ML (2014) Lead accumulation in plants grown in polluted soils. Screening of native species for phytoremediation. J Geochem Explor 137:29–36

Schnoor JL, Light LA, McCutcheon SC, Wolfe NL, Carreia LH (1995 Jul) Phytoremediation of organic and nutrient contaminants. Environ Sci Technol 29(7):318A–323A

Seigneur VJ, Bongrain T, David R, Moreau S, Bruder O, Tennenhaus S, Baratte L, Guichard MA, Guillier A. The state of renewable energies in Europe. Edition 2016. 16. EurObserv'ER Report

Seiple TE, Coleman AM, Skaggs RL (2017) Municipal wastewater sludge as a sustainable bioresource in the United States. J Environ Manag 197:673–680

Shah V, Daverey A (2020) Phytoremediation: a multidisciplinary approach to clean up heavy metal contaminated soil. Environ Technol Innov 18:100774

Sharma HD, Reddy KR (2004) Geoenvironmental engineering: site remediation, waste containment, and emerging waste management technologies. Wiley

Shi W, Liu C, Ding D, Lei Z, Yang Y, Feng C, Zhang Z (2013) Immobilization of heavy metals in sewage sludge by using subcritical water technology. Bioresour Technol 137:18–24

Shiyab S, Chen J, Han FX, Monts DL, Matta FB, Gu M, Su Y (2009) Phytotoxicity of mercury in Indian mustard (Brassica juncea L.). Ecotoxicol Environ Saf 72(2):619–625

Singh A, Fulekar MH (2012) Phytoremediation of heavy metals by *Brassica juncea* in aquatic and terrestrial environment. In: The plant family Brassicaceae. Springer, Dordrecht. pp 153–169

Singh RP, Agrawal M (2008) Potential benefits and risks of land application of sewage sludge. Waste Manag 28(2):347–358

Slatter KA (2013) Nickel accumulation and tolerance in Berkheya Codii and its application in phytoremediation. Master's Thesis, University of Kwazulu, Natal, South Africa

Su Y, Han FX, Chen J, Sridhar BM, Monts DL (2008) Phytoextraction and accumulation of mercury in three plant species: Indian mustard (*Brassica juncea*), beard grass (*Polypogon monospeliensis*), and Chinese brake fern (*Pteris vittata*). Int J Phytoremediation 10(6):547–560

Su Y, Sridhar BM, Han FX, Diehl SV, Monts DL (2007) Effect of bioaccumulation of Cs and Sr natural isotopes on foliar structure and plant spectral reflectance of Indian mustard (*Brassica juncea*). Water Air Soil Pollut 180(1):65–74

Su Y, Han FX, Sridhar BM, Monts DL (2005) Phytotoxicity and phytoaccumulation of trivalent and hexavalent chromium in brake fern. Environ Toxicol Chem: Int J 24(8):2019–2026

Subhashini V, Swamy AV (2013) Phytoremediation of Pb and Ni contaminated soils using Catharanthus roseus (L.). Univ J Environ Res Technol 3(4):465–472

Tessier AP, Campbell PG, Bisson MJ (1979) Sequential extraction procedure for the speciation of particulate trace metals. Anal Chem 51(7):844–851

Thangavel P, Subbhuraam CV (2004) Phytoextraction: Role of Hyperaccumulators in Metal Contaminated Soils. Proceedings of the Indian National Science Academy. Part B. 70:109–130

Thewys T, Kuppens T (2008) Economics of willow pyrolysis after phytoextraction. Int J Phytoremediation 10(6):561–583

Tytła M, Widziewicz K, Zielewicz E (2016) Heavy metals and its chemical speciation in sewage sludge at different stages of processing. Environ Technol 37(7):899–908

Wang FQ, Li YJ, Zhang Q, Qu J (2015) Phytoremediation of cadmium, lead and zinc by Medicago sativa L.(alfalfa): a study of different period. Bulg Chem Commun 47:167–172

Wang JY, Zhang DS, Stabnikova O, Tay JH (2005) Evaluation of electrokinetic removal of heavy metals from sewage sludge. J Hazard Mater 124(1–3):139–146

Xiyuan X, Tongbin C, Zhizhuang AN, Mei LEI, Huang Z, Xiaoyong L, Yingru LIU (2008) Potential of Pteris vittata L. for phytoremediation of sites co-contaminated with cadmium and arsenic: the tolerance and accumulation. J Environ Sci 20(1):62–67

Yang J, Lei M, Chen T, Gao D, Zheng G, Guo G, Lee D (2014) Current status and developing trends of the contents of heavy metals in sewage sludges in China. Front Environ Sci Eng 8(5):719–728

Yang G, Zhang G, Wang H (2015) Current state of sludge production, management, treatment and disposal in China. Water Res 78:60–73

Yashim ZI, Agbaji EB, Gimba CE, Idris SO (2016) Phytoremediation potential of Ricinus communis L. (castor oil plant) in northern Nigeria. Int J Plant Soil Sci 10(5):1–8

Zennegg M, Munoz M, Schmid P, Gerecke AC (2013) Temporal trends of persistent organic pollutants in digested sewage sludge (1993–2012). Environ Int 60:202–208

Zhang W, Yang L, Wang AH, Wang CW, Zhou J (2014) Advance of sludge producing, hazards and disposal methods. Adv Mater Res 1033:369–377. Trans Tech Publications Ltd.

Zhang X, Wang XQ, Wang DF (2017) Immobilization of heavy metals in sewage sludge during land application process in China: a review. Sustainability 9(11):2020

Zhao W, Ding L, Gu X, Luo J, Liu Y, Guo L, Shi Y, Huang T, Cheng S (2015) Levels and ecological risk assessment of metals in soils from a typical e-waste recycling region in southeast China. Ecotoxicology 24(9):1947–1960

Zhou DM, Chen HF, Cang L, Wang YJ (2007) Ryegrass uptake of soil Cu/Zn induced by EDTA/EDDS together with a vertical direct-current electrical field. Chemosphere 67(8):1671–1676

Zorpas AA, Vlyssides AG, Zorpas GA, Karlis PK, Arapoglou D (2001) Impact of thermal treatment on metal in sewage sludge from the Psittalias wastewater treatment plant, Athens. Greece J Hazardous Mater 82(3):291–298

Part III

Phytoremediation Applications for Contaminated Water and Soil

Chapter 8
Phytoremediation of Heavy Metals by *Trapa natans* in Hokersar Wetland, a Ramsar Site of Kashmir Himalayas

Syed Shakeel Ahmad, Zafar A. Reshi, Manzoor A. Shah, Irfan Rashid, and Roshan Ara

Abstract Hokersar wetland is an important Ramsar site of Kashmir Himalayas. Hokersar is an important game reserve of international importance and is a suitable habitat for thousands of resident birds and migratory birds that visit the wetland from Central Asia, China, N-Europe, and Siberia. Currently, the Hokersar is subjected to a number of direct and indirect pressures including metal pollution. In the present study, removal potential of *Trapa natans* for different heavy metals in the Hokersar wetland was studied. The heavy metal concentration in roots and shoots was carried out. In addition, heavy metals were measured in water and sediments of the Hokersar wetland. Enrichment factor, translocation factor, and bioconcentration factor were calculated to evaluate the phytoremediation potential of the macrophyte species. After calculation of the phytoremediation potential of the macrophyte species, it was observed that *T. natans* shows hyperaccumulation of Zn, Pb, Al, and Cr. Moreover, *T. natans*, having BCF > 1 and TF < 1 for Mn indicate that it can be efficiently used for phytostabilization of Mn.

Keywords Hyperaccumulator · heavy metal · macrophytes · phytoremediation · wastewater · wetland

8.1 Introduction

Hokersar wetland is an important Ramsar site of Kashmir Himalayas located 10 km from the Srinagar city. Hokersar is an important game reserve of international importance. The wetland is experiencing heavy metal pollution due to the use of gun shots for hunting and poaching, use of pesticides in adjoining rice fields and apple and other fruit orchards, vehicular transport, etc. (Ahmad et al. 2016). The

---

S. S. Ahmad (✉) · Z. A. Reshi · M. A. Shah · I. Rashid · R. Ara
Department of Botany, University of Kashmir, Srinagar, J & K, India

L. Newman et al. (eds.), *Phytoremediation*, https://doi.org/10.1007/978-3-031-17988-4_8

pollution arising as a result of entry of heavy metals into the wetlands and other water bodies is a big environmental problem and is responsible for the pollution of the environment as well as it impairs human health and aquatic wildlife (Buruiana et al. 2015; Choppala et al. 2014; Janssens et al. 2003; Sanchez 2008; Scheuhammer 1887). Once the heavy metals find entry into animals including human beings, they are responsible for a number of diseases like developmental retardation, various cancers, and kidney damage. They are also responsible for decreased fertility, cellular and tissue damage, cell death, and disjunction of a variety of organs and even death in some instances (Glover-Kerkvliet 1995; Hogstrand and Haux 2001; Oliveira Ribeiro et al. 2000; Oliveira Ribeiro et al. 2002; Rietzler et al. 2001; DamekProprawa and Sawicka-Kapusta 2003). Thus, removal of heavy metals from habitats and ecosystems is of prime importance. Phytoremediation is the removal of contaminants using vegetation from contaminated sites. Phytoremediation is an affordable, efficient, ecologically green, and easily applicable technological solution for the removal of heavy metals from contaminated sites (Maine et al. 2001; Xue et al. 2005; Vymazal 2010). The process of phytoremediation involves the use of uptake capabilities of plant root systems, together with the translocation, bioaccumulation, and contaminant degradation abilities of the plants (Hinchman et al. 1995; Ma et al. 2013). A number of macrophyte species are involved in the removal of heavy metals from contaminated water and soil (Ellis et al. 1994; Hua et al. 2012; Kara et al. 2003; August et al. n.d.; Rai et al. 1995; Sharma and Gaur 1995).

The removal of heavy metals in natural wetlands and the capability of wetlands to purify water efficiently and cheaply have long been reported, and this has led to an extensive research both on natural and constructed wetlands for the removal of contaminants throughout the globe (Hammer 1990; Kadlec and Kadlec 1979; Kadlec and Knight 1996; Kwong and Van Stempvoort 1994; Mays and Edwards 2001). The Kashmir Himalayas are gifted with a number of natural wetlands, but unfortunately, we have very scanty information on the extent of heavy metal contamination and their removal capability by different aquatic macrophyte communities growing in these wetlands except a few attempts in recent past by some workers (Ahmad et al. 2014, 2015, 2016). The present research was carried out to determine the capability of *Trapa natans* to remove different heavy metals, so that it can be employed by researchers across the globe for the removal of heavy metals both in constructed and in natural wetlands.

8.2 Materials and Methods

8.2.1 Study Area

Hokersar wetland (34° 06′ N latitude, 74° 05′ E longitude) is a perennial, protected wildlife reserve and a Ramsar site at an altitude of 1584 m (amsl) about 12 km Northwest of Srinagar city in Kashmir Himalaya, India (Fig. 8.1). The wetland has a fluvial origin and is a permanent but relatively shallow water body that has a

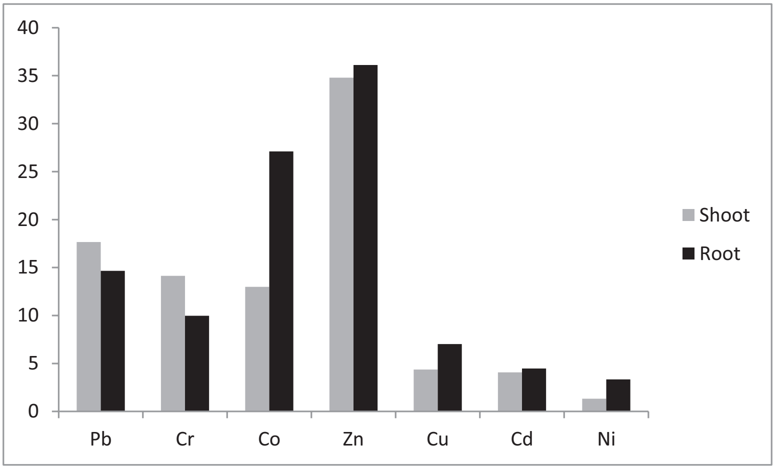


Fig. 8.1 Heavy metals (Pb, Cr, Co, Zn, Cu, Cd, and Ni) in roots and shoots of *Trapa natans*

sub-Mediterranean climate. The Hokersar wetland is composed of Karewa table lands. The Hokersar wetland has lacustrine deposits (clay, silt, sand particles, conglomerates, boulders, and pebbles) of Pleistocene age. Once the wetland was spread to an area of 19.5 km^2. Now, the wetland has shrunk to just 13.26 km^2 because of different anthropogenic pressures. The water enters the wetland through different inlet channels like Doodganga, Dharmuna, and Soyibugh inlets. The water leaves through lone outlet at Soziath provided with needle weir gate. Hokersar wetland is a suitable habitat for a number of migratory and residential avifaunal species. The wetland receives about two million migratory waterfowl during winter migrating from Central Asia, China, N-Europe, and Siberia.

8.2.2 Study Species

Trapa natans L. belongs to the family water nut family or Trapaceae. It is an aquatic, rooted annual herb. The leaves of *Trapa natans* are arranged in the form of a rosette. *Trapa natans* is known by different names which include water chestnut, buffalo nut, bat nut, devil pod, ling nut, or *singhara.* The plant has two types of leaves finely divided, feather-like submerged leaves and undivided floating leaves.

8.2.3 Sampling

Plant samples were randomly collected from two different sites within the wetland and were sealed in airtight polythene bags and transported to the laboratory at 4 °C. The samples of water were collected from five different sites of the wetland.

Prior to sampling, all the sampling equipments were pre-treated as specified by American Public Health Association (APHA 1995). One litre of water sample was collected from each sampling site in high density polythene bottles for the determination of heavy metals. The samples were preserved with 2 ml of conc. HNO_3 per liter and were kept at 4 °C until analyzed. The sampling quality control in water was ensured by introducing bottle blanks and field replicate samples which were analyzed to measure the integrity of the samples and reproducibility, respectively. For the estimation of heavy metals in the sediment to complete the study, the different sediment samples were collected from the different sites of the wetland and were transported to the laboratory in plastic bags. The samples were stored at 4 °C for about 1 week. Prior to sampling, all the sampling equipment were pre-treated as specified by American Public Health Association (APHA 1995).

8.2.4 Chemical Analysis

Water samples (50 mL) were digested with 2 M HNO_3 at 95 °C for 2 h and were made up to 100 mL in volumetric flask with double distilled water. The digestion was done in glassware previously soaked in nitric acid and washed with demineralized water. The digested samples were analyzed for metals in duplicate using AAS Perkin Elmer, model Analyst 800. Sample blanks were also analyzed to correct for any contamination in the course of analysis.

The plant samples were thoroughly washed with distilled water in the laboratory. Shoot (leaves and stalks) and root tissues were separated and oven dried at 60 °C until well-dried. The dried samples were weighed and ground to pass a 40 mesh screen using a Wiley mill. For the estimation of heavy metals in plant samples, diacid digestion (nine parts nitric acid:four parts perchloric acid) was carried out at 80 °C. All the reagents that were used were of analytical grade and the reaction vessels were treated well to avoid external contributions of the metals. Sample blanks were analyzed to correct for possible external contributions of the metals, while replicate samples were also evaluated. All the analyses were done in triplicate to ensure reproducibility of results. The digested samples were analyzed for ten metals (Fe, Al, Mn, Zn, Cu, Pb, Co, Cr, Ni, and Cd) using AAS Perkin Elmer, model Analyst 800.

For the estimation of heavy metals in sediments, the sediment samples were collected from the wetland and transported to the laboratory in plastic bags. The collected sediment samples were stored in the laboratory for 1 week at 4 °C. The dried sediment samples were placed in aluminum trays and dried overnight in an oven at 80 °C. The dried samples were then homogenized by grinding with the help of a mortar and pestle. A sample of 1.0 g of ground sediment was weighed into 100 ml glass block digestion tube and digested with acid mixture (nine parts nitric acid:four parts perchloric acid) during which temperature was raised to about 95 °C until the evolution of nitrous gas stopped and digest became clear. Filtration through a Whatman filter paper was carried out, and after proper, the digest was analyzed for different heavy metals.

8.2.4.1 Data Analysis

The mean and standard error of mean of the metals in plant sample parts were calculated. In addition, translocation factor (TF), enrichment factor, and bioconcentration factors were calculated to know the phytoremediation potential of *Trapa natans.* Translocation factor (TF) was evaluated by calculating the ratio of the concentration of metals (μg/g) in the shoot to the concentration of metals (μg/g) in the root (μg/g) of *Trapa natans*. The enrichment factor was evaluated by calculating the ratio of the concentration of metal in the plant (μg/g) to the concentration of the metal in the water (mg/L). The bioconcentration factor was evaluated b calculating the ratio of concentration of heavy metal in plant root to the concentration of the metal in the soil (Yoon et al. 2006).

8.3 Results and Discussion

The concentration (mg/kg) of different heavy metals in the roots and shoots of *Trapa natans* is presented in Table 8.1. The results are also graphically presented in Figs. 8.1 and 8.2. Among different heavy metals, Fe was found to be in the highest concentration (16,059 ± 302.53), while the lowest concentration was found to be in Ni (1.33 ± 0.30). The macrophytes present in different aquatic ecosystems have an important role in the removal of different contaminants including heavy metals. However, different macrophyte species have different potentials to accumulate different heavy metals. In general, roots of macrophytes accumulate higher concentration of metals than their shoots. Incase of surface floating macrophytes like *Lemna minor* and emergent macrophytes like *Sparganium erectum, Typha angustata* and *Phragmites australis* the heavy metals metals mainly enter the plant through their roots. In case of submerged species, heavy metals mainly enter the plant through their leaves and roots (Denny 1987). Those macrophyte species that have well-developed root rhizome system and having totally submerged leaves the route of heavy metals uptake is mostly from the sediments (Gullizzoni 1991).

Phytoremediation involves the use of special type of plants called hyperaccumulators for the amelioration of different contaminants from the polluted ecosystems (Lasat 2002; Wei et al. 2009). The main criteria to delimit a species as a hyperaccumulator of the different metals are the concentration of the metals in shoots. To classify a plant as a hyperaccumulator, it must possess a concentration of 10,000 μg/g for Zn and Mn, Ba, and Fe; above 1000 μg/g dry mass for Pb, Cu, Ni and Co, Cr; 100 μg/g for Cd (Baker and Brooks 1989; Reeves and Baker 2000; Srivastava et al. 2006). The other criteria that are used to delimit a species as a hyperaccumulator are EF and TF. A hyperaccumulator should have both EF and TF greater than one (Wei et al. 2009; Baker and Brooks 1989). A hyperaccumulator must also have high tolerance to toxic contaminants (Ma et al. 2001).

In the present study on *T. natans,* the highest EF was recorded for Fe which was followed by Mn and Co. This shows that Fe is the most transferred metal into the root followed by Mn and Co in decreasing order. TF greater than one was recorded

Table 8.1 Concentration of heavy metals, EF, TF, and BCF in *Trapa natans*

Heavy Metal	Shoot	Root	EF		TF	BCF
			Shoot	Root		
Pb	17.66 ± 1.67	14.66 ± 2.59	236	258	1.20	0.23
Fe	7165.5 ± 163.69	16,059 ± 302.53	2751	1225	0.45	1.11
Mn	406.1 ± 6.95	1821.2 ± 290.3	2716	606	0.22	1.26
Al	2887 ± 754.68	2666 ± 141.10	340	368	1.08	0.29
Cr	14.14 ± 1.03	9.97 ± 0.37	399	566	399	566
Co	12.99 ± 0.65	27.1 ± 0.45	2710	1299	0.48	0.14
Zn	34.79 ± 2.87	36.12 ± 1.83	580	984	1.70	0.05
Cd	4.07 ± 0.04	4.47 ± 0.43	1118	1018	0.91	0.30
Ni	1.33 ± 0.30	3.34 ± 0.63	111	44	0.40	0.01

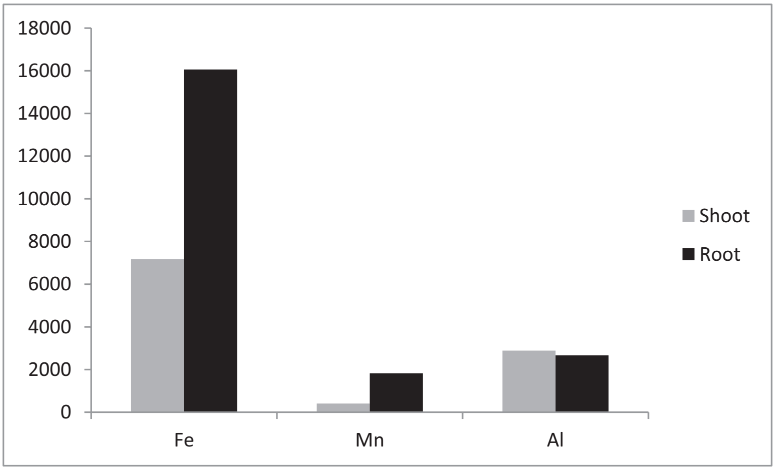


Fig. 8.2 Heavy metals (Fe, Mn, Ni) in roots and shoots of *Trapa natans*

for Zn, Pb, Al, and Cr, while less than one was recorded for Ni, Cu, Cd, Zn, Co, Fe, and Mn. BCF > 1 was obtained for Fe (1.11) and Mn (1.26). The obtained results suggest that *T. natans* is a hyperaccumulator of Zn, Pb, Al, and Cr. Moreover, *T. natans* having BCF > 1 and TF < 1 for Mn can be efficiently used for phytostabilization of Mn. It was also reported by different workers that *Trapa natans* also has a good ability for the phytoremediation of Pb-contaminated water and is an ideal candidate for the removal of wastewater contaminated with Pb (Mansuri et al. 2013). Moreover, He further stated that *T. natans* showed greater bioaccumulation factor than *Phragmites australis* in Anzali wetland. Good phytoremediation potential of *T. natans* has been reported by other workers (Srivastava and Shukla 2014; Verma et al. 2016; Shalini et al. 2014).

References

Ahmad SS, Reshi ZA, Shah MA, Rashid I, Ara R, Andrabi SMA (2014) Phytoremediation potential of *Phragmites australis* in Hokersar wetland—a Ramsar site of Kashmir Himalaya. Int J Phytoremediation 16:1183–1191

Ahmad SS, Reshi ZA, Shah MA, Rashid I, Ara R, Andrabi SMA (2015) Heavy metal accumulation by *Potamogeton natans* and *Ceratophyllum demersum* in a Himalayan RAMSAR site: management implications. Wetland Ecol Manag 24:469. https://doi.org/10.1007/s11273-015-9472-9

Ahmad SS, Reshi ZA, Shah MA, Rashid (2016) Constructed wetlands: role in phytoremediation of heavy metals. In: Ansari AA, Gill SS, Gill R, Lanza GR, Newman L (eds) Phytoremediation, vol 3. In Press

APHA (1995) Standard methods for examination of water and wastewater, 20th edn. American Public Health Association, Washington, DC

August EE, McKnight DM, Hrncir DC, Garhart (n.d.) Agri Biol 3:281–283

Baker AJM, Brooks RR (1989) Terrestrial higher plants which hyperaccumulate metallic elements – a review of their distribution, ecology and phytochemistry. Biorecovery 1:81–126

Buruiana DL, Lefter D, Tiron GL, Balta S, Bordei M (2015) Toxicity of heavy metals on the environment and human health. 15th International Multidisciplinary Scientific Geo Conference SGEM 2015, wwwsgemorg, SGEM2015 Conference Proceedings, ISBN 978–619-7105-40-7 / ISSN 1314–2704, June 18–24, 2015, Book5 2:565–572

Choppala G, Saifullah Bolan N, Bibi S, Iqbal M, Rengel Z, Kunhikrishnan A, Ashwath N, Ok YS (2014) Cellular mechanisms in higher plants governing tolerance to cadmium toxicity. Cr Rev Plant Sci 33:374–391

DamekProprawa M, Sawicka-Kapusta K (2003) Damage to the liver, kidney and testis with reference to burden of heavy metals in yellow necked mice from areas around steel works and zinc smelters in Poland. Toxicology 186:1–10

Denny P (1987) Mineral cycling of wetland plants: a review. Archiv für Hydrobiologie–BeiheftErgebnisse der Limnologie 27:1–25

Ellis JB, Revitt DM, Shutes RBE, Lang Ley JM (1994) The performance of vegetated biofilters for highway runoff control. Sci Total Environ 146/147:543–550

Glover-Kerkvliet J (1995) Environmental assault on immunity. Environ Health Perspect 103:236–239. PMID: 7768222

Gullizzoni P (1991) The role of heavy metals and toxic materials in the physiological ecology of submerged macrophytes. Aquatic Botany 41:87

Hammer DA (1990) Constructed wetlands for wastewater treatment. Lewis Publishers, Michigan

Hinchman RR, Negri M, Gatliff EG (1995) Phytoremediation: using green plants to clean up contaminated soil, groundwater, and wastewater. Argonne National Laboratory Hinchman, Applied Natural Sciences, Inc.

Hogstrand C, Haux C (2001) Binding and detoxification of heavy metals in lower vertabrates with reference to metallo-thionein. Comp Biochem Physiol Part C: Comp Pharmacol 100:137–141

Hua Y, Zhang C, Yin Y, Chen R, Wang X (2012) Phytoremediation potential of three aquatic macrophytes in manganese-contaminated water. Water Environ J 26:335–342

Janssens E, Dauwe T, Pinxten R, Bervoets L, Blust R, Eens M (2003) Effects of heavy metal exposure on the condition and health of nestlings of the great tit (Parus major), a small songbird species. Environ Pollut 126:267–274

Kadlec RH, Kadlec JA (1979) Wetlands and water quality. In: Greeson PE, Clark JR, Clark JE (eds) Wetland functions and values : the state of our understanding. American Water Resources Association, Minneapolis, p 674

Kadlec RH, Knight RL (1996) Treatment wetlands. Lewis Publishers/CRC Press, New York

Kara Y, Aran DB, Kara Y, Ali Z, Genc I (2003) Bioaccumulation of nickel by aquatic macrophyta, *Lemna minor* (Duckweed). Int J Agric Biol

Kwong YTJ, Van Stempvoort DR (1994) Attenuation of acid rock drainage in a natural wetland system. Environ Geochem Sulphide Oxidation ACS Symp Series 550:382–392

Lasat MM (2002) Phytoextraction of toxic metals: a review of biological mechanisms. J Environ Qual 31:109–120

Ma LQ, Komar KM, Tu C (2001) A fern that accumulates arsenic. Nature 409:579

Ma Y, Rajkumar M, Luo Y, Freitas H (2013) Phytoextraction of heavy metal polluted soils using Sedum plumbizincicola inoculated with metal mobilizing Phyllobacterium myrsinacearum RC6b. Chemosphere 93(7):1386–1392

Maine MA, Duarte MV, Suñé NL (2001) Cadmium uptake by floating macrophytes. Water Res 35(11):2629–2634

Mansuri N, Khorasani N, Monavari SM, Karbasi A, Panahandeh M (2013) Heavy metal concentration in soil and plant species (*Phragmites australis, Trapa natans*) from Anzali Wetland (Iran). World J Environ Pollut 3(1):01–04

Mays PA, Edwards GS (2001) Comparison of heavy metal accumulation in a natural wetland and constructed wetlands receiving acid mine drainage. Ecol Eng 16(4):487–500

Oliveira Ribeiro CA, Pelletier E, Pfeiffer WC, Rouleau C (2000) Comparative uptake, bioaccumulation and gill damages of inorganic mercury in tropical and nordiac freshwater fish. Environ Res 831:286–292

Oliveira Ribeiro CA, Schatzmann M, Silva de Assiss HC, Silva PH, Pelletier E, Akaishi FM (2002) Evaluation of tributyl tin subchronic effects in tropical freshwater fish (*Astyanax bimaculatus* L. 1758). Ecotoxicol Environ Saf 51:161–167

Rai UN, Sinha S, Tripathy RD, Chandra P (1995) Wastewater treatability potential of some aquatic macrophytes: removal of heavy metals. Ecol Eng 5:5–12

Reeves RD, Baker AJM (2000) Phytoremediation of toxic metals. Wiley, New York, pp 193–229

Rietzler AC, Fonseca AL, Lopes GP (2001) Heavy metals in tributaries of Ampulha reservoir, Minas Gerais Brazzilian. J Biol 61:363–370

Sanchez ML (ed) (2008) Causes and effects of heavy metal pollution. Nova Science Publishers, Hauppauge, p 392

Scheuhammer AM (1887) The chronic toxicity of aluminium, cadmium, mercury, and lead in birds: a review. Environ Pollut 46:263–295

Shalini S, Arti Y, Shukla DN (2014) Effects of lead and its phytoremediation potential in *Trapa natans* (L.). Asian J Res Chem 7(4):434

Sharma SS, Gaur JP (1995) Potential of *Lemna polyrhiza* for removal of heavy metals. Ecol Eng 4:37–45; KS (2002) Seasonal variability of metals transported through a wetland impacted by mine drainage in the Rocky Mountains. Environ Sci Technol 36(17):3779–3786

Srivastava S, Shukla DN (2014) Effects of lead and its phytoremediation potential in *Trapa natans* (L.). Ecol Environ Conserv Paper 20(4):1745–1748

Srivastava M, Ma LQ, Santos JAG (2006) Three new arsenic hyperaccumulating ferns. Sci Total Environ 364:24–31

Verma A, Bharagava RN, Kumar V, Singh A, Dhusia N, More N (2016) Role of macrophytes in heavy metal removal through rhizo-filtration in aquatic ecosystem. Eur J Biotechnol Biosci 4(10):15–20

Vymazal J (2010) Constructed wetlands for wastewater treatment. Water 2:530–549

Wei S, Zhou Q, Srivastava M, Xiao H, Yanga C, Zhang Q (2009) Kalimeris integrifolia Turcz. Ex DC: An accumulator of Cd. J Hazardous Mater 162:1571–1573

Xue SG, Chen YX, Baker AJM, Reeves RD, Xu XH, Lin Q (2005) Manganese uptake and accumulation by two populations of *Phytolacca Acinosa* ROXB. (Phytolaccacear). Water Air Soil Pollut 160:3–14

Yoon J, Cao X, Zhou Q, Ma LQ (2006) Accumulation of Pb, Cu, and Zn in native plants growing on a contaminated Florida site. Sci Total Environ 368:456–464

Part IV

Phytoremediation Using Microbial Assemblages in Water and Soil

Chapter 9
Spinoffs of Phyoremediation and/or Microorganism Consortium in Soil, Sediment, and Water Treatments and Improvement: Study of Specific Cases and Its Socioeconomic and Environmental Advantages

Hayfa Rajhi and Anouar Bardi

Abstract A large amont of rejected materials and their pollution can create multiple challenges in terms of sustainable development, law, and the environment. Faced with this problem, it is necessary to study and develop methods that make it possible to extract or stabilize pollutants in the biotope matrix (sediment, soils, and water) before storage and possible recovery operations. Different cases were presented, namely, (I)a bioremediation of urban wastewater by microalgae (phytoremedaition), (II) bioremediation of industrial wastewater using anaerobic digestion (using anaerobic microorganisms) and solid fermentation (using fungi), (III) bioremdiation of sediment and sludge using anaerobic consortia (remediation associated with bioenergy production), and (IV) bioremediation using biosurfactant microorganisms' activity. In addition, the effect of an economic and environmental bioremediation study was carefully discussed in this chapter. In fact, the use of bioremediation process is in perfect harmony with recent sustainable environmental development.

Keywords Bioremediation · Phytoremediation · Waste treatment · Consortia · Bioenergy · Sustainable development · Economic growth

---

Hayfa Rajhi and Anouar Bardi contributed equally with all other contributors.

H. Rajhi (✉)
Laboratory of Applied Microbiology, Department of Molecular Biology, Universidad Autonoma de Madrid, Madrid, Spain

A. Bardi
Higher Institute of Management of Gabès, Gabès, Rue Jilani Lahbib, Gabès, Tunisia

L. Newman et al. (eds.), *Phytoremediation*, https://doi.org/10.1007/978-3-031-17988-4_9

9.1 Introduction

Applied Environmental Microbiology Section encompasses two main areas of research in environmental microbiology. The first area concerns the study of microorganisms found in soils, sediments, water, and air, in addition to their relationships with each other and with animals, humans, and plants. The second field of environmental microbiology is that of the study of microorganisms involved in biotechnologies that affect all aspects of human activity, such as food sciences, agriculture, biomass valuation, techniques, depollution, bioremediation and pharmacology, etc. In this context, we can suggest that the bioremediation research was basically based to microorganism's pathways as well as their different environment response behaviors (Rajhi 2012).

Biological methods rely on the metabolism and activity of communities of bacteria, fungi, higher plants to remove, degrade, or stabilize pollutants. We distinguish two main processes: phytoremediation and bioremediation. Phytoremediation is a biological process basically used by plants to treat soil and/or water. In addition, plants have the capacity to extract, accumulate or degrade polluted efficiently. The plant phytoremediation consist to the interaction of roots and microorganisms associated. This bioprocess allows soil and water decontamination from higher organic and mineral-polluted compounds. Phytodepollution technique is a pollution control technology that appears to be effective against a broad spectrum of organic and inorganic pollutants. It can be used on solid (polluted soil), liquid (contaminated water), or gaseous (filtration of air laden with harmful volatile compounds) substrates. Main phytodepollution mechanisms are phytoextraction, phytodegradation, rhizodegradation, and phytostabilization (Perchet 2008).

In Bioremediation process, the microbial strains (bacteria and /or fungi) were invested to degarde the wastes. The bioremediation is bioprocess that has a huge applications, including cleaning soil water, soil, industrial sludge. There are microorganisms capable of efficiently degrading pollutants such as petroleum products, oils and greases, and hydrocarbons. In addition to eliminating compounds that have harmful effects on the environment, this technique makes it possible to reduce sanitation costs. Microorganisms need nutrients and a carbon source to provide the energy necessary for their growth and survival. Bioremediation is multidisciplinary, thus taking into account microbiology, engineering, ecology, ecotoxicology, soil science, and chemistry. Several methods use microorganisms as the main actor in bioremediation (Perchet 2008). Like other treatments, bioremediation processes can be grouped into two sub-parts: the first devoted to "in situ" depollution treatments and the second to "off-site" treatments. In situ treatments are required in cases where pollutants have penetrated deep into the soil and are distributed over large areas, making excavation too expensive. These treatments aim to activate biodegradation processes and improve the accessibility of microorganisms to oxygen (Perchet 2008). Biological treatment by soil aeration (or bioventing) is a promising technology which consists of stimulating the in situ biodegradation of pollutants in the soil by supplying the microflora in place with the necessary oxygen. Oxygen is provided by injecting air into the contaminated area. For this method to be effective, it is necessary for the porous medium to have a good content of mineral elements and a soil colonized by microorganisms suitable for pollution, so that bioventing technique can be envisaged. Regarding the treatment of soils by injection of hydrogen peroxide (H_2O_2), some bacteria can use H_2O_2 as an oxygen source up to concentrations of 1 g/L, which represents O_2 contents 50 times higher than those measured in water saturated with the air. Thus, the use of H2O2 was considered for the treatment of polluted areas. This treatment can only be advantageous if the contaminated soil is sufficiently permeable to allow effective percolation. The addition of hydrogen peroxide can lead to precipitation of iron, which can lead to clogging of soils. It is important to control the decomposition of hydrogen peroxide. Indeed, too rapid decomposition runs the risk of over-saturating the water with O_2 which will tend to degas and block the circulation of fluids. Too slow decomposition reduces microbial metabolism and the speed of decontamination. Treatment of soils associated with that of the water ground, this type of treatment results in pumping water from the water ground, which is surface treated (filtration, stripping, and biological treatment), often re-aerated, supplemented with mineral nutrients sometimes with microorganisms before being reinjected into the soil. Injection of microorganisms may be necessary in the case of specific pollutants having a microorganism suitable for degradation. However, the use of this technique is limited and cannot be used in case of contaminated deeply soil. Most of the time, using these off-site processes reduces processing times. (I) The aim of reactor or bioslurry treatments, is to mix microorganisms and pollutants in order to facilitate their degradation. For bioreactors in anaerobic condition, the final objective is to mineralize the pollutant or to reduce its bioavailability or that of metabolites by binding them irreversibly to the matrix. (II) Composting process, the soil is mixed with agricultural by-products (alfalfa straw, sugar beet stalks, and vegetable waste). (III) The treatment in biotertre (or biopile) consists in stimulating or optimizing the metabolism of microorganisms to break down soil pollutants. This technique is carried out under cover, with treatment of gases and juices produced (leachate), aeration, humidification, and addition of nutrients (nitrogen and phosphorus) to the substrate to be decontaminated (Perchet 2008). (IV) Controlled spreading (or landfarming) or controlled landfarming was for a long time the only biodegradation process used (on a small scale) for polluted materials with little hydrocarbon content. It requires large areas with a spreading plan that is difficult to put into action (many players to be convinced and controls to be carried out). (V) Laggooning used for the treatment of wastewater or mine water, lagooning technique consists in developing, downstream of zones generating these pollution, areas through which the effluents flow. This technique is a purification process which consists in maintaining the wastewater in shallow ponds for a long period during which the action of microorganisms, plants, wind, and sun, with or without artificial aeration, causes the slow degradation of organic matter. (Rajhi et al. 2018, 2020).

In this chapter, a summary of results of the research work carried out was presented. Different cases were presented, namely, (I) a bioremediation of urban wastewater by microalgae (phytoremedaition), (II) bioremediation of industrial wastewater using anaerobic digestion (using anaerobic microorganisms) and solid fermentation (using fungi), (III) bioremdiation of sediment and sludge using anaerobic consortia (remediation associated with bioenergy production), and (IV) bioremediation using biosurfactant microorganisms activity. In addition, an economic and environmental bioremediation study effect was carefully discussed.

9.2 Phytoremediation

9.2.1 Definition of Phytoremediation

Phytoremediation is a bioprocess that uses the metabolism of plants and (algae/microalgae) to transform, to degrade, to concentrate, and to stabilize or to volatilize pollutants (organic and inorganic molecules, metals, and radioelements) contained in contaminated soil/sediment or water. More precisely, it is a set of in situ techniques (which can be installed directly on the contaminated site) relying on plants to extract, degrade, or immobilize contaminants from soils, sediments, sludge, water from surface or underground, and in the air.

Phytoremediation is an efficient economic bioremediation strategy based on solar energy conversion.

9.2.2 The Different Phytoremediation Processes (by Plants)

Different phytoremediation processes were based on the following different processes such as extraction, stabilization, degradation, and volatilization.

9.2.2.1 Phytoextraction

In this bioprocess, plants can remove contaminants, such as trace metal and metalloid compounds, as well as different organic contaminants, from the soil and accumulate them in their aerial parts which can then be harvested. This is the most used method. Plants can acidify the rhizosphere or even secrete ligands capable of chelating metal ions. Sometimes, mycorrhizal fungi form symbiosis with plant roots and aid in uptake of metals when soil concentrations are low, and conversely, can help plants resist phytotoxic levels (Peer et al. 2005).

9.2.2.2 Phytostabilization

Plants reduce the bioavailability of soil–rhizosphere contaminants by chemical immobilization, such as precipitation, stabilization, absorption as well as a prevention of lateral depth movements via erosion/and leaching. Plant stabilization can prevent the dispersion of contaminants in surface and groundwater. A vegetated land cover minimizes wind and water erosion. In addition, this technique can prevent the animal against direct with pollutants. Plants can minimize the formation of contaminated leachate and limit the migration of dissolved contaminants into groundwater. In contrast, a risk of pollutants conversion into less bioavailable forms can be occurred when these precipitate in the rhizosphere (Giasson et al. 2005).

9.2.2.3 Phytodegradation

Plants absorb and break down organic pollutants in their tissues, as well as can secrete an enzyme of degradation in the rhizosphere. Decontamination is carried out in the rhizosphere by microorganisms, which growth and activity were stimulated by plants. The degradation of organic compounds can be complete (generating inorganic elements such as CO_2 and H_2O/Cl_2), but it can also be incomplete, leading to the stable intermediates' formation (called metabolites), which can be stored in the plant. This type of remediation can be used, among other things, to remedy contamination problems with petroleum hydrocarbons (Pilon-Smits 2005).

9.2.2.4 Phytovolatilization

Organic and inorganic compounds are extracted from the soil by plants, transported in their vascular system, and then exposed to the atmosphere through transpiration, which can be completely volatilized, and therefore, it is not necessary to harvest and treat used plants (Olson et al. 2004). However, the risk of pollutants air transfer into atmosphere must be examined before the process implements. Phytovolatilization is used for chlorinated solvents (such as trichloroethylene, herbicides, insecticides, hydrocarbons, and certain metalloids, such as mercury, arsenic, and selenium. Volatile organic compounds can simply be released into the atmosphere by plants. However, components such as selenium must be transformed in the plant before being volatilized (this transformation simultaneously decreases their toxicity). Mycorrhizal fungi can facilitate the absorption of mercury and selenium, two elements that have a gas phase (Glass 1999).

9.2.2.5 Rhizofiltration

This technique can treat the municipal as the industrial wastewater, surface runoff, or water that infiltrates the soil in agricultural areas, leachate from mines and landfills, or contamination of water and underground water. Contaminants targeted include metallic trace elements, radionuclides, selenium, nutrients, certain organic compounds, such as pesticides, or acid mine drainage (Newman et al. 1997).

9.2.3 Phytoremediation by Microorganisms: Phytoremediation Wastewater by Microalgae (Study Case of Urban Wastewater)

The assessment of the treatment of treatment (phytoremediation) by microalgae on wastewater must cover three major axes, namely: agricultural impact, environmental impact, and socio-economic impact. Several socio-economic benefits can be highlighted during the use of this process, which consists of comparing the physicochemical and microbiological quality of the sewage before and after a phytoremediation process by microalgae, namely, bioenergetic benefits, environmental benefits, and economic and social benefits.

9.2.3.1 Bioenergetic Benefits: Valorization of Fatty Acids Produced by Phytoremediation in Biodiesel

Phytoremediation-treated water shows a very important content of lipid constituents. In fact, lipid compounds are present only after the treatment of water by phytoremediation, which highlights the importance of this process already applied in this research; in this case, the use of this high lipid content in the production of biodiesel (a third generation biofuel). On the other hand, no fatty acid has been detected with the exit wastewater already treated in the treatment plant. In fact, microalgae have greater treatment potential than has been planned and can eliminate many nutrients from water, with greater efficiency than classic wastewater treatment. From an economic point of view, it seems that it would be more interesting to use these microorganisms in secondary rather than tertiary treatment. In particular, the cost of electricity energy supplied and usable during secondary treatment in a station can be replaced by energy produced in biodiesel.

9.2.3.2 Environmental Impact and Agricultural Impact

Purified waters already treated with phytoremediation are devoid of heavy metals and are rich in phosphorus and nitrogen, which constitute a good irrigation substrate in agriculture and can bring out several positive impacts on the environment, on the economy and society.

9.2.3.2.1 Environmental Benefits

Wastewater treatment by the phytoremediation process can reduce the environmental impact of polluted wastewater discharges too loaded into the Gulf of Gabes. Similarly, this treatment can contribute to the improvement of the quality of bathing water and the regeneration of the Gulf of Gabes Marine Ecosystem. In addition, we can observe a sharp fall in the contents of minerals and heavy metals, particularly cadmium and chromes which are completely eliminated after the application of this method. In fact, the elimination rate reaches 100%. Another time, it is observed that the purpose of phytoremediation has been successfully achieved. In fact, the treatment of wastewater by microalgae is in perfect harmony with respect to the environment and offers advantage a cost-effective means of elimination of nutrients and biomass production (Rajhi et al. 2020; Fig. 9.1).

The Gulf region of Gabes has different environment characteristics, namely, a climate with very high humidity and wealth in light intensity (a fairly important light whose presence was continuous throughout the year). Similarly, the region of Gabès has long suffered an important amount of polluted water highly charged with organic materials and which come from the release of wastewater partially treated directly into the sea as well as chemical waste such as the phosphogypse that are rejected with big quantities in marine waters by the industrial zone (Rajhi et al. 2020). This will necessarily allow large-scale recycling of waste in the region, with the resulting environmental and energy benefits. Experimental research already carried out in this study was very close to natural weather parameters of the region defined by an annual temperature of 18.56 °C a year and an average overall solar radiation of 207.1 (w/m^2). The batch experimental parameters are defined by a temperature of 25 °C and a luminous intensity of 100 W. CO_2 and phosphorus, which are key factors in fatty acid production, come from industrial zone which is a few meters from the wastewater treatment

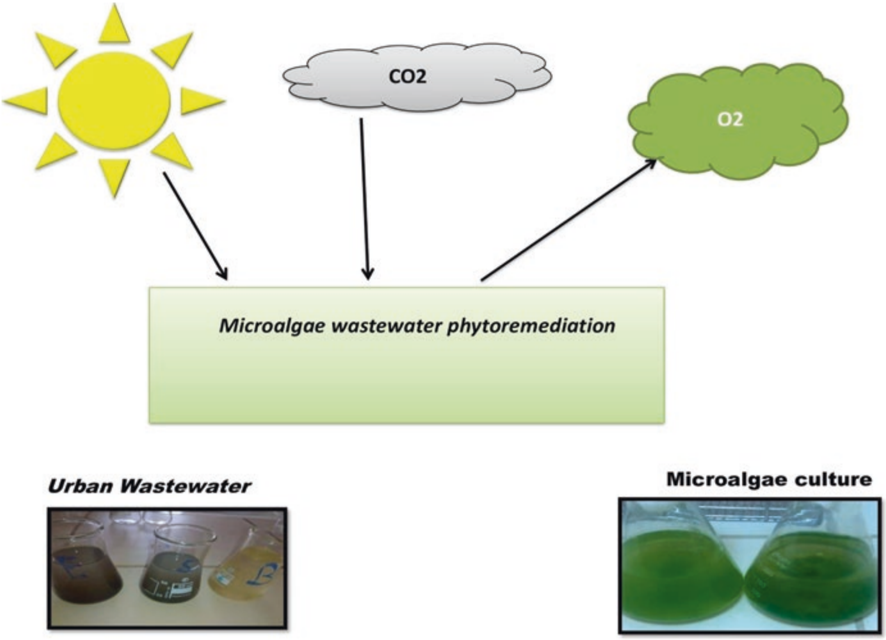


Fig. 9.1 Simplified process of urban wastewater treatment by microalgae enrichment

station. In fact, strategic conditions described above can facilitate a very effective and large-scale natural treatment (Rajhi et al. 2020).

9.2.3.2.2 Advantage of Agronomy

The reuse of treated sewage that is devoid from any chemical, organic and biological contamination in the soil irrigation can constitute an important agronomy challenge (Rajhi et al. 2020).

9.3 Biological Treatment of Industrial Wastewater

9.3.1 Biological Treatment of Industrial Wastewater [Case Study of Olive Mill Waste Water (OMW) Treatment in Arid Zone]

A complete study was made on the olive mill wastewater (OMW) in the South Tunisian for their valorization. The study included the chemical and microbiological characterization of two types of margins: fresh OMW (FOMW), directly from the extraction oiler to a three-phase continuous system, and the other deposited in evaporation ponds (DOMW). The purpose of this natural treatment was to consider ecological assets of the arid region. This comparative study was followed by an assessment of the spreading of these two types of OMW on the soil fertility of the olive field. In addition, an essay of FOMW's strengths in antibacterial activity against standard clinical bacteria. Indeed, a significant increase in pH value of 6 was recorded after the margin layout in evaporation ponds. A fall of the CE to 8.94 A ms/cm-1 was recorded after the OMW layout more than 1 year in evaporation ponds. This fall has been accompanied by a fall in biological oxygen demand (BOD5) and chemical oxygen demand (COD) of 61.05 and 116.37 (G/L) to 55.67 and 103.82 (G/L), respectively. In addition, a significant increase in degradation of phenolic compounds and lipids has been observed after the arrangement of OMW in evaporation ponds. A comparative ground comparative study with OMWF and OMWD shows significant soil fertility after ground spreading with DOMW. The ground treated with DOMW showed an important organic matter compared with the ground treated with FOMW. Indeed, we note that the irrigated site with DOMW has shown [an important value of the germination index (170.55%)] compared with it found in the irrigated soil with FOMW (61.65%) (Rajhi et al. 2018) (Fig. 9.2).

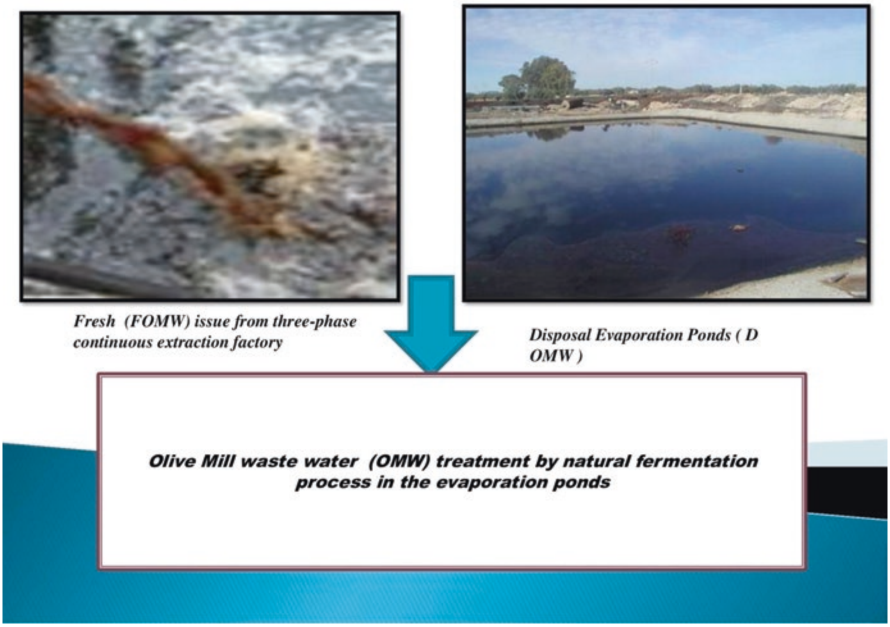


Fig. 9.2 Olive mill waste water (OMW) treatment by natural fermentation process in the evaporation ponds

9.3.2 Biological Treatment of Industrial Wastewater (Case Study: Anaerobic Biodegradation of Chlorinated Organics in Bioaugmented with **Desulfitobacterium spp.***”)*

The biodegradation of 2,4,6-trichlorophenol (246TCP) was studied using a reactor (EGSB) and a reactor (FBBR) filled with activated carbon. The result of FISH shows that the methanogenic arrow community has been maintained in the EGSB reactor, while in the FBBR reactor, this community has been gradually developed up to its final stability threshold. The desulfitobacterium community has also been maintained in reactors, although the proportion of D. chlororespirans has increased in the FBBR reactor, which explains that this species can withstand the toxicity of 246TCP and this best that the species *D. Hafniense* (Puyol et al. 2011).

9.3.3 Biological Treatment of Industrial Wastewater (Case Study: Anaerobic Treatment of Wastewater from Used Industrial Oil Recovery)

A study of "Anaerobic Treatment of Wastewater from Used Industrial Oil Recovery" focused on the anaerobic biodegradation of wastewater of residual industrial oils. Biodegradability tests have shown that these wastewater can be partially biodegradable under anaerobic conditions at a mesophilic temperature. Anaerobic treatment using an EGSB reactor has occurred as an optimal option for wastewater treatment. Long-term treatment has allowed the diversity of granular mud, thus modifying and considerably its microbial composition. Methane production was even stimulated by the addition of wastewater at low concentrations.

(Garcia-Mancha et al. 2012).

9.3.4 Biological Treatment of Industrial Wastewater (Case Study of OMW Treatment)

The valorization of by-products of the olive tree to produce on the one hand, a livestock food with high energy value, and on the other hand of the high industrial and biotechnological enzymes, and by the fermentation in solid medium, from the isolated mushrooms of olive by-products. Through this research action, an essay can offered a new way to the valorization of three coproducts of the olive tree at the same time, namely, the size, the OMW, and numbers, and this by the use of new processes which is the fermentation in solid medium, and which is defined as a fermentation or a culture of microorganisms on a solid medium or substrate in the absence of free water. Similarly, by this research, action has been treated the detoxification of effluents of oils in particular OMWs, which already have serious environmental problems that are mainly attributed to the presence of recalcitrant compounds difficult to degrade, such as phenolic compounds, in high concentration (4–15 $G.L^{-1}$), and which are responsible for phytotoxic and antimicrobial effects.

OMW is rich in organic matter especially phenolic compounds and has an acidic pH. As a result, OMW require different processing technologies to eliminate pollutant agents with harmful effects on the environment. In this work, a comparative study was conducted between the chemical treatment of the OMW by the (fenton-similar) method and another biological treatment. Ten species of fungi were used from margins from different trituration units. Three species, namely, *Rhizopus Oryzae*, *Aspergillus Niger,* and *Commune Penicillium*, have been chosen to treat OMW through a biological process. Different inoculum concentrations of these species have been used to determine the most optimum inoculum for more efficient biological treatment. Results obtained have shown that the biological treatment of OMW appears to be the most effective as the chemical treatment. In fact, most isolated mold species showed a significant decrease in phenolic compound contents.

Similarly, chemical oxygen demand (COD) and the rate of OMW discoloration have been very important particularly with the highest suspension of spores, in this case (10^7spora/ml). The *Rhizpous* Oryzae species showed a higher discoloration rate of the order of 82%, which led to an oxidation of phenolic compounds of 6, 5–3.1 g/l and a degradation of the COD of 72.7%.

9.3.5 Biological Treatment of Industrial Wastewater (Environmental Bioremediation by Lipopeptides Biosurfactants Microorganisms Produced)

Biosurfactants are mainly produced by microorganisms growing aerobically, using one or more carbon sources, such as carbohydrates, oils, or hydrocarbons. These microorganisms are usually yeasts, fungi, or bacteria. The main physiological role of biosurfactant is to allow microorganisms to grow on substrates insoluble by reducing the interfacial tension between the water and the substrate, making the latter more easily accessible to cells. Biosurfactant-producing microorganisms have been isolated from a large diversity of environments, including soil, seawater, marine sediments, fields of oil, and even extreme environments. Many extremophilic microorganisms are found in several media marine extremes, such as hydrothermal vents, hot springs, salt lakes, and deep sea floors. The ability of these microorganisms to tolerate temperatures, extremes, salinity, and pressuredemonstrates their great potential for processes biotechnology. Bacterial genera known to produce biosurfactants include *Pseudomonas, Bacillus, Mycobacterium, Nocardia, Flavobacterium, Corynebacterium, Clostridium, Acinetobacter, Thiobacillus, Serratia, Arthrobacter, Alcanivorax, and Halomonas* (Mnif et al. 2021). Although many species produce biosurfactants, the regulation of their synthesis is still poorly understood, except for strains of Pseudomonas aeruginosa and Bacillus subtilis which are the most studied bacteria (Mnif et al. 2021).

9.4 Bioremediation and Bioenergy of Sludge and Sediments

Many policies were interested in the problem related to the reduction of fossil fuel reserves and prospects of climate change that makes the search for the source a priority of renewable new energy vectors; especially, in recent years, we see a serious environmental change, such as (I) global climate change, (II) depletion of fossil fuel reserves, and (III) increasing quantities of waste caused by the high industrial activity and the highest population growth in urban areas (IV). A strong increase in energy demand and a pressing needs for alternative energy (Rajhi 2012).

Hydrogen, nowadays, represents one of the most promising sources of renewable energy. It is currently produced by very intensive thermal and electrochemical processes; this refers to the need for high energy consumption which is associated with the growing demand for the use of other non-renewable energies. There are two possible mechanisms for this biological production of hydrogen, namely, the reduction photo and the obscure or acidic fermentation.

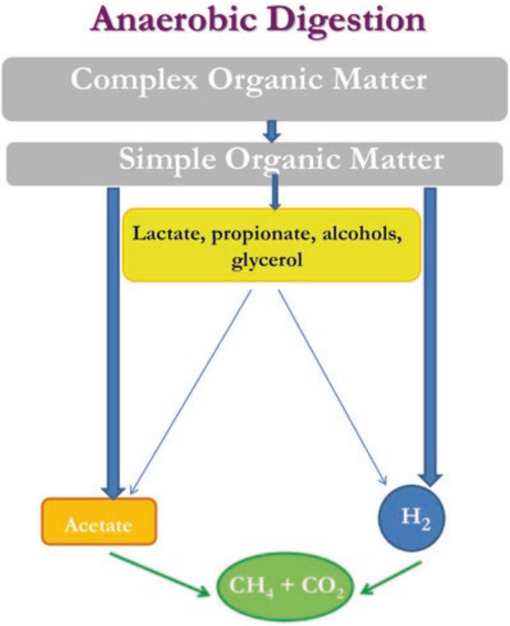
Among the most important benefits of this organic hydrogen production, it can be evoked at the same time its high efficiency and low cost. Nevertheless, this production may encounter a major problem during its realization which may be due to the partial pressure of hydrogen. Indeed, if this pressure reaches very high values, hydrogen-producing bacteria (such as clostridium) may change their metabolism by driving either a mere reduction of this hydrogen production is its total removal. A study realized by Rajhi 2012 proposed the production of hydrogen by organic fermentation using isolated and identified bacteria, and to solve if it comes to the problem of inhibition or change of bacterial metabolism that is necessarily to influence this hydrogen production. Optimizations of different parameters were fixed in goal to promote an efficient hydrogen production, such as pH, substrate and temperature. Results of this study will eventually be applied at a reactor that will be enriched by hydrogen-producing bacteria. This reactor will be useful for the purification of wastewater, and at the same time, the production of hydrogen under the most optimal conditions is possible.

The original approach of this work consisted in avoiding the accumulation of H_2 by its extraction by applying the void. During anaerobic digestion of organic matter, hydrogen produced is consumed by hydrogen consumers, mainly Methanogenic archèes. This is why, moreover, that to obtain H_2 as a final product, methanogenesis (biomethanation) must be avoided. Regarding the choice of inoculum, the production of biomass and solid and liquid waste draws special attention insofar as it can transform a large quantity of organic waste into energy resources.

In this study, an isolation of hydrogen producing species from several sources, such as an anaerobic granular mud of an anaerobic Sludge BED (U.A.S.B) reactor, an anaerobic digestive mud Municipal solid waste, an activated domestic treatment plant, and anaerobic sediments of a river (Rio Tinto, in the south of Spain). In addition, optimization of pH and the temperature on H_2 production by isolated species and by enrichment culture are also presented and discussed. Intermediate dark fermentation products have also been examined (Figs. 9.3 and 9.4).

All species isolated in this work belong to the genus *Clostridium*. These bacteria are metabolically universal, and capable of using a wide range of carbon sources. In addition, *K. pneumoniae*, *C. Kluyveri,* and *C. bifermentas* have been identified, using different culture media and a granular sludge as inoculum. A significant fluctuation in the hydrogen production of one species to another has been observed, which can be explained by the diversity of metabolisms of each species. If we only consider the dco consumed, the production becomes higher than 300 ml h_2 g^{-1} consumed COD, or even higher than 450 ml h_2 g^{-1} COD consumed for *C. diolis* rt2 and *C. beijerinckii* uam, which corresponds to at 2.5–4 mole-h_2-mole of glucose consumed. For most species studied, the optimum pH for the production of hydrogen was 6.5, with the exception of R12 (pH 5.5), H17 (pH 7.5), and H5 (pH 5.5–7.5). In general, the optimum pH allows microorganisms to produce and achieve maximum hydrogen production. Nevertheless, hydrogenase activity in hydrogen fermentation

Fig. 9.3 Simplified diagram of anaerobic digestion



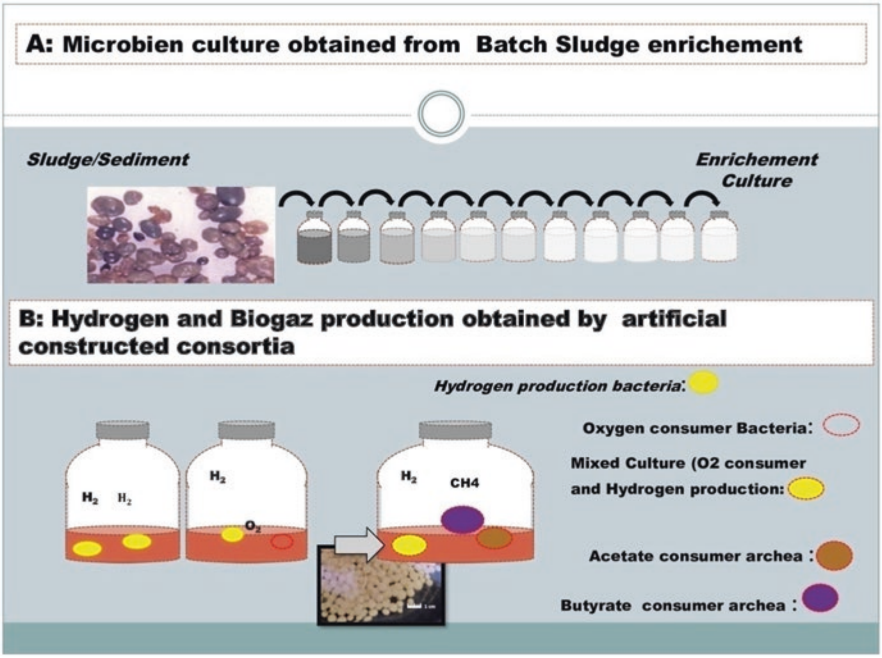


Fig. 9.4 (**a**) Enrichment culture of granular sludge batch culture treatment. (**b**) Bioenergy production (hydrogen and biogas) by microbial consortia

can be eliminated by weak or large pH values. For most species studied and enriched crops, 35 °C was the best temperature for the production of hydrogen except for R12 (30 °C) and H17 (25 °C). For most cases, we note that weak hydrogen production occurred in 25 and 40 °C; this indicates that the production of hydrogen in Clostridium has been removed at a low and high temperature. From then on 40 °C can be considered as a critical temperature in the enriched crop. This explains that a fairly high temperature may terminate some essential enzymes and proteins associated with cell growth and hydrogen production.

The analysis of final fermentation products has shown a butyrate accumulation and acetate. The species H1, H5, RT1, RT2, and UAM made a butyric ferment using the MR medium as a substrate, heterolactic fermentation, or acid-mixed fermentation produced with R14 and R12 using as a substrate. Regarding the *EC*, the butyrate was the most important final product, with the exception of tests made at a temperature of 40 °C, in which the fermentation of lactic acid seems to occur. That the production of hydrogen was made by a butyric fermentation, which constitutes in our view, the typical fermentation of effective production of H_2. Yet, alcoholic fermentation and propionic were observed, respectively, by R6 and H5 using meat extract as a single source of carbon. Note that the amount of fermentation products and the metabolic route depend on both species and changes in metabolism incumbent by changes in temperature, pH, and substrate. Mixed acid fermentation, heterolactic fermentation, propionic fermentation, and butyric fermentation are considered as the most important metabolic roads in this study on the granular mud using different substrates (synthetic environments and industrial and domestic wastewater) (Rajhi et al. 2016).

The hydrogen production can be inhibited at a hydrogen gas pressure more than 0.5 atm. In this context, the hydrogen extraction by vacuum application process is plausible. In fact, results show a positive effect of hydrogen extraction by applying vacuum to the degradation of organic matter and significant changes in metabolic roads. The vacuum application avoids changing acidogenesis toward the fermentation of solvents, associated with the production of hydrogen toward the production of smaller substrates (namely, butanol and ethanol). In all studied tests, the vacuum application has allowed the oxidation of final fermentation and substrate products: which has decreased the final COD. Regarding the emptiness effect in the EC, an increase in bacterial biodiversity has been observed and the disappearance of hydrogenotrophic methanogens. The combination of *C. Saccharobutylicum* H1 and *C. Roseum* H5 shows a significant production of hydrogen which is capable of degrading the complex organic matter containing both carbohydrates and proteins. A consortium includes streptomyces SP. In addition, hydrogen-producing species could allow an accumulation of biomass in a bioreactor and establish anaerobic conditions in the environment without adding any reduction agents. In addition, the introduction of a bacteria likely to degrade the butyrate (*Syntrophobacter Wolinii*) and an archy likely to consume acetate (*Methanosaeta Concilii*) could decrease the final fermentation products (especially butyrate and acetate) and allow methane production (Rajhi et al. 2013a).

9.5 Contribution of Phytoremediation/Bioremediation Processes to Recent Developments in the Economics of Sustainable Development

Bioremediation is a process for the biological treatment of waste, whether liquid (urban or industrial wastewater) or solid (contaminated soil, contaminated sediments, and sludge), using microorganisms. This biological remediation of waste involves microorganisms (generally bacteria, fungi, and microalgae) to decontaminate effluents (liquid and/or solid). Consequently, these microorganisms become main players in this bioremediation technique. These microorganisms through their decontamination of waste can also produce energy (bioenergy), which can be biogas (methane and hydrogen). Likewise, and in the case where these microorganisms are photosynthetic (the case of photosynthetic bacteria and microalgae), a large amount of lipids can be supplied by these microorganisms; these lipids can in turn be converted into biodiesel (we are talking about third generation energy here). This denotes several advantages that can be produced when using the microorganism bioremediation process, namely: socioeconomic and environmental benefits.

Phytoremediation is a process used to decontaminate wastewater, the main players of which are microalgae. Its advantage is that it fixes CO_2 as a greenhouse gas. In general, the treated wastewater by phytoremediation displays an important lipid contain, which evaluates the importance of this bioprocess, notably in this case use of this high lipid compound into biodiesel production (a third generation biofuel). In addition, any fatty acid was detected with the outlet wastewater already treated in the treatment plant. In fact, phytoremediation displays a greater bioprocess potential than classical wastewater treatment method. From an economic point of view, it seems more interesting to use these microalgae phytoremediation in a secondary treatment rather than a tertiary one. Especially, the energy electricity energy cost can be supplied in plant tratemet can be replaced by energy produced in biodiesel. Bioenergy: is a process that consists of biologically treating waste, contaminated sediments, sludge, and wastewater using microorganisms and producing bioenergy (hydrogen and biogas). Using this process (namely, the case of the bioproduction of hydrogen by acid fermentation), we can solve the problem linked to the decrease in fossil fuel reserves and climate change, which make the search for renewable energy sources a priority. In addition, its use in hydrogen-fuel cells makes it a promising alternative to hydrocarbons to power land vehicles. Indeed, nowadays, all the governments of the world agree on the need to put in place policies that allow the development of renewable or alternative energies.

The use of these two bioremediation processes is in perfect harmony with recent developments in the economics of sustainable development in which the environmental costs of growth are taken into account. These techniques can, therefore, be considered as a contribution to research on biological remediation processes for waste resulting from economic activity while highlighting international standards of respect for the environment which aim to preserve the environment and the reduction of environmental costs linked to economic growth.

Indeed, human productive activity has always been accompanied by unexpected health consequences and negative externalities exerting external effects harmful to the environment and disastrous consequences on human health due to high levels of concentrations of polluting elements resulting from of industrial, agricultural, and service production in urban areas. Industrialization policies, for example, implemented for several decades all over the world and have been an important step in the anthropization of the planet and the biosphere through the use of fossil energy reserves and its environmental consequences. Intensive growth has resulted in increasing predation on natural resources offered to us by the planet and harmful effects on the environment. This mode of development can be generalized to all countries when we realize that the growth model of industrial countries has resulted in significant climatic disturbances (global warming, various pollution, and depletion of natural resources) and by an unprecedented degradation of the environment.

Actually, sustainable development has become one of the major challenges of contemporary economies, due to the ecological limits that economic growth faces. The implementation of adequate environmental policies which will be in perfect harmony with recent developments in the economics of sustainable development in which environmental costs of growth are taken into account and whose supporters advocate green growth (green business) and the sustainability of economic development that preserves the environment and safeguards the interests of future generations and improves the well-being of individuals has become the way essential for preserving the environment and restoring the right to life for future generations. Several questions arise at this level, namely: is economic growth compatible with the preservation of the environment? Can the damage of growth on the natural and human environment be repaired? Can we expect economic growth and scientific and technical progress to solve all these problems? Is the market capable of regulating and correcting human behavior in the direction of sustainable development? What policy can the state pursue in favor of sustainable development? Should it encourage economic agents by adopting a tax or subsidy system in favor of "green growth"? Can we set up a "polluting rights" market to limit greenhouse gas emissions? What instruments do the public authorities have to effectively carry out climate and environmental policies? Consequently, the awareness of national political decision-makers on the environmental risks of economic growth and, therefore, of the interest of integrating environmental standards into economic production cycles has paved the way for a new model of governance in management. The environmental constraint weighing on growth and the socio-economic dynamics of development provide an approach method integrating the economic, ecological, and social dimensions.[1]

---

[1] This trend in the economics of sustainable development shows the extent to which the health-environment field must integrate multiple, different and complementary disciplines, approaches and points of view, in this case the economic, ecological and social dimensions.

9.5.1 Sustainable Development and the Negative Effects of the Economic System on the Environment

Economic development is a qualitative process of transformation of economic, social, cultural, demographic, and mental structures that accompanies and promotes the economic growth of a country. We insist here on the structural (industrialization, urbanization, wage employment, institutionalization, etc.) and qualitative (transformation of mentalities, behaviors, etc.) aspects of long-term development. Development translates into the advancement of the well-being of the population. Human well-being is a qualitative and subjective notion that expresses the satisfaction that an individual derives from life.[2] According to the Brundtland Report of 1987, the sustainable development is "development which meets the needs of present generations without compromising the ability of future generations to meet theirs". It is about having a way of growth that allows the next generation to have at least as much well-being as our own generation, in particular not to (too much) destroy the ecosystem, part of which is non-renewable. In other words, development is sustainable if the capacity of society to produce well-being remains constant. The idea is that an economy must both meet the needs of the present generations (equity in the sharing of wealth at the global level and fight against poverty and hunger) and thus allow their well-being but also allow the generations to future generations can meet their needs and achieve a level of well-being at least equal to the present generations (taking the environment into account in economic calculations). Two implications emerge from the "Brundtland" commission: (i) taking into account the concept of need, and more particularly the essential needs of the most deprived, to whom the highest priority should be given. (ii) Resources are limited: "the idea of the limitations that the state of our techniques as well as our social organization impose on the capacity of the environment to meet current and future needs". Sustainable development, therefore, combines two concepts, namely: development and sustainability. Indeed, according to the theses of the economics of sustainable development, growth and development have several limits: their impact on the environment depletes natural resources and mankind's natural heritage, and at the social level, there is a persistence of inequalities and the social divide remains in many countries, not all countries benefit from growth: persistence of inequalities between developed and developing countries. As soon as we witness the birth of a new concept of sustainable development, that is to say "a development which meets the needs of the present without compromising the ability of future generations to meet theirs" and which advocates solidarity between generations (reduction of

---

[2] It should be noted that economic development is the expression of a strong and sustained expansion of material production (growth of the Gross Domestic Product (GDP) or of national income) associated with a reduction in monetary poverty and progress in health and education and the universalization of real freedoms. Development is a qualitative phenomenon taking into account the economic and social dimensions, it is measured thanks to the HDI.

greenhouse gas emissions), and between peoples (fair trade), participation of all in the preservation of the environment, precautionary principle (risk prevention).

The Brundtland report advocates a new model of governance in the management of the environmental constraint that weighs on growth and the socio-economic dynamics of development, and this by providing a method of approach integrating the economic, ecological, and social dimensions. Growth is said to be sustainable when it is consistent with sustainable development. Sustainable development is not only about preserving the environment, it must make compatible the creation of wealth, the satisfaction of basic needs, and the preservation of the environment for future generations. Thus, due to the importance of the risk of environmental degradation, in recent years, we have witnessed an awareness of the value of sustainable development or sustainable development which tries to respond to two aspects linked to the degradation of the environment. environment linked to the increasing rate of the level of economic activity and, therefore, to economic growth, namely: sustainable development as a response to the environmental costs of growth (i.e., economic development which seeks to reconcile the economic, social, and environmental dimensions of development) and sustainable development that meets the needs of the present without compromising the ability of future generations to meet theirs. Given that natural resources are irreplaceable and that a preserved environment should be left to future generations.

9.5.2 The Three Pillars of Sustainable Development

The three pillars of sustainable development (Fig. 9.5): (I) the economic pillar: economic development—more equitable place of developing countries in the world economy; (II) the environmental pillar: taking into account the environmental dimension of growth, respect for biodiversity and ecosystems, reduction of polluting emissions, and non-destruction of natural capital; and (III) the social pillar: fight against inequalities and poverty (social consequences of economic activity, problem of inequalities, working, and living conditions).

The concept of sustainable development, therefore, combines three dimensions: economic (creating wealth and improving material living conditions), social (meeting health, education, housing, employment, prevention of exclusion, and intergenerational equity), and environmental (preserve the diversity of species and natural and energy resources). Economists will have to make their contribution in order to present a solution that will reconcile the economic, social, and ecological dynamics of growth. It is a question of answering the question of knowing how countries should proceed in order to be able to increase the well-being of the world population, fight against social inequalities and safeguard the dynamics of the biosphere (Vivien 2008). This debate must be organized around the two concepts introduced by the Brundtland report, namely: the concept of needs and that of limitations. Two theoretical projects have thus emerged: the first focuses on meeting needs, and

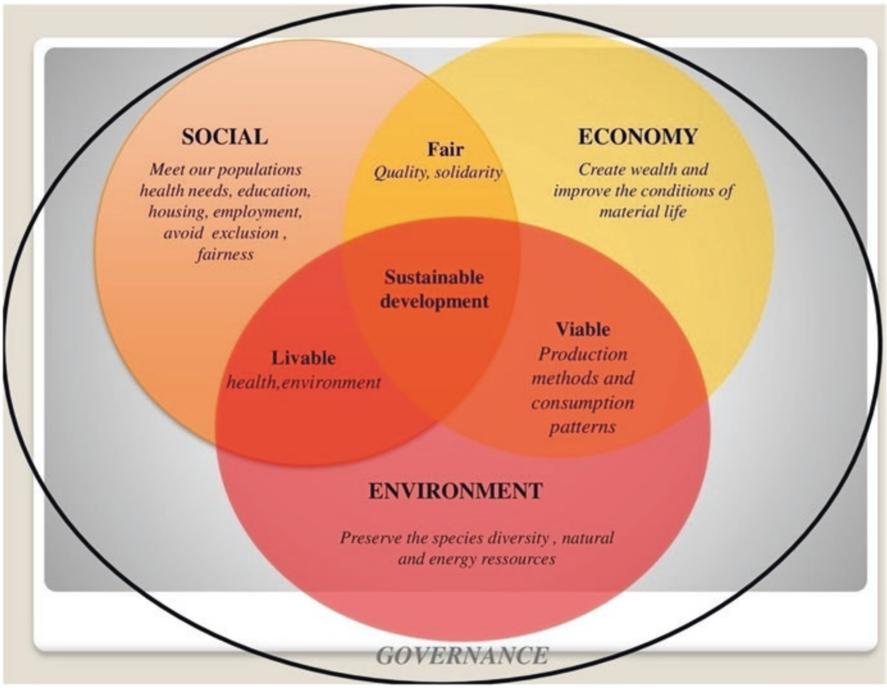


Fig. 9.5 Three pillars of sustainable development

examines the links that may exist between growth and development. The second focuses on the environmental constraint weighing on the socio-economic dynamics of growth.

9.5.3 Is Economic Growth Compatible with the Preservation of the Environment?

The economic analysis of sustainable development, which is based on the preservation of development possibilities for future generations, is concerned with the level and evolution of the stocks of each type of capital (accumulation and destruction) as well as the decisive question of the degree of substitution between these different capitals as well as how to overcome the ecological limits encountered by economic growth (depletion of energy resources and fish stocks, deforestation, increase in the concentration of greenhouse gases, etc.). In connection with climate policy, which will make it possible to analyze the instruments available to public authorities to carry out environmental policies in the face of externalities suffered by the environment and market failures?

9.5.3.1 The Economic Growth and Development Results from the Interaction of Several Types of Capital

The economic analysis of sustainable, or sustainable, development emphasizes the preservation of possibilities for future development. By relying on the classic analysis of production in which the product flows result from the mobilization of factors production, such as the productive capital and labor the usual analyzes. It, therefore, broadens the notion of productive capital and adopts a patrimonial approach, which different capital stocks are taken into account. We can thus make a distinction between natural, physical, human, and social and institutional capital. Development, therefore, results from the accumulation of the different four types of capital.

Natural capital brings together the various resources of nature capable of generating a productive service (wealth of the sea, the soil, the subsoil, etc.). It corresponds to natural resources (such as water, soil, coal, oil, fauna, flora, etc.), ecosystems, and biodiversity which provide populations with material well-being or not. It can take the form of a stock of renewable or exhaustible resources which make it possible to produce well-being by its exploitation for productive purposes. Direct source of good to be, it represents the essential support of our life. Some natural resources are non-renewable, others are renewable (regenerate on their own) as long as they are not over-exploited (e.g., fishery resources). The physical capital is a good produced in the past by man and used as a means of production (building, machine, material, etc.). It is the set of means of production, including fixed capital (capital goods) and circulating capital (intermediate goods). This stock of durable goods available to a community is used to produce goods and services capable of meeting the needs of the population and improving their well-being. The progressive wear and tear of this capital are taken into account through the concept of depreciation.

The human capital can also be accumulated by humans and includes the physical and intellectual capacities of an individual or a group of individuals; it can be accumulated through training, initial or professional. It brings together all of: individual wealth made up of know-how, interpersonal skills and knowledge (acquired during initial or continuing training, learning, and social and professional experiences) which provide advantages (particularly in terms of well-being) both individually and collectively. According to G Becker, labor power is capital: it is possible to invest in human capital in order to improve its productivity. It is possible to integrate the level of health into it.

Concerning, the social and the institutional capital: set of social networks, norms, values, and institutions which make it possible to increase trust between the actors in a given society. This increased confidence brings individual interests and collective interests together and thus promotes the well-being of populations. Institutions are the set of human frameworks and constraints that structure political, economic, and social interactions. Legislative apparatus, other norms, formal or informal, values, can contribute to the well-being of populations as well as to economic growth. Institutional capital brings together these institutions. Political, institutional, and legal arrangements, therefore, correspond to institutional capital. These institutions have the following functions: protection (of property, contracts, resources, etc.), surveillance (of competition), regulation (respect for economic balances), coverage (insurance and social protection), and arbitration (of social conflicts). These different types of capital contribute to conventionally measured production and can thus contribute to the well-being of populations. However, they can also contribute in ways that are more difficult to measure. If we take the example of a natural resource, such as the forest, this can constitute a measurable productive capital (exploitation of tree species, firewood, etc.), but also absorb part of the gas production, greenhouse effect (unmeasured productive service), be conducive to hiking (most often non-market productive service) or even arouse the pure well-being or wonder of those who cross it.

9.5.3.2 Sustainable or Sustainable Development and the Debate on the Substitutability of Capital

9.5.3.2.1 Sustainability, Growth and Environment

The notion of sustainability, of economic growth and its link with environmental constraints has become an inescapable necessity that should be realized in the economics of sustainable development. This approach to the sustainability of development makes it possible to ask crucial questions. Is the current global level of production sustainable? Is not the environmental constraint on the growth of wealth so restrictive that it calls into question its viability? To these questions, only one answer emanates from neoclassical economists; the solution is growth. Their argument is based on a theorization leading to an environmental Kuznets curve (Kuznets 1955). The idea behind it is that there is clear evidence that although economic growth normally causes environmental degradation in the early stages, in the end the best—and probably the only—path to regaining a decent environment in the country. Most of the country is getting rich. The environmental Kuznets curve (inverted U) is a possible representation of this notion of sustainability, of economic growth and its link with the environmental constraint responding to the hypothesis of substitutability between capitals. As with social inequalities, polluting emissions would initially increase as average income increases. Second, new “cleaner” technologies would reverse the trend. If we consider the environmental Kuznets curve as a satisfactory representation of the relationship between economic growth and the environment, then not only is growth not contradictory with the preservation of the environment, but, correctly oriented, it is a condition of this preservation. The basic essential elements of this representation of the link between growth and the environment are well-recognized by economists, and the growth of production requires more exploitation of resources and generates more waste and pollutants. The idea is that beyond a certain development threshold, a company will move toward cleaner activities; therefore, the ratio of emissions to the increase in per capita GDP is falling. In other words, as the GDP increases (growth), the rejection rate tends to stagnate. Once this stage has passed, a company has the capacity to invest part of its wealth in the research and development of means of production that are more respectful of the environment, which tends to lower emissions while increasing GDP. These effects would be expressed by principles of social evolution and political demands.

In general, the Kuznets environmental curves can be highlighted in some data concerning some local environmental issues (such as air pollution) but not in others (such as soil renewal or biodiversity). We must also add that the effects of climate change such as the disappearance of species and the loss of biodiversity are irreversible. Although some empirical studies indicate that economic growth may be associated with improvement in some environmental indicators, this does not imply that economic growth is sufficient to improve the state of the environment in general.

9.5.3.2.2 Sustainable Development: Strong Sustainability (or Sustainability)/ Low Sustainability (or Sustainability) Sustainable or Sustainable Development Integrates Three Dimensions

The economic dimension (growth in wealth must be possible), the social dimension (this wealth must be equitably shared in the world and between generations), the environmental dimension (resources and the planet must be preserved). Economic analysis is based on the possibilities for development and improved well-being for future generations; in accordance with the heritage approach adopted, it bases the sustainability criteria on the evolution of stocks of the four types of capital mentioned above. A debate remains on the substitutability[3] of these four types of capital and, therefore, on the means to ensure the sustainability of our development. Two conceptions of sustainable development should, therefore, be distinguished: weak sustainability in which capital is substitutable and strong sustainability in which capital is not substitutable. Those in favor of "weak sustainability" believe that nature is productive capital like any other. Therefore, it can be considered substitutable. If it becomes scarce, its price will become higher and economic agents will strive to find productive technologies that will make more use of other factors of production that have become relatively less expensive. Technical progress can then push back the limits of economic growth. The freedom of agents, which pushes them to seek the optimal technology to produce, may, therefore, be sufficient to ensure the sustainability of production growth and our development. Humans have been able to save and even reintroduce animal species, rebuild endangered natural environments. A polluted river can be cleaned up, a destroyed forest replanted, there reconstituted biodiversity. It suffices to maintain a capacity to produce economic well-being at least equal to that of the present generations. To ensure this, the level of total capital (natural and built) must be kept constant. They consider that damage to natural capital is, to some extent at least, irreversible: the damage caused to the environment remains partly irreparable and certain exhaustible resources are

---

[3] Sustainability is a situation in which the current level of well-being can at least be maintained for future generations, which supposes measuring the quantitative and qualitative evolution of the stocks of heritage on the basis of our well-being.

irreplaceable. In this hypothesis, it cannot be enough to keep the global capital constant. Natural capital must be the subject of specific conservation. The factors of production are not all substitutable. Technological innovations alone cannot push the limits of economic growth. Indeed, following a very intense production cycle, the evolution of “natural capital” can be compromised by the rise in environmental costs which have become quite significant.

These high environmental costs are linked to the following: (I) excessive drain on non-reproducible natural resources, (II) excessive drain on natural resources or their degradation which leads to an erosion of biodiversity, (III) fairly significant damage linked to pollution (negative externality), while the expenditure for nature protection is very negligible (the expenditure for the treatment of polluted water, for example, is quite low or even non-existent), (IV) the massive use of fossil energy (oil and coal) which contributes to the increase in greenhouse gases and, therefore, to global warming, and (V) atmospheric pollution linked to industrial economic activity and lifestyle, which exerts a negative externality, and increases greenhouse gases, responsible for warming and climate change. In the pessimistic version of the concept of sustainability (strong sustainability (or sustainability), damage to natural capital is, at least to a certain extent, irreversible. Some damage is irreparable, some resources are not renewable, and others are overexploited.

Natural capital must, therefore, be the subject of specific conservation and other capitals cannot be substituted for it, capitals are complementary, that is to say, the use of one type of capital necessarily implies that of other capitals. In the optimistic version of the conception of sustainability (low sustainability, nature is a productive capital like the others, natural capital is, therefore, substitutable, in particular by human capital and physical capital. his price will increase, economic agents will be encouraged to find technologies that save this factor or use other factors (e.g., oil).

The essential idea results from this analysis of the concept and criteria relating to the sustainability of sustainable development (Vivien 2005) is that it is necessary to transmit to future generations the same global capital stock composed of four types of substitutable capital (natural, human, physical, and institutional). It is above all a question of transmitting or preserving to future generations the same stock of natural capital. As a result, natural capital can be substituted for other forms of capital (human, social, and technical which incorporates new technology). In this case, it is up to the state (institutional capital) to promote substitution between different types of capital, for example, by supporting technological changes that save nature, and by educating individuals on the benefits of sustainable development.

9.5.4 What Environmental Policies to Put in Place by Governments?

Environmental degradation and climate change resulting from industrialization (release of pollutants into nature) can be analyzed as pollution which, in economic analysis, corresponds to a negative externality. In such situations, individual economic agents only take into account in their decisions the private costs and benefits of their actions, thus neglecting the costs incurred by humans. Since there is an externality, there is necessarily a market failure in a laissez-faire situation: in the presence of a negative externality, the private cost is lower than the social cost, so that the action at the origin of the externality tends to be chosen excessively with regard to what is socially desirable. In the event of obvious market failures, it will be imperative to intervene by the public authority, which must conduct a climate policy with a view to reducing the effects of pollutants on the environment. It is also desirable that global agreements force countries to conduct the measures. Necessary efforts reconcile their environmental policies to limit the damage caused to the environment, which is not without posing serious difficulties. Several instruments for carrying out climate policies by the public authorities in order to reduce greenhouse gas emissions, since these are responsible for global warming/disruption, given that atmospheric pollution linked to economic activity and to life exerts negative externalities. There are two types of economic instruments for managing the climate issue: some are based on coercion and others on incentive. Negative externalities can in fact be combated by regulation, that is to say coercion, and/or by the implementation of instruments aimed at internalizing them: it is then a question of ensuring that the private costs borne by the producers of externalities include social costs, that is to say the damage suffered by other agents. Two instruments can be mobilized for this internalization of social costs: environmental taxes, which correct the prices of existing markets and "emission rights" markets (polluting rights market), which make it possible to generate a decentralized price for emissions. The taxation of economic activities and the market for rights to pollute are economic tools, where we will encourage economic agents to modify their behavior (consumption or production). It should be noted, however, that each instrument has advantages for some and disadvantages for others (producer, worker, consumer, and state). Nevertheless, it should be noted that these instruments must be combined carefully in order to derive maximum benefit from them and increase their use in efficiency for the preservation of the environment and human health.

9.6 Conclusions

The economics of sustainable development is nowadays one of the major challenges of contemporary economies, due to the ecological limits encountered by economic growth. The establishment of adequate environmental policies (climate policies, regulations, taxes, etc.) in which the environmental costs of growth and the negative externalities resulting from industrialization and consequently the sustainability of economic development which will be taken into account, preserves the environment and safeguards the interests of future generations and improves the well-being of individuals, has become an essential necessity for national and international political decision-makers in the search for economic, ecological, political, and social solutions for the preservation of the environment and the restoration of the rights to life for future generations. The use of bioremediation and phytoremediation processes to remedy pollution and environmental degradation is nowadays one of the favorable and serious solutions which seek to put in place adequate bioenergy policies likely to preserve the environment. These processes are correct with economic sustainable recent developments in which the environmental growth costs are taken into account. These techniques can, therefore, be considered as a contribution to research on waste bioremediation bioprocess resulting from economic activity while highlighting international standards of respect for the environment which aim to preserve the environment.

Acknowledgements Hayfa Rajhi is grateful to Pr. Jose Luis Sanz Martion (Professor of Microbiology in University Autonoma Madrid–Laboratory of Applied Microbiology) for his supervision and teaching throughout these years in terms of Microbiology and waste Bioremediation field (especially the anaerobic microbiology) as well as the molecular microorganisms techniques. This chapter is specially dedicated to Jose Luis Sanz Martin and his laboratory member.

References

Garcia-Mancha N, Puyol D, Monsalvo VM, Rajhi H, Mohedano AF, Rodriguez JJ (2012) Anaerobic treatment of wastewater from used industrial oil recovery. J Chem Technol Biotechnol 87:1320. https://doi.org/10.1002/jctb.3753

Giasson P, Jaouich A, Gagné S, Moutoglis P (2005) Phytoremediation of zinc and cadmium: a study of arbuscular mycorrhizal hyphae. Remediat J 15(4):113–122

Glass DJ (1999) Current market trends in phytoremediation. Int J Phytoremediation 1(1):1–8

Kuznets S (1955) Economic growth and income inequality. Am Econ Rev 45(1):1–28

Mnif I, Rajhi R, Bouallegue A, Trabelsi N, Ghribi D (2021) Characterization of lipopeptides biosurfactants produced by a newly isolated strain bacillus subtilis ZNI5: potential environmental application. J Polym Environ. https://doi.org/10.21203/rs.3.rs-308797/v1

Newman LA, Strand SE, Choe N, Duffy J, Ekuan G, Ruszaj M, Shurtleff BB, Wilmoth J, Heilman P, Gordon MP (1997) Uptake and biotransformation of trichloroethylene by hybrid poplars. Environ Sci Technol 31(4):1062–1067

Olson P, Reardon K, Pilon-Smits E (2004) Ecology of rhizosphere bioremediation. In: Phytoremediation: transformation and control of contaminants (vol. 121), p. 317

Peer WA, Baxter IR, Richards EL, Freeman JL, Murphy AS (2005) Phytoremediation and hyperaccumulator plants. In: Molecular biology of metal homeostasis and detoxification. Springer, pp 299–340

Perchet TMG (2008) Sediment bioremediation study contaminated by compounds organic persistent niters (Tessis doctoral)

Pilon-Smits E (2005) Phytoremediation. Ann Rev Plant Biol 56:15–39

Puyol D, Rajhi H, Mohedano AF, Rodríguez JJ, Sanz JL (2011) Anaerobic biodegradation of 2,4,6-trichlorophenol in expanded granular sludge bed and fluidized bed biofilm reactors bioaugmented with *Desulfitobacterium* spp. Water Sci Technol. https://doi.org/10.2166/wst.2011.556

Rajhi H (2012) Biohydrogen production by dark fermentation. A Date of defence: in October 19th, 2012. Place: Department of Molecular Biology, Center of Molecular Biology (CBM), Autónoma university of Madrid (UAM), Madrid - Spain. http://hdl.handle.net/10486/12889

Rajhi H, Diaz EE, Rojas P, Sanz JL (2013a) Microbial consortia for hydrogen production enhancement. Curr Microbiol. https://doi.org/10.1007/s00284-013-0328-3

Rajhi H, Conthe M, Puyol D, Diaz EE, Sanz JL (2013b) Dark fermentation: isolation and characterization of hydrogen producing strains from different sludge's. Int Microbiol. https://doi.org/10.2436/20.1501.01.180

Rajhi H, Puyol D, Diaz E, Martínez M, Sanz JL (2016) Vacuum promotes metabolic shifts and increase biogenic hydrogen production in dark fermentation systems. Front Environ Sci Eng 10:513–521

Rajhi H, Mnif I, Abichou M, Rhouma A (2018) Assessment and valorization of treated and non-treated olive mill wastewater (OMW) in the dry region. Int J Recycl Org Waste Agric 2018(7):199–210. https://doi.org/10.1007/s40093-018-0206-x

Rajhi H, Bardi A, Sadok S, Moussa M, Turki S (2020) Phytoremediation of samples extracted from wastewater treatment plant and their socioeconomic impact. Water Sci Technol 82(8):2020

Vivien F-D (2005) Sustainable development. Paris, La Découverte, Repères collection

Vivien F-D (2008) Sustainable development: progress, shortcomings and future needs. Cahiers Français, n ° 347, November–December

Chapter 10
Applying Amendments for Metal(loid) Phytostabilization: Effects on Soil Biogeochemical and Microbiological Processes

Manhattan Lebrun, Lukáš Trakal, Domenico Morabito, and Sylvain Bourgerie

Abstract The pollution of soil by metal(loid)s gathered research attention due to its negative environmental and health impact. Especially, research is focusing on the phytoremediation of these soils and how to improve its success. In this goal, plant selection and amendment application can be performed to ameliorate plant growth. This chapter will focus on the phytostabilization of metal(loid)-contaminated soils, with a focus on *Salicaceae* as potential phytostabilizor and the effects of diverse amendments, organic and inorganic, on the different components of the soil–plant continuum, i.e., soil, metal(loid)s, microorganisms, and plant, especially the physiological response of the plant roots to amendments.

Keywords Metal(loid)s · Phytostabilization · Biogeochemical processes · Microbiological processes · *Salicaceae*

10.1 Introduction

Soil pollution is an important concern worldwide, with more than 10 million of sites polluted around the world, making pollution the third most important threat to soil (Rodríguez Eugenio et al. 2018). This pollution is the result of two types of sources,

---

M. Lebrun (✉)
INRAE USC1328, LBLGC EA1207, University of Orléans, Orléans, France

UMR Ecosys, INRAE, AgroParisTech, Université Paris-Saclay, Thiverval-Grignon, France
e-mail: manhattan.lebrun@inrae.fr

L. Trakal
Department of Environmental Geosciences, Faculty of Environmental Sciences, Czech University of Life Sciences Prague, Praha 6 Suchdol, Czech Republic

D. Morabito · S. Bourgerie
INRAE USC1328, LBLGC EA1207, University of Orléans, Orléans, France

L. Newman et al. (eds.), *Phytoremediation*, https://doi.org/10.1007/978-3-031-17988-4_10

i.e., natural (volcanic eruption, soil crust weathering, continental dust, and erosion) and anthropogenic (mining and industrial activities, transport, waste disposal, military, and nuclear operations), with the latter being responsible for the major part of the pollution (Gong et al. 2018; Gupta et al. 2019; Panagos et al. 2013; Saxena et al. 2019).

Thus, soils can be polluted by diverse pollutants, organic or inorganic (Rodríguez Eugenio et al. 2018), among which, metals and metalloids (thereafter called metal(loid)s) are the most important ones, encountered in more than 50% of the polluted area worldwide and in almost 35% of the European polluted area (European Commission. Joint Research Centre. Institute for Environment and Sustainability, 2014; Khalid et al. 2017). Contrary to organic pollutants, metal(loid)s are non-degradable and thus accumulate in the soil. They have negative effects on the environment with many consequences: impairment of plant growth and microorganism activity, reduction of biodiversity, etc. Moreover, metal(loid)s can enter the food chain and be thus consumed by the human population, which can cause important health issues, as most metal(loid)s are carcinogenic and able to induce chronic diseases.

Due to such environmental and health concerns, metal(loid)-contaminated soils and their remediation have become a priority. Remediation refers to the lowering of the harmful effects of pollutants, especially the reduction of people exposure and the amends of soil functions (Payá Pérez and Rodríguez Eugenio 2018). Remediation can be performed by physical, chemical, or biological methods, which have been reviewed in many papers (Derakhshan Nejad et al. 2018; Gong et al. 2018; Khalid et al. 2017; Liu et al. 2018). For decades, the most used remediation techniques were physical and chemical methods, as presented in Table 10.1.

The advantage of these conventional physical and chemical techniques is that they provide rapid results. However, their disadvantages are their high cost, difficulty to install on a large scale, and their negative effects on the soil, such as the destruction of the soil structure and its biological activities and sometimes even the induction of a secondary pollution. Therefore, over the last decades, a more ecological remediation technique has been developed, phytoremediation.

Phytoremediation is defined as the use of plants, and their associated microorganisms, to reduce the toxic effects of contaminants in soil (Ashraf et al. 2019; Saxena et al. 2019). It has several advantages compared to physical and chemical remediation: it is up to five times less expensive, environmentally friendly, operationally simple, aesthetically pleasing and has the public acceptance (Liu et al. 2018). Phytoremediation is divided into four main processes (Fig. 10.1), i.e., phytodegradation, phytovolatilization, phytoextraction, and phytostabilization. Phytodegradation concerns the degradation of organic pollutants by plant metabolism, which is especially active in the rhizosphere area, through the interaction of the plant root system and the associated microorganisms; in this case, it is called rhizodegradation (Mirck et al. 2005; Wenzel 2009). In the phytovolatilization process, the pollutant is taken up by the plant, converted into a volatile form, followed by its release into the atmosphere. This technique is only applicable for some organic pollutants as well as arsenic and mercury. However, when the pollutants are

Table 10.1 Physical and chemical remediation techniques (Derakhshan Nejad et al. 2018; Gong et al. 2018; Khalid et al. 2017; Liu et al. 2018)

Type	Method	Definition	Results
Physical	Soil replacement	Removal of the contaminated soil from the site, replacement (partial or complete) by clean soil	Dilution of pollution level
Physical	Surface capping	Instalment of a geotextile cover on the soil surface, covered by seeded garden soil	Reduction of water leaching and support of vegetation
Physical	Soil encapsulation	Installation of physical barriers, at the bottom, on the sides and on the surface of the contaminated soil	Immobilization of the soil, prevention of contamination spreading
Physical	Thermal desorption	Heating of the soil	Volatilization, and recovery, of metal(loid)s
Chemical	Soil washing	Application of extractant solution	Removal of the metal(loid)s
Chemical	Solidification/ stabilization	Application of binding agents	Immobilization of metal(loid)s or transformation into less toxic forms
Chemical	Vitrification	Heating of the soil at very high temperature (1600–200 °C)	Transformation of the soil into a glass-like material of lower volume
Chemical	Electrokinetic	Instalment of cathode and anode into the soil and application of an electric current	Migration and collect of the metal(loid)s at the cathode (positively charged elements) and the anode (negatively charged elements)
Chemical	Oxidation/ neutralization/ reduction	Application of diverse solutions to the soil	Detoxification, precipitation or stabilization of the metal(loid)s

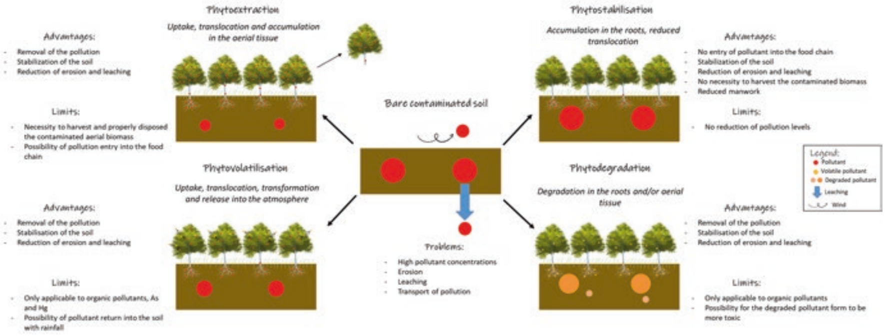


Fig. 10.1 Different phytoremediation techniques

released into the atmosphere, there is a risk of potential return into the soil during rain events (Ali et al. 2013; Khalid et al. 2017). Although these techniques constitute an interesting remediation process, through the degradation or transformation of the pollutants to a potentially less toxic form, they are mainly applicable for organic pollutants, while the other two techniques (phytoextraction and phytostabilization) can be used for both organic and inorganic pollutants.

Phytoextraction is considered as a real cleaning technique, in which the pollutants are uptake from the soil by the roots, and then translocated and accumulated in the aerial biomass. This contaminated biomass is then harvested and needs to be properly treated. In some cases, the extracted elements have an economical interest, and the process is called phytomining (da Conceição Gomes et al. 2016; Khalid et al. 2017; Liu et al. 2018). However, there is a need to decontaminate the biomass produced to remove the pollutants, which induce the implementation of a process that will cost time and money. Moreover, plants used in phytoextraction usually have a low biomass production and reduced root system (Liu et al. 2018). Therefore, the quantity of pollutants extracted is low and corresponds only to the first few centimetres of the soil, where roots have developed, and consequently, the complete extraction of the soil pollution could take several hundred years. Thus, when metal(loid) contamination level is high and spread, the last phytoremediation technique is often more suitable, i.e., phytostabilization, which will be detailed in the following section

This chapter focuses on phytostabilization, presenting the potential species that can be used, especially *Salicaceae*, as well as the necessity to add amendments to improve its success. The effect of these amendments on the different components of the soil–plant–microorganism continuum is considered. This chapter will answer the following questions: (i) what are the effects of amendment on the soil physicochemical properties and metal(loid) behaviour? (ii) What are the physiological responses of plant roots to amendment application? (iii) How the microbial community is affected by the addition of amendments? (Fig. 10.2).

10.2 Phytostabilization to Contain Metal(loid) Pollution and Reduce Its Negative Effects

Contrary to phytoextraction, phytostabilization is not a decontamination per se, in the sense that pollutants are not accumulated into the aerial parts but rather stabilized at the root zone, i.e., the rhizosphere (Ashraf et al. 2019; Khalid et al. 2017; Liu et al. 2018) (Fig. 10.1). The pollutants are stabilized through three ways: (i) they are accumulated inside the root, (ii) they are adsorbed on the root surface, or (iii) they are complexed with root exudates. Phytostabilization does not request the aerial biomass to be harvested and properly disposed, which reduces the cost of the process. Moreover, the reduction of the pollutant translocation toward and thus accumulation in the plant upper parts reduces the risk of pollution entry into the

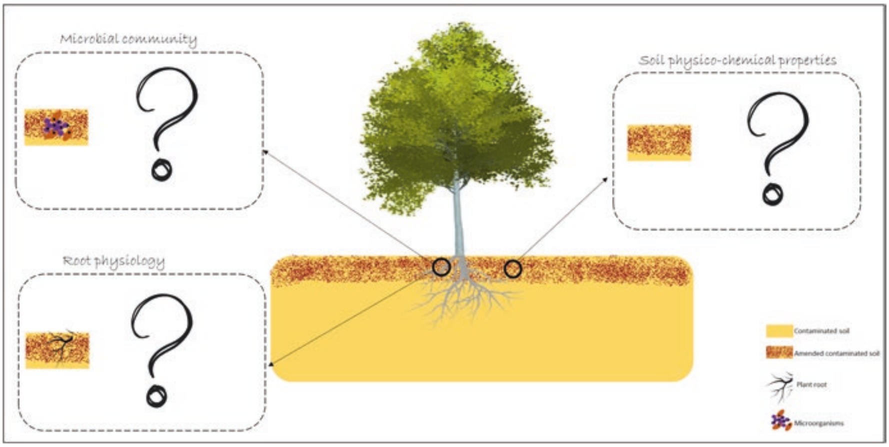


Fig. 10.2 Objectives to answer in the chapter

food chain (Tack and Meers 2010). Finally, since aerial pollutant concentration is low, this biomass can be used for energy production or other industrial processes, making an economic profit out of the process; in this case, such strategy is called phytomanagement.

The success of phytostabilization will depend on the plant species used and their capacity to tolerate pollutants and grow on the polluted soil. Thus, to increase the phytostabilization success, the selection of the adequate plant species must be performed and the use of specific amendments should be considered to ameliorate soil conditions.

10.2.1 Salicaceae, *Species with a Good Potential for Phytostabilization*

The success of phytostabilization is driven by the ability of the plants to grow; thus, the selection of the adequate species is essential.

Several studies focused on the use of herbaceous species to remediate metal(loid)-contaminated soils, such as *Agrostis* (Lebrun et al. 2021d, e; Nandillon et al. 2021), *Coronopus didymus* (Sidhu et al. 2017), *Pteris vittata* (Wan et al. 2017), and *Viola principis* (Wan et al. 2017). However, these species produce a low biomass and a reduced root system. Another strategy would be to use species native from the polluted area, which acquired tolerance toward the pollutants. For instance, Lebrun et al. (2021f) tested two native species, *Alnus* sp. and *Betula* sp., for the remediation of a former mine technosol. They found that these two species were able to develop on the contaminated soil. However, *Betula* sp. translocated high amounts of As, Fe, and Pb to its aerial parts, making it unsuitable for phytostabilization. In another study, Nandillon et al. (2021) compared two ecotypes of *Agrostis capillaris*, one collected on a contaminated site and a commercial one. They found that the endemic ecotype was more suitable than the commercial one for the phytoremediation of the contaminated soil. Bech et al. (2012) collected five plant species from a mine and showed that these species were suited for phytoextraction purposes. However, except in some cases, these species produced a low biomass, and moreover, they usually show high translocation of the metal(loid)s to the aerial biomass, making them not suitable for phytostabilization.

For this reason, research on phytostabilization is now focusing on testing the potential of tree species like *Salicaceae*, which are characterized by a fast growth, a high biomass production and a deep and wide root system. Moreover, these species have been demonstrated to be tolerant to metal(loid)s in several studies. For instance, in hydroponic studies, *Salix integra* was shown tolerant to Pb (196 μM) (Wang et al. 2014), *Populus deltoids* and *Populus* × *canadensis* to Cu and Zn (30 μM) (Benyó et al. 2016), *Populus* × *euramericana* to Cu (1 mM) (Borghi et al. 2007), *Salix alba*, *Salix matsudana* and *Salix nigra* to Cd, Ni and Pb (10^{-4} M) (Borišev et al. 2009), *Salix integrrra* to As (80 μM) (Chen et al. 2014), and *Salix discolor*, *Salix eriocephala*, *Salix exidua*, *Salix nigra,* and *Salix elucida* to Cu (25 μM) (Kuzovkina et al. 2004).

In addition, laboratory experiments using potted soil and field experiments have been performed. They demonstrated the tolerance of willows and poplars toward diverse metal(loid)s, such as Fe, Pb, Cd, Cu, and Zn, and their potential in phytoremediation, and particularly phytostabilization (Baldantoni et al. 2014; Bart et al. 2016; Courchesne et al. 2017).

However, compared to non-contaminated soils, willows and poplars growing on contaminated soils showed much lower biomass production (Bart et al. 2016; Ciadamidaro et al. 2013, 2014), which can affect phytoremediation efficiency. Therefore, soil condition improvers can be required.

10.2.2 Amendments to Improve Soil Conditions

Soils polluted by metal(loid)s are usually characterized by extreme conditions, i.e., an acidic pH, a low nutrient and a low organic matter contents, an absence of structure, and high pollution levels. Therefore, plant establishment is difficult, which reduces phytoremediation efficiency. One solution to overcome such harsh conditions is to apply amendments, which are aimed to (i) supply nutrients for plants and microorganisms, (ii) improve the soil physico-chemical properties, and (iii) immobilize metal(loid)s. Both organic and inorganic amendments can be used (Rizwan et al. 2017), and many of them demonstrated efficacy in metal(loid) remediation studies (Egene et al. 2018; Fresno et al. 2018; Houben et al. 2012; Kiran et al. 2017; Mahar et al. 2015; Rocco et al. 2018).

However, some amendments have gathered research interest over the last decades: organic amendments, such as carbon-based amendments, compost and manure and metal oxides and iron-based amendments.

10.2.2.1 Organic Amendments

Biochar is defined as the product of pyrolysis of biomass (Paz-Ferreiro et al. 2014). Pyrolysis temperature is usually comprised between 200 °C and 1000 °C (Yu et al. 2019) and all kinds of feedstocks that contain carbon, even waste materials, can be used to produce biochar (Qian et al. 2015). The properties of biochar are highly dependent on the feedstock used and the pyrolysis conditions, such as temperature, heating rate, and residence time. However, almost all biochars are characterized by the same property ranges: (i) biochar is considered as a very stable material, with a half-life of several thousand years (Zama et al. 2018); (ii) biochar pH is mostly alkaline and usually increases with the rise in pyrolysis temperature (Kwak et al. 2019; Sun et al. 2014; Yang et al. 2018); (iii) the specific surface area of the biochar is high, from a few centimetres per gram to several meter per gram, and as pH, it usually increases with pyrolysis temperature (Cantrell et al. 2012; Wu et al. 2016); (iv) biochar is mainly made of carbon, with low levels of hydrogen, oxygen and other elements (Al-Wabel et al. 2019; de Sousa Lima et al. 2018); and (v) it has a porous structure (Paz-Ferreiro et al. 2014), which makes it capable to hold high quantities of water (Lebrun et al. 2018b).

Furthermore, biochar can be modified, for example, on its surface, in order to improve its properties for a specific usage. Such modified material is called functionalized or activated biochar/carbon. The modification of the biochar surface can be physical (steam, gas, and magnetization) or chemical (amino acid and element fixation) (Rajapaksha et al. 2016; Tan et al. 2017). The benefits of biochar functionalization are multiple, i.e., increase in surface area and ash content, rise in cation exchange capacity, modification of pH, and functional groups. (Payne and Abdel-Fattah 2005; Qian et al. 2013; Rajapaksha et al. 2016; Samsuri et al. 2013; Trakal et al. 2018). All these changes affect how the metal(loid)s, soil, and plants will respond to biochar application.

Composts and manures are commonly used as organic fertilizers in agriculture. Compost is produced from the microbiological degradation of organic wastes (Diacono and Montemurro 2010; Huang et al. 2016), while manure is composed of litter and animal droppings at a more or less fermentation state. Both composts and manures are characterized by a high content in humic substances and nutrients as well as microorganisms (Fischer and Glaser 2012; Huang et al. 2016). Moreover, they usually have an alkaline pH, a high electrical conductivity (EC), and an elevated moisture (Alvarenga et al. 2014; Farrell and Jones 2010; Rossini-Oliva et al. 2017; Touceda-González et al. 2017).

Composts and manures are interesting amendments in phytoremediation due to their potential to improve the poor fertility of contaminated soils. Indeed, in addition to high metal(loid) concentrations, polluted soils often lack of essential nutrients, such as nitrogen, phosphorus, and potassium, which are present in high amounts in composts and manure.

10.2.2.2 Iron Oxides and Iron-Based Amendments

Metal oxides are interesting stabilizing amendments, and they are characterized by a low particle size and a low solubility. In addition, they have a high sorption capacity toward metal(loid)s (Komárek et al. 2013), especially iron oxides, which are highly studied and are the focus of this section. Diverse precursors of iron oxides can be added to a polluted soil, such as iron grit (Fe(0)), (nano)zero valent iron (Fe(0)), and redmud. Iron grit is a commercial product mainly composed of iron, while redmud is considered as a waste, formed during the alumina production through the Bayer process (Bhatnagar et al. 2011), and its annual production is estimated at about 90–120 million of tons (Hua et al. 2017; Liu et al. 2007). Redmud is characterized by a high pH, a high surface area and as having a high level of Fe and other elements, such as arsenic and aluminium (Derakhshan Nejad and Jung 2017; Garau et al. 2007, 2011; Lee et al. 2011, 2014).

In the following sections, we will detail the effects of these amendments on the soil, the plant, with a focus on the root physiological response, and the microbial community.

10.3 The Effects of Amendments

10.3.1 The Effects of Amendments on the Soil

One of the first purposes of applying amendment is to ameliorate soil conditions, especially to reduce soil acidity and immobilize metal(loid)s, which have been demonstrated in many studies. For instance, several types of composts were applied to metal(loid)-contaminated sites: mixed solid waste compost, green waste compost, vermicompost, a compost made of peat moss, softwood bark, green compost and seaweed, a compost derived from a mixture of animal manure and vegetable waste, a sewage sludge compost and a compost from sewage sludge and olive waste. In these studies, they were efficient to increase soil pH, soil organic matter content, and nutrient availability and reduce the mobility and availability of diverse metal(loid)s; however, they induced a mobilization of As in some cases (Alvarenga et al. 2014; Ferreira et al. 2018; Lebrun et al. 2019; Nandillon et al. 2019; Rossini-Oliva et al. 2017).

Similar to compost, biochar has been much studied in phytoremediation and showed efficiency to improve soil physico-chemical properties and immobilize metal(loid)s. These studies tested biochars derived from different feedstocks, such as grape stalk, olive mill waste, poultry manure, etc. Following the application of these biochar to metal(loid)-contaminated soils, soil pH, electrical conductivity, and organic matter content increased, while metal(loid)s were immobilized, and nutrient content was increased in some cases (Trakal et al. 2017; Hmid et al. 2015; Marchand et al. 2016). Functionalized biochars were also tested for their ability to improve soil growing conditions; however, results are more various: the functionalization of a grape stalk and a nutshell biochars by amorphous manganese oxides or magnetization improved their sorption capacity for metal(loid)s (Trakal et al. 2016, 2018); the steam activation of a coconut biochar improved its sorption capacity toward Pb, but did not ameliorate its effect on soil pH and Pb immobilization compared to the pristine biochar (Lebrun et al. 2021g), while the study of diverse activated carbons demonstrated that they were not efficient for As and Pb immobilization (Lebrun et al. 2021a). These studies show that biochar is generally efficient to improve soil properties and immobilize metal(loid)s. This has also been demonstrated in many other studies. Studies also showed that biochar effects depend on several biochar production factors: (i) the pyrolysis temperature; (ii) the feedstock; (iii) the particle size of the biochar; and (iv) soil characteristics. For instance, date palm biochar was more efficient when pyrolyzed at higher temperature (Al-Wabel et al. 2019), rice straw biochar was more effective than bamboo biochar (Lu et al. 2017), while lightwood biochar was better than pinewood biochar (Lebrun et al. 2018b); the fine particle biochars were more rapid to induce beneficial effects than coarser ones (Lebrun et al. 2018a), and the same biochar applied to two metal(loid)-contaminated sites only showed positive outcomes on the most acidic and least fertile soil (Lebrun et al. 2017), while it had no effect when added to a neutral contaminated soil (Lebrun et al. 2018a).

The last type of amendments gathering attention in phytoremediation studies and being the focus of this chapter is iron-based amendments, which showed efficiency in the improvement of soil properties and the immobilization of metal(loid)s, especially arsenic, contrary to compost and biochar. For instance, redmud increased soil pH, electrical conductivity, and decreased metal(loid) mobility in different studies (Lee et al. 2014; Liang et al. 2012; Feigl et al. 2012).

Taken together, the studies showed that amendments were efficient to increase pH, nutrient availability, and immobilize metal(loid)s. The rise in soil pH has been attributed to the high pH of the amendments, the dissolution of protons and cations, as well as the presence of functional groups (on the biochar surface) which can bind H^+ (Fischer and Glaser 2012; Lebrun et al. 2018b, c, 2021g). Following amendment application, nutrient availability is increased due to the addition of them from the amendments themselves and the modifications of the soil conditions, especially pH (Fresno et al. 2018). Finally, metal(loid)s are immobilized by amendments due to their effect on soil pH (Houben et al. 2012; Lebrun et al. 2018c, 2021g) and a direct sorption of the elements on the amendment surface, which has been demonstrated in several studies, especially for biochar and redmud (Castaldi et al. 2010; Lebrun et al. 2018d, 2021g). Regarding arsenic, the mobilization often observed following compost amendment can be attributed to its high organic matter and phosphorus content, which compete with arsenic for sorption site (Egene et al. 2018; Fresno et al. 2017).

Finally, although these three amendment types demonstrated efficiency in the amelioration of the soil physical and chemical properties, due to their different properties and effects on soil, better outcomes can be expected when they are used in combination. Such amendment combinations have been tested in several researches, demonstrating contrasting effects: combining hardwood biochar and green waste compost was better than single amendment for soil condition improvements, but not metal(loid) immobilization (Beesley et al. 2010); Fe-loaded biochar, combined to zero-valent iron, was shown to be a good candidate for As stabilization (Li et al. 2018); combining biochar and redmud was not more efficient than their single application to increase pH and immobilize Pb (Lebrun et al. 2021g); and the combination of biochar with zero valent iron grit was more effective than biochar to stabilize Cu (Oustriere et al. 2017).

10.3.2 The Effects of Amendments on Plant Growth and Metal(loid) Accumulation

Following their effects on the soil and on their metal(loid)s contents, amendments can ameliorate plant growth, which is a positive outcome in phytostabilization. Amendments can also influence metal(loid) accumulation in plants. For instance, when applied to metal(loid) contaminated soils, compost ameliorated the growth of *Agrostis tenuis* (Alvarenga et al. 2014), *Brassica alba*, *Brassica nigra* and *Brassica carinata* (Brunetti et al. 2012), *Zea mays* (Rehman et al. 2016), *Salix viminalis* (Lebrun et al. 2019), and *Phaseolus vulgaris* (Nandillon et al. 2019). The study of Rehman et al. (2016) also showed that following compost amendments, metal(loid) accumulation in plants was increased.

Biochar amendment is also known to ameliorate plant growth, such as demonstrated in the studies of Brennan et al. (2014) (maize), Abbas et al. (2018) (wheat), Lebrun et al. (2018b) (*Salix viminalis*), Lebrun et al. (2018c) (*Salix viminalis* and *Populus euramericana*), and Lebrun et al. (2021a) (*Trifolium repens*). However, in some cases, biochar can have no effect or even negatively affect plant growth (Marchand et al. 2016). Biochar also affected metal(loid) plant accumulation, either increasing their concentration or decreasing it (Abbas et al. 2018; Lebrun et al. 2018b, c).

Finally, iron-based amendments were also demonstrated as efficient plant growth improver and to affect metal(loid) accumulation: redmud on *Trifolium repens* (Lebrun et al. 2021a), redmud on *Salix dasyclados* (Lebrun et al. 2021g), zero valent iron on *Panax notoginseng* (Yan et al. 2013), and redmud on *Miscanthus sinensis* and *Pteridium aquilinum* (Lee et al. 2014).

Similar to the assessment of amendment combinations on soil properties and metal(loid) accumulation, their effects on plants growth were also evaluated: no difference between the combined and single application of a hardwood biochar and a green waste compost was found on *Lolium perenne* shoot length (Beesley et al. 2010); *Brassica campestris* biomass was increased by biochar but not when combined to zero valent iron, while all decreased As accumulation (Li et al. 2018); the combination biochar + redmud was not more efficient than the single amendments to improve *Salix dasyclados* growth (Lebrun et al. 2021g). These studies showed that on plants, amendment combination is generally not better than single amendment.

10.3.3 The Specific Response of Roots to Amendments

Roots are an important organ for plants. They serve as an anchor for plants, and assure plant nutrition. They are also known to modify soil properties and bacterial community, through their metabolism activity. Many studies evaluated the effect of a metal(loid) contamination on plant physiology, especially on the roots; however, these studies were mainly performed in hydropony (Demirevska-Kepova et al. 2004; Drzewiecka et al. 2017; Pawlak-Sprada et al. 2011), which does not take into account the effect that the soil itself, and its properties, could have on metal(loid) behaviour and thus their toxicity to the plant. Few studies were performed under soil growing conditions (Dresler et al. 2017a, b; Ullah et al. 2019).

However, although the effects of amendments on soil physico-chemical properties and plant growth have been much studied, their effect on plant root physiology has been poorly studied. Since roots are sensitive to changes in their growing media, the effects of amendments on soil properties and metal(loid) mobility/availability will induce a specific root response, which needs to be deeper evaluated, more precisely the root architecture, the root exudation pattern, the root proteome profiles, and the root oxidative stress markers.

Brennan et al. (2014) evaluated how the application of biochar to a former copper mine affected the root traits of maize. They measured a positive effect of biochar on most of the growing parameters evaluated. Especially, biochar increased root length and surface area, as well as affected the root diameter classes, by increasing the proportion of small roots and reducing the ones of larger roots. Moreover, root architecture (root length density and specific root length) and morphology (root length/root volume ratio and root tissue density) were also significantly affected by biochar amendment. They attributed such observations primary to the reduction in Cu availability (Brennan et al. 2014).

Another root parameter deeply affected by soil conditions is the root exudation. Through photosynthesis, plants produce assimilates that are transferred to the roots and can be excreted. These root exudates are composed of low molecular weight organics, i.e., sugars, amino acids, carboxylic acids and phenolics, carboxylates, and high molecular weight compounds, i.e., proteins and mucilage (Bais et al. 2006; Bertin et al. 2003). The amount and composition of root exudates were shown to be affected by plant stress (Bertin et al. 2003). For instance, in a hydroponic study, Mora et al. (2009) evaluated the effect of Mn on ryegrass root exudates and observed an increase in carboxylate exudation with increasing Mn concentration in the growing medium. They hypothesized that the exudation of carboxylates such as oxalate and citrate decreased Mn availability in the rhizosphere and thus helped in the tolerance to Mn (Mora et al. 2009). Similarly, increasing application of Cd increased the exudation of organic acids by maize, which was more visible for the tolerant cultivar than the sensitive one (Javed et al. 2017). Still on maize, Lapie et al. (2019) observed that Cd application decreased the exudation of carbon, sugars, and amino acids but not proteins. Based on these observations that metal(loid) stress could affect plant root exudation, Lebrun and collaborators tried to evaluate how biochar, compost, and iron grit amendments could influence the exudation of organic acids by *Salix viminalis* roots (Lebrun et al. 2021b). They found that with the application of biochar and/or compost, the exudation of citric, fumaric, and malic acids increased, while the ones of succinic and tartaric acids increased with iron grit. This demonstrated an increase in organic acid exudation with the reduction of metal(loid) stress by amendments.

The analysis of the leaf and root tissues proteome of plants subjected to abiotic constraints have shown changes in various metabolic pathways linked to several metabolic pathways (Bonhomme et al. 2009; Durand et al. 2012; Liu et al. 2017; Rodziewicz et al. 2014). More precisely, studies showed that metal(loid) contamination affected the root proteome profiles. For instance, Li et al. (2009) analyzed the proteomic response of roots of *Elsholtzia splendens* to Cu and concluded that a redirection of the plant metabolism toward cellular metabolism and redox homeostasis could be an important mechanism for Cu tolerance. Liu et al. (2017) compared the proteomic response to arsenic of a sensitive and resistant cultivars of poplar and identified a protein, the DNA repair/toleration, playing a key role in arsenic tolerance. Gutierrez-Carbonell et al. (2013) performed a deeper analysis, evaluating the effect of increasing Zn concentrations on the root proteome of *Beta vulgaris* and observed differences between low and medium Zn concentrations and high Zn concentration. In more detail, mitochondrial transport chain and oxidative phosphorylation were slightly affected at low-medium concentration, while at high Zn metabolism, defence system toward oxidative stress was negatively affected, demonstrating a shutdown of the metabolism (Gutierrez-Carbonell et al. 2013). Finally, Sharmin et al. (2012) studied the response of *Miscanthus sinensis* roots to Cr and observed, following the proteome analysis, that the up-regulated proteins were related to vacuole and mitochondria transportation, protein stabilization, mitochondrial respiration, defence and detoxification mechanisms, and cell division, while the down-regulated proteins showed that Cr inhibited carbon flux and glycolysis.

However, the influence of amendments on the root proteome profile is still poorly evaluated. In 2020, Lebrun and collaborators assessed the effect of applying biochar, compost, and iron grit on the root proteome profile of *Salix viminalis* grown on an As- and Pb-contaminated soil (Lebrun et al. 2020a). They found that the proteins affected by amendments belonged to eight functional classes: energy, protein destination and storage, secondary metabolism, disease and defence, intracellular traffic, metabolism, signalling, and protein synthesis. The results showed differences between the amendment treatments. More precisely, under biochar and/or compost amendment, plants overcame metal(loid) stress by eliciting signalling and defence mechanisms, as well as through the redirection of the metabolism toward primary and secondary metabolisms, whereas in the biochar + iron grit condition, plants still suffered from oxidative stress, leading to the impairment of protein degradation.

Finally, plant exposure to metal(loid) stress induces the overproduction of reactive oxygen species (ROS), leading to oxidative stress (Xu et al. 2019). To overcome such oxidative stress and try to maintain ROS at a normal level, plants developed diverse enzymatic and non-enzymatic antioxidant mechanisms. However, under stress, these mechanisms can be overlapped, leading to oxidative damage inside the plants. For instance, Verma and Dubey (2003) grew rice in the presence of Pb and found that the presence of this pollutant in the growing media led to high levels of lipid peroxidation together with an increase in antioxidant enzyme activities. Moreover, other studies also showed that under metal(loid) stress, phenolic compound levels increased (Jaskulak et al. 2018), which is related to their ROS scavenging activity (Kovacik and Kledjus 2008).

Few studies also evaluated the effect of amendment application on the oxidative stress markers in plants. For instance, a combination of redmud with either biochar or activated carbon was added to a former mine technosol (Lebrun et al. 2020b). This amendment induced a decrease in phenolic and salicinoid compound concentration, demonstrating a reduction of oxidative stress with the amendments. Similarly, the antioxidant activity decreased in the amended conditions. However, no amendment effect was measured on enzyme activities and chelation capacity decreased only in one amended substrate (redmud + chemically activated carbon). Finally, the root cell wall composition was studied and the results showed that amendment application did not affect the root cell wall.

To resume, metal(loid) effect on plant root physiology has been much studied, while only a few studies focused on the physiological responses of the root to amendment application. However, these few studies demonstrated that amendment addition to soil affected the root architecture, the root exudate composition as well as the proteome profiles and oxidative stress. More studies are needed to better understand the physiological response of plants to amendments, on a more biochemical level.

10.3.4 Modification of Soil–Microbial Community by Amendments

Soil is a habitat for many microorganisms (Thavamani et al. 2017), especially bacteria, which are the most abundant microorganisms that can be found in soil, estimated between 10^8 and 10^9 cells per gram of soil (Yu et al. 2019). Microorganisms are essential in the remediation of metal(loid)-polluted soil (Ojuederie and Babalola 2017). Even though metal(loid)s cannot be degraded, their behaviour, i.e., mobility, availability, and toxicity, can be affected by microorganisms. Moreover, bacteria have been reviewed to possess diverse metal(loid) tolerance mechanisms (Etesami 2018; Yin et al. 2019): extracellular and intracellular sequestration, active export of metal(loid) ions, and detoxification. Some bacteria also have plant growth promoting properties, which improve plant growth, and thus remediation success (Babu et al. 2013; He et al. 2009).

In addition to their role in phytoremediation success enhancement, as microorganisms are very sensitive to changes in their growing media, they could be used to evaluate the efficiency of a phytoremediation process. Furthermore, since amendments greatly affect soil properties, as demonstrated in the previous sections, microorganisms will be affected by amendment application. For instance, the microbial biomass of the rhizosphere of *Salix viminalis* plants grown on a former mine technosol was observed to be differentially affected by hardwood biochar amendment, depending on the biochar particle size and application rate (Lebrun et al. 2018b).

In addition to the microbial biomass, the activity and the composition of the soil–microbial community constitute an indicator of soil health.

There are two main laboratory tests to evaluate microbial activity, the assessment of the soil enzyme activities, informing on the biochemical status of the soil, and the measurement of the community-level physiological profiles (CLPP), measuring the functional diversity of the microbial community (Al Marzooqi and Yousef 2017; Alvarenga et al. 2014; Mierzwa-Hersztek 2016; Lombi et al. 2002).

It has been shown that amendments, by modifying soil properties and metal(loid) availability, affected the soil–microbial activity (Khadem and Raiesi 2017; Khan et al. 2007; Touceda-González et al. 2017). For instance, the application of biochar, compost, and/or iron grit modified the activity of acid and alkaline phosphatase and the hydrolytic activity, while it increases the functional diversity, evaluated by the CLPP (Lebrun et al. 2021b). On the same soil, the addition of activated carbon, biochar, and/or redmud affected the hydrolytic activity of the microbial community, as well as its β-glucosidase, and alkaline phosphatase activities, and the effect depended on the amendment, and all amendments increased the functional diversity and activity of the microbial community (Lebrun et al. 2021c). Similarly, in the study ofNie et al. (2018) showed that sugarcane bagasse biochar increased the urease, catalase, and invertase activities of the soil. In other studies, several enzyme activities were found to increase in the soil following the addition of compost (Alvarenga et al. 2014; Rossini-Oliva et al. 2017), or redmud (Lee et al. 2011; Lee et al. 2009).

In addition to the microorganism activity, amendments can modify the microbial community structure, by favouring specific strains while negatively affecting others. The effect of amendments on the community structure can be assessed through next generation sequencing (NGS) or phospholipid fatty acid (PLFA) assay. For instance, PLFA measured following the application of a corn biochar or a bamboo biochar to a soil contaminated with both metals and organic pollutants showed that biochar affected the microbial diversity, increased Gram negative bacteria, while having not effect on Gram positive bacteria, *Actinobacteria*, and fungi (Ni et al. 2018). Using next generation sequencing, Garau et al. (2007) found that redmud modified the microbial structure of a multi-contaminated soil, by inhibiting *Actinobacteria* and promoting *β-proteobacteria*, *Bacteroidetes,* and *Chlorobi*. Similarly, Lebrun et al. (2021b) observed a modification of the microbial community structure following the addition of biochar, compost, and/or iron grit to a former mine technosol, with effects depending on the amendment treatments. On the same mine soil, activated carbon, biochar, and/or redmud was applied (Lebrun et al. 2021c). Only the application of redmud significantly increased the number of operational taxonomic units (OTUs), while biochar and redmud increased the number of phyla, and the number of reads was not affected by amendments. The Shannon diversity index at the OTU and phylum levels decreased with the application of activated carbon.

10.4 Concluding Remarks and Future Perspectives

This chapter focused on giving an overview of the effects of amendment application on the soil, metal(loid)s, and plants in a phytoremediation context. More precisely, we tried to answer three main questions (Fig. 10.3).

1. *What are the effects of amendments on the soil physico-chemical properties and metal(loid) behaviour?*

This question has been the subject of many studies over the last decades, which showed that in general, amendment application reduced soil acidity and improved the nutrient and organic matter levels in the soil as well as its water content. Amendments were also shown efficient to immobilize metal(loid)s, although differences were observed between them: biochar and compost were mostly effective in immobilizing cation elements, but tended to mobilize anions, especially arsenic, whereas iron-based amendments were capable of immobilizing both cations and anions. Finally, the studies demonstrated that in addition to amendment type (biochar/compost/redmud), the feedstock, particle size, and application rate of an amendment type, and its association with another one, were important elements affecting the response of soil and metal(loid)s to amendment.

2. *What are the physiological responses of plant roots to amendment application?*

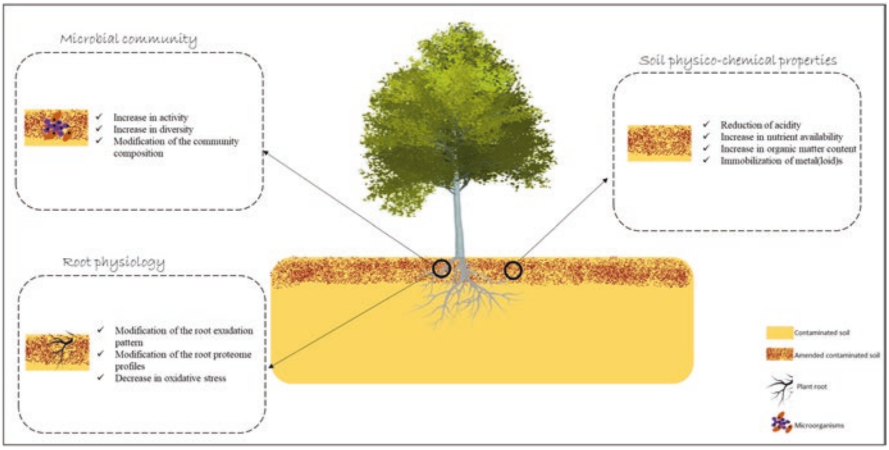


Fig. 10.3 Effects of amendments on the soil, the microbial community, and the root physiology

This question has not been often studied, much of the studies focusing on the plant response to metal(loid)s and not to amendments. However, few published studies demonstrated that amendments had an effect on the root architecture, exudation pattern, proteome profiles, and oxidative stress markers. However, this subject still needs deeper analysis.

3. *How the microbial community is affected by the addition of amendments?*

Similar to the soil and plant roots, soil microorganisms are highly sensitive to metal(loid) pollution. Moreover, their answer to amendment application demonstrated that in general, the improvement of the soil properties and immobilization of metal(loid)s by amendment application also ameliorated the activity and diversity of the soil–microbial community, and modified its composition.

To conclude, amendment application to polluted soils is a good option to improve soil properties and immobilize metal(loid)s, therefore, increasing plant growth and thus phytoremediation success. However, although the influence of metal(loid)s on plant physiology has been demonstrated, these studies were mainly performed in artificial hydroponic conditions and rarely on soils. Furthermore, the physiologic response of plants to amendments, in a real phytostabilization context, has been poorly studies and thus needs to be more precisely evaluated.

References

Abbas T, Rizwan M, Ali S, Adrees M, Mahmood A, Zia-ur-Rehman M, Ibrahim M, Arshad M, Qayyum MF (2018) Biochar application increased the growth and yield and reduced cadmium in drought stressed wheat grown in an aged contaminated soil. Ecotoxicol Environ Saf 148:825–833. https://doi.org/10.1016/j.ecoenv.2017.11.063

Al Marzooqi F, Yousef LF (2017) Biological response of a sandy soil treated with biochar derived from a halophyte (Salicornia bigelovii). Appl Soil Ecol 114:9–15. https://doi.org/10.1016/j.apsoil.2017.02.012

Ali H, Khan E, Sajad MA (2013) Phytoremediation of heavy metals—concepts and applications. Chemosphere 91:869–881. https://doi.org/10.1016/j.chemosphere.2013.01.075

Alvarenga P, de Varennes A, Cunha-Queda AC (2014) The effect of compost treatments and a plant cover with *Agrostis tenuis* on the immobilization/mobilization of trace elements in a mine-contaminated soil. Int J Phytoremediation 16:138–154. https://doi.org/10.1080/15226514.2012.759533

Al-Wabel MI, Usman ARA, Al-Farraj AS, Ok YS, Abduljabbar A, Al-Faraj AI, Sallam AS (2019) Date palm waste biochars alter a soil respiration, microbial biomass carbon, and heavy metal mobility in contaminated mined soil. Environ Geochem Health 41:1705–1722. https://doi.org/10.1007/s10653-017-9955-0

Ashraf S, Ali Q, Zahir ZA, Ashraf S, Asghar HN (2019) Phytoremediation: environmentally sustainable way for reclamation of heavy metal polluted soils. Ecotoxicol Environ Saf 174:714–727. https://doi.org/10.1016/j.ecoenv.2019.02.068

Babu AG, Kim J-D, Oh B-T (2013) Enhancement of heavy metal phytoremediation by Alnus firma with endophytic Bacillus thuringiensis GDB-1. J Hazard Mater 250–251:477–483. https://doi.org/10.1016/j.jhazmat.2013.02.014

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. https://doi.org/10.1146/annurev.arplant.57.032905.105159

Baldantoni D, Cicatelli A, Bellino A, Castiglione S (2014) Different behaviours in phytoremediation capacity of two heavy metal tolerant poplar clones in relation to iron and other trace elements. J Environ Manag 146:94–99. https://doi.org/10.1016/j.jenvman.2014.07.045

Bart S, Motelica-Heino M, Miard F, Joussein E, Soubrand M, Bourgerie S, Morabito D (2016) Phytostabilization of As, Sb and Pb by two willow species (S. viminalis and S. purpurea) on former mine technosols. Catena 136:44–52. https://doi.org/10.1016/j.catena.2015.07.008

Bech J, Duran P, Roca N, Poma W, Sánchez I, Barceló J, Boluda R, Roca-Pérez L, Poschenrieder C (2012) Shoot accumulation of several trace elements in native plant species from contaminated soils in the Peruvian Andes. J Geochem Explor 113:106–111. https://doi.org/10.1016/j.gexplo.2011.04.007

Beesley L, Moreno-Jiménez E, Gomez-Eyles JL (2010) Effects of biochar and greenwaste compost amendments on mobility, bioavailability and toxicity of inorganic and organic contaminants in a multi-element polluted soil. Environ Pollut 158:2282–2287. https://doi.org/10.1016/j.envpol.2010.02.003

Benyó D, Horváth E, Németh E, Leviczky T, Takács K, Lehotai N, Feigl G, Kolbert Z, Ördög A, Gallé R, Csiszár J, Szabados L, Erdei L, Gallé Á (2016) Physiological and molecular responses to heavy metal stresses suggest different detoxification mechanism of Populus deltoides and P. × canadensis. J Plant Physiol 201:62–70. https://doi.org/10.1016/j.jplph.2016.05.025

Bertin C, Yang X, Weston LA (2003) The role of root exudates and allelochemicals in the rhizosphere. Plant Soil 256:67–83. https://doi.org/10.1023/A:1026290508166

Bhatnagar A, Vilar VJP, Botelho CMS, Boaventura RAR (2011) A review of the use of red mud as adsorbent for the removal of toxic pollutants from water and wastewater. Environ Technol 32:231–249. https://doi.org/10.1080/09593330.2011.560615

Bonhomme L, Monclus R, Vincent D, Carpin S, Lomenech A-M, Plomion C, Brignolas F, Morabito D (2009) Leaf proteome analysis of eight *Populus ×euramericana* genotypes: genetic variation in drought response and in water-use efficiency involves photosynthesis-related proteins. Proteomics 9:4121–4142. https://doi.org/10.1002/pmic.200900047

Borghi M, Tognetti R, Monteforti G, Sebastiani L (2007) Responses of Populus×euramericana (P. deltoides×P. nigra) clone Adda to increasing copper concentrations. Environ Exp Bot 61:66–73. https://doi.org/10.1016/j.envexpbot.2007.03.001

Borišev M, Pajević S, Nikolić N, Pilipović A, Krstić B, Orlović S (2009) Phytoextraction of Cd, Ni, and Pb using four willow clones (Salix spp.). Pol J Environ Stud 18(4):553–561

Brennan A, Jiménez EM, Puschenreiter M, Alburquerque JA, Switzer C (2014) Effects of biochar amendment on root traits and contaminant availability of maize plants in a copper and arsenic impacted soil. Plant Soil 379:351–360. https://doi.org/10.1007/s11104-014-2074-0

Brunetti G, Farrag K, Soler-Rovira P, Ferrara M, Nigro F, Senesi N (2012) The effect of compost and Bacillus licheniformis on the phytoextraction of Cr, Cu, Pb and Zn by three brassicaceae species from contaminated soils in the Apulia region, Southern Italy. Geoderma 170:322–330. https://doi.org/10.1016/j.geoderma.2011.11.029

Cantrell KB, Hunt PG, Uchimiya M, Novak JM, Ro KS (2012) Impact of pyrolysis temperature and manure source on physicochemical characteristics of biochar. Bioresour Technol 107:419–428. https://doi.org/10.1016/j.biortech.2011.11.084

Castaldi P, Silvetti M, Enzo S, Melis P (2010) Study of sorption processes and FT-IR analysis of arsenate sorbed onto red muds (a bauxite ore processing waste). J Hazard Mater 175:172–178. https://doi.org/10.1016/j.jhazmat.2009.09.145

Chen L, Gao S, Zhu P, Liu Y, Hu T, Zhang J (2014) Comparative study of metal resistance and accumulation of lead and zinc in two poplars. Physiol Plant 151:390–405. https://doi.org/10.1111/ppl.12120

Ciadamidaro L, Madejón E, Puschenreiter M, Madejón P (2013) Growth of Populus alba and its influence on soil trace element availability. Sci Total Environ 454–455:337–347. https://doi.org/10.1016/j.scitotenv.2013.03.032

Ciadamidaro L, Madejón P, Madejón E (2014) Soil chemical and biochemical properties under Populus alba growing: three years study in trace element contaminated soils. Appl Soil Ecol 73:26–33. https://doi.org/10.1016/j.apsoil.2013.08.003

Courchesne F, Turmel M-C, Cloutier-Hurteau B, Constantineau S, Munro L, Labrecque M (2017) Phytoextraction of soil trace elements by willow during a phytoremediation trial in Southern Québec. Canada Int J Phytoremediation 19:545–554. https://doi.org/10.1080/15226514.2016.1267700

da Conceição Gomes MA, Hauser-Davis RA, de Souza AN, Vitória AP (2016) Metal phytoremediation: general strategies, genetically modified plants and applications in metal nanoparticle contamination. Ecotoxicol Environ Saf 134:133–147. https://doi.org/10.1016/j.ecoenv.2016.08.024

de Sousa Lima JR, de Moraes Silva W, de Medeiros EV, Duda GP, Corrêa MM, Martins Filho AP, Clermont-Dauphin C, Antonino AC, Hammecker C (2018) Effect of biochar on physicochemical properties of a sandy soil and maize growth in a greenhouse experiment. Geoderma 319:14–23. https://doi.org/10.1016/j.geoderma.2017.12.033

Demirevska-Kepova K, Simova-Stoilova L, Stoyanova Z, Hölzer R, Feller U (2004) Biochemical changes in barley plants after excessive supply of copper and manganese. Environ Exp Bot 52:253–266. https://doi.org/10.1016/j.envexpbot.2004.02.004

Derakhshan Nejad Z, Jung MC (2017) The effects of biochar and inorganic amendments on soil remediation in the presence of hyperaccumulator plant. Int J Energy Environ Eng 8:317–329. https://doi.org/10.1007/s40095-017-0250-8

Derakhshan Nejad Z, Jung MC, Kim K-H (2018) Remediation of soils contaminated with heavy metals with an emphasis on immobilization technology. Environ Geochem Health 40:927–953. https://doi.org/10.1007/s10653-017-9964-z

Diacono M, Montemurro F (2010) Long-term effects of organic amendments on soil fertility. A review. Agron Sustainable Dev 30:401–422. https://doi.org/10.1051/agro/2009040

Dresler S, Rutkowska E, Bednarek W, Stanisławski G, Kubrak T, Bogucka-Kocka A, Wójcik M (2017a) Selected secondary metabolites in Echium vulgare L. populations from nonmetalliferous and metalliferous areas. Phytochemistry 133:4–14. https://doi.org/10.1016/j.phytochem.2016.11.001

Dresler S, Wójciak-Kosior M, Sowa I, Stanisławski G, Bany I, Wójcik M (2017b) Effect of short-term Zn/Pb or long-term multi-metal stress on physiological and morphological parameters of metallicolous and nonmetallicolous Echium vulgare L. populations. Plant Physiol Biochem 115:380–389. https://doi.org/10.1016/j.plaphy.2017.04.016

Drzewiecka K, Mleczek M, Gąsecka M, Magdziak Z, Budka A, Chadzinikolau T, Kaczmarek Z, Goliński P (2017) Copper and nickel co-treatment alters metal uptake and stress parameters of Salix purpurea × viminalis. J Plant Physiol 216:125–134. https://doi.org/10.1016/j.jplph.2017.04.020

Durand TC, Sergeant K, Carpin S, Label P, Morabito D, Hausman J-F, Renaut J (2012) Screening for changes in leaf and cambial proteome of Populus tremula×P. alba under different heat constraints. J Plant Physiol 169:1698–1718. https://doi.org/10.1016/j.jplph.2012.06.016

Egene CE, Van Poucke R, Ok YS, Meers E, Tack FMG (2018) Impact of organic amendments (biochar, compost and peat) on Cd and Zn mobility and solubility in contaminated soil of the Campine region after three years. Sci Total Environ 626:195–202. https://doi.org/10.1016/j.scitotenv.2018.01.054

Etesami H (2018) Bacterial mediated alleviation of heavy metal stress and decreased accumulation of metals in plant tissues: mechanisms and future prospects. Ecotoxicol Environ Saf 147:175–191. https://doi.org/10.1016/j.ecoenv.2017.08.032

European Commission. Joint Research Centre. Institute for Environment and Sustainability (2014) Progress in the management of contaminated sites in Europe. Publications Office, LU

Farrell M, Jones DL (2010) Use of composts in the remediation of heavy metal contaminated soil. J Hazard Mater 175:575–582. https://doi.org/10.1016/j.jhazmat.2009.10.044

Feigl V, Anton A, Uzigner N, Gruiz K (2012) Red mud as a chemical stabilizer for soil contaminated with toxic metals. Water Air Soil Pollut 223:1237–1247. https://doi.org/10.1007/s11270-011-0940-4

Ferreira PAA, Marchezan C, Ceretta CA, Tarouco CP, Lourenzi CR, Silva LS, Soriani HH, Nicoloso FT, Cesco S, Mimmo T, Brunetto G (2018) Soil amendment as a strategy for the growth of young vines when replanting vineyards in soils with high copper content. Plant Physiol Biochem 126:152–162. https://doi.org/10.1016/j.plaphy.2018.03.003

Fischer D, Glaser B (2012) Synergisms between compost and biochar for sustainable soil amelioration. In: Kumar S (ed) Management of organic waste. InTech. https://doi.org/10.5772/31200

Fresno T, Peñalosa JM, Santner J, Puschenreiter M, Moreno-Jiménez E (2017) Effect of Lupinus albus L. root activities on As and Cu mobility after addition of iron-based soil amendments. Chemosphere 182:373–381. https://doi.org/10.1016/j.chemosphere.2017.05.034

Fresno T, Moreno-Jiménez E, Zornoza P, Peñalosa JM (2018) Aided phytostabilisation of As- and Cu-contaminated soils using white lupin and combined iron and organic amendments. J Environ Manag 205:142–150. https://doi.org/10.1016/j.jenvman.2017.09.069

Garau G, Castaldi P, Santona L, Deiana P, Melis P (2007) Influence of red mud, zeolite and lime on heavy metal immobilization, culturable heterotrophic microbial populations and enzyme activities in a contaminated soil. Geoderma 142:47–57. https://doi.org/10.1016/j.geoderma.2007.07.011

Garau G, Silvetti M, Deiana S, Deiana P, Castaldi P (2011) Long-term influence of red mud on As mobility and soil physico-chemical and microbial parameters in a polluted sub-acidic soil. J Hazard Mater 185:1241–1248. https://doi.org/10.1016/j.jhazmat.2010.10.037

Gong Y, Zhao D, Wang Q (2018) An overview of field-scale studies on remediation of soil contaminated with heavy metals and metalloids: technical progress over the last decade. Water Res 147:440–460. https://doi.org/10.1016/j.watres.2018.10.024

Gupta N, Yadav KK, Kumar V, Kumar S, Chadd RP, Kumar A (2019) Trace elements in soil-vegetables interface: translocation, bioaccumulation, toxicity and amelioration – a review. Sci Total Environ 651:2927–2942. https://doi.org/10.1016/j.scitotenv.2018.10.047

Gutierrez-Carbonell E, Lattanzio G, Sagardoy R, Rodríguez-Celma J, Ríos Ruiz JJ, Matros A, Abadía A, Abadía J, López-Millán A-F (2013) Changes induced by zinc toxicity in the 2-DE protein profile of sugar beet roots. J Proteome 94:149–161. https://doi.org/10.1016/j.jprot.2013.09.002

He L-Y, Chen Z-J, Ren G-D, Zhang Y-F, Qian M, Sheng X-F (2009) Increased cadmium and lead uptake of a cadmium hyperaccumulator tomato by cadmium-resistant bacteria. Ecotoxicol Environ Saf 72:1343–1348. https://doi.org/10.1016/j.ecoenv.2009.03.006

Hmid A, Al Chami Z, Sillen W, De Vocht A, Vangronsveld J (2015) Olive mill waste biochar: a promising soil amendment for metal immobilization in contaminated soils. Environ Sci Pollut Res 22:1444–1456. https://doi.org/10.1007/s11356-014-3467-6

Houben D, Pircar J, Sonnet P (2012) Heavy metal immobilization by cost-effective amendments in a contaminated soil: effects on metal leaching and phytoavailability. J Geochem Explor 123:87–94. https://doi.org/10.1016/j.gexplo.2011.10.004

Hua Y, Heal KV, Friesl-Hanl W (2017) The use of red mud as an immobiliser for metal/metalloid-contaminated soil: a review. J Hazard Mater 325:17–30. https://doi.org/10.1016/j.jhazmat.2016.11.073

Huang M, Zhu Y, Li Z, Huang B, Luo N, Liu C, Zeng G (2016) Compost as a soil amendment to remediate heavy metal-contaminated agricultural soil: mechanisms, efficacy, problems, and strategies. Water Air Soil Pollut 227:359. https://doi.org/10.1007/s11270-016-3068-8

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 Manag 218:71–78. https://doi.org/10.1016/j.jenvman.2018.04.052

Javed MT, Akram MS, Tanwir K, Javed Chaudhary H, Ali Q, Stoltz E, Lindberg S (2017) Cadmium spiked soil modulates root organic acids exudation and ionic contents of two differentially cd tolerant maize (Zea mays L.) cultivars. Ecotoxicol Environ Saf 141:216–225. https://doi.org/10.1016/j.ecoenv.2017.03.027

Khadem A, Raiesi F (2017) Influence of biochar on potential enzyme activities in two calcareous soils of contrasting texture. Geoderma 308:149–158. https://doi.org/10.1016/j.geoderma.2017.08.004

Khalid S, Shahid M, Niazi NK, Murtaza B, Bibi I, Dumat C (2017) A comparison of technologies for remediation of heavy metal contaminated soils. J Geochem Explor 182:247–268. https://doi.org/10.1016/j.gexplo.2016.11.021

Khan S, Cao Q, Hesham AE-L, Xia Y, He J (2007) Soil enzymatic activities and microbial community structure with different application rates of Cd and Pb. J Environ Sci 19:834–840. https://doi.org/10.1016/S1001-0742(07)60139-9

Kiran YK, Barkat A, Cui X, Feng Y, Pan F, Tang L, Yang X (2017) Cow manure and cow manure-derived biochar application as a soil amendment for reducing cadmium availability and accumulation by Brassica chinensis L. in acidic red soil. J Integr Agric 16:725–734. https://doi.org/10.1016/S2095-3119(16)61488-0

Komárek M, Vaněk A, Ettler V (2013) Chemical stabilization of metals and arsenic in contaminated soils using oxides – a review. Environ Pollut 172:9–22. https://doi.org/10.1016/j.envpol.2012.07.045

Kovacik J, Kledjus B (2008) Dynamics of phenolic acids and lignin accumulation in metal-treated Matricaria chamomilla roots. Plant Cell Rep 27:605–609

Kuzovkina YA, Knee M, Quigley MF (2004) Cadmium and copper uptake and translocation in five willow (*Salix* L.) species. Int J Phytoremediation 6:269–287. https://doi.org/10.1080/16226510490496726

Kwak J-H, Islam MS, Wang S, Messele SA, Naeth MA, El-Din MG, Chang SX (2019) Biochar properties and lead(II) adsorption capacity depend on feedstock type, pyrolysis temperature, and steam activation. Chemosphere 231:393–404. https://doi.org/10.1016/j.chemosphere.2019.05.128

Lapie C, Leglize P, Paris C, Buisson T, Sterckeman T (2019) Profiling of main metabolites in root exudates and mucilage collected from maize submitted to cadmium stress. Environ Sci Pollut Res 26:17520–17534. https://doi.org/10.1007/s11356-019-05168-0

Lebrun M, Macri C, Miard F, Hattab-Hambli N, Motelica-Heino M, Morabito D, Bourgerie S (2017) Effect of biochar amendments on As and Pb mobility and phytoavailability in contaminated mine technosols phytoremediated by Salix. J Geochem Explor 182:149–156. https://doi.org/10.1016/j.gexplo.2016.11.016

Lebrun M, Miard F, Hattab-Hambli N, Bourgerie S, Morabito D (2018a) Assisted phytoremediation of a multi-contaminated industrial soil using biochar and garden soil amendments associated with Salix alba or Salix viminalis: abilities to stabilize As, Pb, and Cu. Water Air Soil Pollut 229:163. https://doi.org/10.1007/s11270-018-3816-z

Lebrun M, Miard F, Nandillon R, Hattab-Hambli N, Scippa GS, Bourgerie S, Morabito D (2018b) Eco-restoration of a mine technosol according to biochar particle size and dose application: study of soil physico-chemical properties and phytostabilization capacities of Salix viminalis. J Soils Sediments 18:2188–2202. https://doi.org/10.1007/s11368-017-1763-8

Lebrun M, Miard F, Nandillon R, Léger J-C, Hattab-Hambli N, Scippa GS, Bourgerie S, Morabito D (2018c) Assisted phytostabilization of a multicontaminated mine technosol using biochar amendment: early stage evaluation of biochar feedstock and particle size effects on As and Pb accumulation of two Salicaceae species (Salix viminalis and Populus euramericana). Chemosphere 194:316–326. https://doi.org/10.1016/j.chemosphere.2017.11.113

Lebrun M, Miard F, Renouard S, Nandillon R, Scippa GS, Morabito D, Bourgerie S (2018d) Effect of Fe-functionalized biochar on toxicity of a technosol contaminated by Pb and As: sorption and phytotoxicity tests. Environ Sci Pollut Res 25:33678–33690. https://doi.org/10.1007/s11356-018-3247-9

Lebrun M, Miard F, Nandillon R, Scippa GS, Bourgerie S, Morabito D (2019) Biochar effect associated with compost and iron to promote Pb and As soil stabilization and Salix viminalis L. growth. Chemosphere 222:810–822. https://doi.org/10.1016/j.chemosphere.2019.01.188

Lebrun M, De Zio E, Miard F, Scippa GS, Renzone G, Scaloni A, Bourgerie S, Morabito D, Trupiano D (2020a) Amending an As/Pb contaminated soil with biochar, compost and iron grit: effect on Salix viminalis growth, root proteome profiles and metal(loid) accumulation indexes. Chemosphere 244:125397. https://doi.org/10.1016/j.chemosphere.2019.125397

Lebrun M, Miard F, Scippa GS, Hano C, Morabito D, Bourgerie S (2020b) Effect of biochar and redmud amendment combinations on Salix triandra growth, metal(loid) accumulation and oxidative stress response. Ecotoxicol Environ Saf 195:110466. https://doi.org/10.1016/j.ecoenv.2020.110466

Lebrun M, Bourgerie S, Morabito D (2021a) Effects of different biochars, activated carbons and redmuds on the growth of trifolium repens and As and Pb stabilization in a former mine technosol. Bull Environ Contam Toxicol 108:403. https://doi.org/10.1007/s00128-021-03271-y

Lebrun M, Miard F, Bucci A, Fougère L, Nandillon R, Naclerio G, Scippa GS, Destandau E, Morabito D, Bourgerie S (2021b) The rhizosphere of Salix viminalis plants after a phytostabilization process assisted by biochar, compost, and iron grit: chemical and (micro)-biological analyses. Environ Sci Pollut Res 28:47447

Lebrun M, Miard F, Van Poucke R, Tack FMG, Scippa GS, Bourgerie S, Morabito D (2021c) Effect of fertilization, carbon-based material, and redmud amendments on the bacterial activity and diversity of a metal(loid) contaminated mining soil. Land Degrad Dev 32:2618–2628. https://doi.org/10.1002/ldr.3929

Lebrun M, Michel C, Joulian C, Morabito D, Bourgerie S (2021d) Rehabilitation of mine soils by phytostabilization: does soil inoculation with microbial consortia stimulate Agrostis growth and metal(loid) immobilization? Sci Total Environ 791:148400. https://doi.org/10.1016/j.scitotenv.2021.148400

Lebrun M, Nandillon R, Miard F, Le Forestier L, Morabito D, Bourgerie S (2021e) Effects of biochar, ochre and manure amendments associated with a metallicolous ecotype of Agrostis capillaris on as and Pb stabilization of a former mine technosol. Environ Geochem Health 43:1491–1505. https://doi.org/10.1007/s10653-020-00592-5

Lebrun M, Nandillon R, Miard F, Scippa GS, Bourgerie S, Morabito D (2021f) Application of amendments for the phytoremediation of a former mine technosol by endemic pioneer species: alder and birch seedlings. Environ Geochem Health 43:77–89. https://doi.org/10.1007/s10653-020-00678-0

Lebrun M, Van Poucke R, Miard F, Scippa GS, Bourgerie S, Morabito D, Tack FMG (2021g) Effects of carbon-based materials and redmuds on metal(loid) immobilization and growth of *Salix dasyclados* Wimm. On a former mine Technosol contaminated by arsenic and lead. Land Degrad Dev 32:467–481. https://doi.org/10.1002/ldr.3726

Lee S-H, Lee J-S, Jeong Choi Y, Kim J-G (2009) In situ stabilization of cadmium-, lead-, and zinc-contaminated soil using various amendments. Chemosphere 77:1069–1075. https://doi.org/10.1016/j.chemosphere.2009.08.056

Lee S-H, Kim EY, Park H, Yun J, Kim J-G (2011) In situ stabilization of arsenic and metal-contaminated agricultural soil using industrial by-products. Geoderma 161:1–7. https://doi.org/10.1016/j.geoderma.2010.11.008

Lee S-H, Ji W, Lee W-S, Koo N, Koh IH, Kim M-S, Park J-S (2014) Influence of amendments and aided phytostabilization on metal availability and mobility in Pb/Zn mine tailings. J Environ Manag 139:15–21. https://doi.org/10.1016/j.jenvman.2014.02.019

Li F, Shi J, Shen C, Chen G, Hu S, Chen Y (2009) Proteomic characterization of copper stress response in Elsholtzia splendens roots and leaves. Plant Mol Biol 71:251–263. https://doi.org/10.1007/s11103-009-9521-y

Li L, Zhu C, Liu X, Li F, Li H, Ye J (2018) Biochar amendment immobilizes arsenic in farmland and reduces its bioavailability. Environ Sci Pollut Res 25:34091–34102. https://doi.org/10.1007/s11356-018-3021-z

Liang Z, Peng X, Luan Z (2012) Immobilization of Cd, Zn and Pb in sewage sludge using red mud. Environ Earth Sci 66:1321–1328. https://doi.org/10.1007/s12665-011-1341-0

Liu Y, Lin C, Wu Y (2007) Characterization of red mud derived from a combined Bayer process and bauxite calcination method. J Hazard Mater 146:255–261. https://doi.org/10.1016/j.jhazmat.2006.12.015

Liu Y, Damaris RN, Yang P (2017) Proteomics analysis identified a DRT protein involved in arsenic resistance in Populus. Plant Cell Rep 36:1855–1869. https://doi.org/10.1007/s00299-017-2199-8

Liu L, Li W, Song W, Guo M (2018) Remediation techniques for heavy metal-contaminated soils: principles and applicability. Sci Total Environ 633:206–219. https://doi.org/10.1016/j.scitotenv.2018.03.161

Lombi E, Zhao F-J, Wieshammer G, Zhang G, McGrath SP (2002) In situ fixation of metals in soils using bauxite residue: biological effects. Environ Pollut 118:445–452. https://doi.org/10.1016/S0269-7491(01)00295-0

Lu K, Yang X, Gielen G, Bolan N, Ok YS, Niazi NK, Xu S, Yuan G, Chen X, Zhang X, Liu D, Song Z, Liu X, Wang H (2017) Effect of bamboo and rice straw biochars on the mobility and redistribution of heavy metals (Cd, Cu, Pb and Zn) in contaminated soil. J Environ Manag 186:285–292. https://doi.org/10.1016/j.jenvman.2016.05.068

Mahar A, Wang P, Li R, Zhang Z (2015) Immobilization of lead and cadmium in contaminated soil using amendments: a review. Pedosphere 25:555–568. https://doi.org/10.1016/S1002-0160(15)30036-9

Marchand L, Pelosi C, González-Centeno MR, Maillard A, Ourry A, Galland W, Teissedre P-L, Bessoule J-J, Mongrand S, Morvan-Bertrand A, Zhang Q, Grosbellet C, Bert V, Oustrière N, Mench M, Brunel-Muguet S (2016) Trace element bioavailability, yield and seed quality of rapeseed (Brassica napus L.) modulated by biochar incorporation into a contaminated technosol. Chemosphere 156:150–162. https://doi.org/10.1016/j.chemosphere.2016.04.129

Mierzwa-Hersztek M (2016) Effect of poultry litter biochar on soil enzymatic activity, ecotoxicity and plant growth. Appl Soil Ecol 8:144

Mirck J, Isebrands JG, Verwijst T, Ledin S (2005) Development of short-rotation willow coppice systems for environmental purposes in Sweden. Biomass Bioenergy 28:219–228. https://doi.org/10.1016/j.biombioe.2004.08.012

Mora MD, Rosas A, Ribera A, Rengel Z (2009) Differential tolerance to Mn toxicity in perennial ryegrass genotypes: involvement of antioxidative enzymes and root exudation of carboxylates. Plant Soil 320:79–89. https://doi.org/10.1007/s11104-008-9872-1

Nandillon R, Miard F, Lebrun M, Gaillard M, Sabatier S, Bourgerie S, Battaglia-Brunet F, Morabito D (2019) Effect of biochar and amendments on Pb and As phytotoxicity and phytoavailability in a technosol. Clean (Weinh) 47:1800220. https://doi.org/10.1002/clen.201800220

Nandillon R, Lebrun M, Miard F, Gaillard M, Sabatier S, Morabito D, Bourgerie S (2021) Contrasted tolerance of Agrostis capillaris metallicolous and non-metallicolous ecotypes in the context of a mining technosol amended by biochar, compost and iron sulfate. Environ Geochem Health 43:1457–1475. https://doi.org/10.1007/s10653-019-00447-8

Ni N, Shi R, Liu Z, Bian Y, Wang F, Song Y, Jiang X (2018) Effects of biochars on the bioaccessibility of phenanthrene/pyrene/zinc/lead and microbial community structure in a soil under aerobic and anaerobic conditions. J Environ Sci 63:296–306. https://doi.org/10.1016/j.jes.2017.05.023

Nie C, Yang X, Niazi NK, Xu X, Wen Y, Rinklebe J, Ok YS, Xu S, Wang H (2018) Impact of sugarcane bagasse-derived biochar on heavy metal availability and microbial activity: a field study. Chemosphere 200:274–282. https://doi.org/10.1016/j.chemosphere.2018.02.134

Ojuederie O, Babalola O (2017) Microbial and plant-assisted bioremediation of heavy metal polluted environments: a review. Int J Environ Res Public Health 14:1504. https://doi.org/10.3390/ijerph14121504

Oustriere N, Marchand L, Lottier N, Motelica M, Mench M (2017) Long-term cu stabilization and biomass yields of Giant reed and poplar after adding a biochar, alone or with iron grit, into a contaminated soil from a wood preservation site. Sci Total Environ 579:620–627. https://doi.org/10.1016/j.scitotenv.2016.11.048

Panagos P, Van Liedekerke M, Yigini Y, Montanarella L (2013) Contaminated sites in Europe: review of the current situation based on data collected through a European network. J Environ Public Health 2013:1–11. https://doi.org/10.1155/2013/158764

Pawlak-Sprada S, Arasimowicz-Jelonek M, Podgórska M, Deckert J (2011) Activation of phenylpropanoid pathway in legume plants exposed to heavy metals. Part I. Effects of cadmium and lead on phenylalanine ammonia-lyase gene expression, enzyme activity and lignin content. Acta Biochim Pol 58(2):211–216. https://doi.org/10.18388/abp.2011_2267

Payá Pérez A, Rodríguez Eugenio N (2018) Status of local soil contamination in Europe revision of the indicator “Progress in the management contaminated sites in Europe”. European Commission, Joint Research Centre

Payne K, Abdel-Fattah T (2005) Adsorption of arsenate and arsenite by iron-treated activated carbon and zeolites: effects of pH, temperature, and ionic strength. J Environ Sci Health Part A 40:723–749. https://doi.org/10.1081/ESE-200048254

Paz-Ferreiro J, Lu H, Fu S, Méndez A, Gascó G (2014) Use of phytoremediation and biochar to remediate heavy metal polluted soils: a review. Solid Earth 5:65–75. https://doi.org/10.5194/se-5-65-2014

Qian W, Zhao A, Xu R (2013) Sorption of As(V) by aluminum-modified crop straw-derived biochars. Water Air Soil Pollut 224:1610. https://doi.org/10.1007/s11270-013-1610-5

Qian K, Kumar A, Zhang H, Bellmer D, Huhnke R (2015) Recent advances in utilization of biochar. Renew Sust Energ Rev 42:1055–1064. https://doi.org/10.1016/j.rser.2014.10.074

Rajapaksha AU, Chen SS, Tsang DCW, Zhang M, Vithanage M, Mandal S, Gao B, Bolan NS, Ok YS (2016) Engineered/designer biochar for contaminant removal/immobilization from soil and water: potential and implication of biochar modification. Chemosphere 148:276–291. https://doi.org/10.1016/j.chemosphere.2016.01.043

Rehman MZ, Rizwan M, Ali S, Fatima N, Yousaf B, Naeem A, Sabir M, Ahmad HR, Ok YS (2016) Contrasting effects of biochar, compost and farm manure on alleviation of nickel toxicity in maize (Zea mays L.) in relation to plant growth, photosynthesis and metal uptake. Ecotoxicol Environ Saf 133:218–225. https://doi.org/10.1016/j.ecoenv.2016.07.023

Rizwan M, Ali S, Abbas F, Adrees M, Zia-ur-Rehman M, Farid M, Gill RA, Ali B (2017) Role of organic and inorganic amendments in alleviating heavy metal stress in oilseed crops. In: Ahmad P (ed) Oilseed crops. Wiley, Chichester, pp 224–235. https://doi.org/10.1002/9781119048800.ch12

Rocco C, Seshadri B, Adamo P, Bolan NS, Mbene K, Naidu R (2018) Impact of waste-derived organic and inorganic amendments on the mobility and bioavailability of arsenic and cadmium in alkaline and acid soils. Environ Sci Pollut Res 25:25896–25905. https://doi.org/10.1007/s11356-018-2655-1

Rodríguez Eugenio N, McLaughlin MJ, Pennock D (2018) Soil pollution: a hidden reality. FAO

Rodziewicz P, Swarcewicz B, Chmielewska K, Wojakowska A, Stobiecki M (2014) Influence of abiotic stresses on plant proteome and metabolome changes. Acta Physiol Plant 36:1–19. https://doi.org/10.1007/s11738-013-1402-y

Rossini-Oliva S, Mingorance MD, Peña A (2017) Effect of two different composts on soil quality and on the growth of various plant species in a polymetallic acidic mine soil. Chemosphere 168:183–190. https://doi.org/10.1016/j.chemosphere.2016.10.040

Samsuri AW, Sadegh-Zadeh F, Seh-Bardan BJ (2013) Adsorption of As(III) and As(V) by Fe coated biochars and biochars produced from empty fruit bunch and rice husk. J Environ Chem Eng 1:981–988. https://doi.org/10.1016/j.jece.2013.08.009

Saxena G, Purchase D, Mulla SI, Saratale GD, Bharagava RN (2019) Phytoremediation of heavy metal-contaminated sites: eco-environmental concerns, field studies, sustainability issues, and future prospects. In: de Voogt P (ed) Reviews of environmental contamination and toxicology, vol 249. Springer International Publishing, Cham, pp 71–131. https://doi.org/10.1007/398_2019_24

Sharmin SA, Alam I, Kim K-H, Kim Y-G, Kim PJ, Bahk JD, Lee B-H (2012) Chromium-induced physiological and proteomic alterations in roots of Miscanthus sinensis. Plant Sci 187:113–126. https://doi.org/10.1016/j.plantsci.2012.02.002

Sidhu GPS, Singh HP, Batish DR, Kohli RK (2017) Tolerance and hyperaccumulation of cadmium by a wild, unpalatable herb Coronopus didymus (L.) Sm. (Brassicaceae). Ecotoxicol Environ Saf 135:209–215. https://doi.org/10.1016/j.ecoenv.2016.10.001

Sun Y, Gao B, Yao Y, Fang J, Zhang M, Zhou Y, Chen H, Yang L (2014) Effects of feedstock type, production method, and pyrolysis temperature on biochar and hydrochar properties. Chem Eng J 240:574–578. https://doi.org/10.1016/j.cej.2013.10.081

Tack FMG, Meers E (2010) Assisted phytoextraction: helping plants to help us. Elements 6:383–388. https://doi.org/10.2113/gselements.6.6.383

Tan X, Liu S-b, Liu Y, Gu Y, Zeng G, Hu X, Wang X, Liu S-h, Jiang L (2017) Biochar as potential sustainable precursors for activated carbon production: multiple applications in environmental protection and energy storage. Bioresour Technol 227:359–372. https://doi.org/10.1016/j.biortech.2016.12.083

Thavamani P, Samkumar RA, Satheesh V, Subashchandrabose SR, Ramadass K, Naidu R, Venkateswarlu K, Megharaj M (2017) Microbes from mined sites: harnessing their potential for reclamation of derelict mine sites. Environ Pollut 230:495–505. https://doi.org/10.1016/j.envpol.2017.06.056

Touceda-González M, Álvarez-López V, Prieto-Fernández Á, Rodríguez-Garrido B, Trasar-Cepeda C, Mench M, Puschenreiter M, Quintela-Sabarís C, Macías-García F, Kidd PS (2017) Aided phytostabilisation reduces metal toxicity, improves soil fertility and enhances microbial activity in Cu-rich mine tailings. J Environ Manag 186:301–313. https://doi.org/10.1016/j.jenvman.2016.09.019

Trakal L, Veselská V, Šafařík I, Vítková M, Číhalová S, Komárek M (2016) Lead and cadmium sorption mechanisms on magnetically modified biochars. Bioresour Technol 203:318–324. https://doi.org/10.1016/j.biortech.2015.12.056

Trakal L, Raya-Moreno I, Mitchell K, Beesley L (2017) Stabilization of metal(loid)s in two contaminated agricultural soils: comparing biochar to its non-pyrolysed source material. Chemosphere 181:150–159. https://doi.org/10.1016/j.chemosphere.2017.04.064

Trakal L, Michálková Z, Beesley L, Vítková M, Ouředníček P, Barceló AP, Ettler V, Číhalová S, Komárek M (2018) AMOchar: amorphous manganese oxide coating of biochar improves its efficiency at removing metal(loid)s from aqueous solutions. Sci Total Environ 625:71–78. https://doi.org/10.1016/j.scitotenv.2017.12.267

Ullah R, Hadi F, Ahmad S, Jan AU, Rongliang Q (2019) Phytoremediation of lead and chromium contaminated soil improves with the endogenous phenolics and proline production in parthenium, cannabis, euphorbia, and rumex species. Water Air Soil Pollut 230:40. https://doi.org/10.1007/s11270-019-4089-x

Verma S, Dubey RS (2003) Lead toxicity induces lipid peroxidation and alters the activities of antioxidant enzymes in growing rice plants. Plant Sci 164:645–655. https://doi.org/10.1016/S0168-9452(03)00022-0

Wan X, Lei M, Yang J (2017) Two potential multi-metal hyperaccumulators found in four mining sites in Hunan Province, China. Catena 148:67–73. https://doi.org/10.1016/j.catena.2016.02.005

Wang S, Shi X, Sun H, Chen Y, Pan H, Yang X, Rafiq T (2014) Variations in metal tolerance and accumulation in three hydroponically cultivated varieties of salix integra treated with lead. PLoS One 9:e108568. https://doi.org/10.1371/journal.pone.0108568

Wenzel WW (2009) Rhizosphere processes and management in plant-assisted bioremediation (phytoremediation) of soils. Plant Soil 321:385–408. https://doi.org/10.1007/s11104-008-9686-1

Wu W, Li J, Niazi NK, Müller K, Chu Y, Zhang L, Yuan G, Lu K, Song Z, Wang H (2016) Influence of pyrolysis temperature on lead immobilization by chemically modified coconut fiber-derived biochars in aqueous environments. Environ Sci Pollut Res 23:22890–22896. https://doi.org/10.1007/s11356-016-7428-0

Xu X, Yang B, Qin G, Wang H, Zhu Y, Zhang K, Yang H (2019) Growth, accumulation, and antioxidative responses of two Salix genotypes exposed to cadmium and lead in hydroponic culture. Environ Sci Pollut Res 26:19770–19784. https://doi.org/10.1007/s11356-019-05331-7

Yan XL, Lin LY, Liao XY, Zhang WB, Wen Y (2013) Arsenic stabilization by zero-valent iron, bauxite residue, and zeolite at a contaminated site planting Panax notoginseng. Chemosphere 93:661–667. https://doi.org/10.1016/j.chemosphere.2013.05.083

Yang X, Igalavithana AD, Oh S-E, Nam H, Zhang M, Wang C-H, Kwon EE, Tsang DCW, Ok YS (2018) Characterization of bioenergy biochar and its utilization for metal/metalloid immobilization in contaminated soil. Sci Total Environ 640–641:704–713. https://doi.org/10.1016/j.scitotenv.2018.05.298

Yin K, Wang Q, Lv M, Chen L (2019) Microorganism remediation strategies towards heavy metals. Chem Eng J 360:1553–1563. https://doi.org/10.1016/j.cej.2018.10.226

Yu H, Zou W, Chen J, Chen H, Yu Z, Huang J, Tang H, Wei X, Gao B (2019) Biochar amendment improves crop production in problem soils: a review. J Environ Manag 232:8–21. https://doi.org/10.1016/j.jenvman.2018.10.117

Zama EF, Reid BJ, Arp HPH, Sun G-X, Yuan H-Y, Zhu Y-G (2018) Advances in research on the use of biochar in soil for remediation: a review. J Soils Sediments 18:2433–2450. https://doi.org/10.1007/s11368-018-2000-9

Chapter 11
Rhizodegradation: The Plant Root Exudate and Microbial Community Relationship

Kwang Mo Yang, Toemthip Poolpak, and Prayad Pokethitiyook

Abstract Understanding the interaction of plants and microbes during rhizodegradation of organic contaminants is critical for developing effective bioremediation technologies. Plant secretes about 20% of their fixed carbons from photosynthesis into their root zone in the forms of sugar, amino acids, phenolics, flavonoids, and many other compounds. These chemical cocktails of plant metabolites, also known as root exudates, provide a viable nutrient source for soil microbial communities where nutrient availability is known to be limited. In general, contaminant concentration in the environment is inversely correlated to the concentration of plant root exudates. There are higher microbial biomass and contaminant transformation rate as root exudates promote microbial growth and catabolic activities. Due to this evidence, environmental scientists sought to figure out the suitable plant-microbe pairs that show the highest remediation capability suited to the specific organic contaminants.

Keywords Rhizodegradation · Rhizosphere bacteria · Root exudates · Plant microbe interactions

11.1 Introduction

Rapid development, urbanization, and excessive agricultural practices over the last century have introduced myriads of contaminants into the environment. Toxic contaminants such as petroleum hydrocarbons (PHCs), polycyclic aromatic

---

K. M. Yang · T. Poolpak · P. Pokethitiyook (✉)
Department of Biology, Faculty of Science, Mahidol University, Bangkok, Thailand

Center of Excellence on Environmental Health and Toxicology (EHT), OPS, MHESI, Thailand
e-mail: prayad.pok@mahidol.ac.th

L. Newman et al. (eds.), *Phytoremediation*, https://doi.org/10.1007/978-3-031-17988-4_11

hydrocarbons (PAHs), polychlorinated biphenyls (PCB), toxic dyes, pesticides, herbicides, and organic solvents are amongst the most commonly found forms of organic contaminants in the environment (Viguri et al. 2002; Hafner and Hites 2003; Qu et al. 2019). The major sources of these contaminants are industrial activities, oil refineries, motor vehicles, improper waste management, and agrochemical and pharmaceutical industries. Once these organic pollutants enter the environment, they accumulate and persist due to their toxicity and resistance to degradation. The environmental partitioning behaviors of individual contaminants differ according to their physio-chemical properties. However, most organic contaminants end up in organic-rich media such as soil and sediments (Chiou et al. 1998; Viguri et al. 2002; Wu et al. 2019). Soil is a complex mixture of chemicals that can be continuously exposed to low to medium levels of contamination from the direct input of organic wastes and depository particulates from the atmosphere (Ma et al. 2013; Qu et al. 2019). Consequently, these contaminants in the environment deteriorate the soil quality and pose a serious threat to their surrounding biota, including human beings. Hence, research on clean-up technologies has dragged many interests to environmental scientists during past decades.

It has been widely accepted that the traditional remediation technologies involving physical and chemical treatments for most contaminated sites are expensive and destructive. Recently, the use of green technologies has become a prioritized search in both scientific communities and industries. One promising technology that gained the attention of several scientists over the years is the use of plants to remediate contaminated soil, also known as phytoremediation. Phytoremediation is a cost-effective and environmentally friendly method that uses a living plant to clean up contaminants in the air, soil, and water. Plants can uptake organic contaminants and directly degrade organic contaminants using laccases, peroxidases, and phenol oxidases (Muratova et al. 2009; Martin et al. 2014; Dubrovskaya et al. 2017). However, most persistent organic pollutants (POPs) are known for their poor solubility in water which limits the uptake and translocation within the plants (Burken and Schnoor 1998; Gao and Zhu 2004). The removal of organic contaminants in the soil is mainly attributed to microbial biodegradation (Gao and Zhu 2004). Plants promote the bioactivity of rhizosphere microorganisms to degrade organic contaminants by providing mechanical support, water, oxygen, and nutrients into the rhizosphere. In addition, plants strategically deposit up to one-third of all photosynthetic fixed carbons into the rhizosphere in the forms of soluble sugars, amino acids, organic acids, phenolic compounds, flavonoids, and other macromolecules (Badri and Vivanco 2009). These ‘root exudates’ serve as viable carbon sources for soil microorganisms and allow them to increase their biomass and metabolic activities, which drive the mineralization of organic contaminants (Miya and Firestone 2001; Liu et al. 2015; Rohrbacher and St-Arnaud 2016; Yang et al. 2021). Accordingly, studies have shown that the rhizosphere is several orders of magnitude richer in microbial biomass compared to the non-rhizosphere in both contaminated and non-contaminated soil (Wang et al. 2008; Rohrbacher and St-Arnaud 2016; Yang et al. 2021). A phenomenon that biological, chemical, and physical changes in soils occur because of root exudates is also known as the ‘rhizosphere effect’. In return, microorganisms provide protection against pathogenic infection or chemical stress, increase the solubility of nutrients, and secrete phytohormones to promote plant growth (Hou et al. 2015; Urana et al. 2019). The symbiotic relationship between plants and microorganisms leads to increased flow of nutrients, enzymes, and biosurfactants to the soil which aids biodegradation of organic contaminants in polluted soil, which is still an open area that needs to be further investigated.

11.2 Bioremediation of Organic Contaminants in the Soil

11.2.1 Microbial Degradation of Organic Contaminants

Microorganisms have been on Earth for more than 3.5 billion years. Their biological transformation of environmental chemicals is the founding principle that sustains all ecosystems. Microorganisms are known to be present in almost every environment on Earth including the most extreme environments such as hot springs and permafrost. It is not surprising that they have evolved numerous catabolic pathways to break down diverse organic contaminants. The soil microbes transform organic contaminants and use them as electron donors to generate energy. During the past decades, various researchers have characterized and isolated many bacterial species to decontaminate toxic pollutants in the environment (Grishchenkov et al. 2000; Sowada et al. 2014; Kafilzadeh et al. 2016). Bacterial strains such as *Pseudomonas sp.* and *Brevibacillus sp.* have been reported to feed exclusively on hydrocarbons (Grishchenkov et al. 2000). Some microorganisms such as *Micrococcus luteus* are reported to mineralize complex organic contaminants (benzo[a]pyrene) as a sole carbon source (Sowada et al. 2014). However, most microorganisms are not equipped with catabolic genes and enzymes to mineralize complex organic contaminants; hence, degradation of complex organic contaminants such as high molecular weight PAHs can be only achieved by a consortium of microorganisms.

11.2.2 Bioremediation

Bioremediation utilizes the concept of natural microbial catabolic capabilities of microorganisms to transform organic contaminants into less toxic metabolites and ultimately mineralize them into carbon dioxide and water. Bioremediation offers a cost-effective method to clean up soil contaminated with organic contaminants. Although bioremediation technology may not be applicable to all types of environmental pollutants, it has been demonstrated to be particularly effective on remediation of soil contaminated with petrochemicals (Balba et al. 1998; Xu et al. 2014; Lu et al. 2019). Bioremediation requires specific microorganisms that are capable of degrading the pollutants as well as manipulation of environmental conditions. In general, bioremediation technology could be simply divided into two main processes, biostimulation and bioaugmentation (Fig. 11.1). Biostimulation focuses on enriching the environment for the indigenous microbes to degrade the pollutants at their full potential. Nutrients such as nitrogen, phosphorus, oxygen, and sometimes even carbon sources are provided to stimulate the local microorganisms. However, bioaugmentation is a process of inoculating the cultured microorganism(s) with known abilities to transform contaminants to enhance degradation of the pollutants. In most cases, bioaugmentation is coupled with biostimulation to provide the optimal condition for the introduced microorganisms to successfully utilize toxic compounds. Inoculation of consortia is found to be more effective compared to the single species inoculation as different species may utilize different intermediates which results in faster degradation.

The efficiency of bioremediation is determined by multiple factors such as the bioavailability of the contaminants, soil texture, pH, water holding capacity, temperature, and nutrient availability. Some examples of in situ and ex situ bioremediation technology are summarized in Table 11.1. Now, researchers focus on finding non-destructive methods to manipulate these factors to enhance the effectiveness of bioremediation.

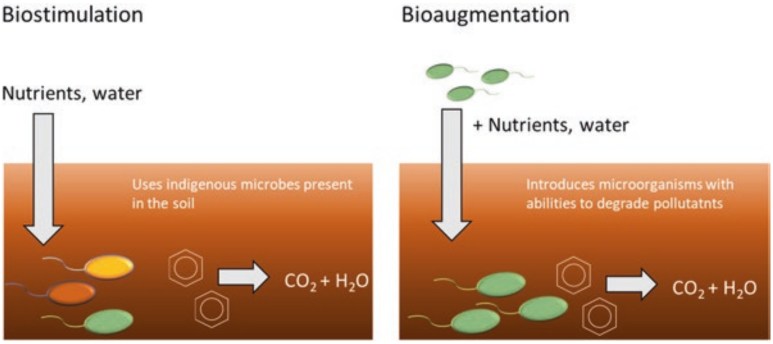


Fig. 11.1 Comparison of biostimulation and bioaugmentation

Table 11.1 Examples of in situ and ex situ bioremediation technology

Technology	Examples	Advantage	Disadvantage
In situ bioremediation	Bioventing Bioaugmentation Biostimulation Phytoremediation	Cost-effective Non-invasive Environmentally friendly	Environmental constraints Monitoring difficulties Highly dependent on indigenous microbes Time-consuming
Ex situ bioremediation	Composting Land farming Biopile Bioreactor	Rapid degradation Optimized environmental condition	Soil excavation required Space requirement Increased treatment cost

11.2.3 Phytoremediation of Organic Contaminants

Phytoremediation is a cost-effective and environmentally friendly method that uses a living plant to clean up contaminants in the air, soil, and water. Soil is a heterogeneous habitat that shows a high variance in contaminant partitioning behavior depending on its physicochemical properties. The partitioning behaviors of organic contaminants in a plant are determined by the nature of individual constituents (Pokethitiyook 2017). In general, phytoremediation of organic contaminants in the soil can be categorized into three main mechanisms, which are phytoextraction, phytovolatilization, and rhizodegradation (Fig. 11.2). Plants can directly uptake organic contaminants and translocate them into aboveground parts (phytoextraction), which may end up in plant tissues and vacuoles. These groups of organic contaminants are typically resistant to biodegradation or chemical decomposition such as poly- and perfluoroalkyl substances (PFASs). For volatile organic compounds (VOCs) such as methyl tert-butyl ether (MTBE) and trichloroethylene (TCE), plants translocate the contaminant to the shoots and transpirate the compounds to the atmosphere (phytovolatilization) (Limmer and Burken 2016). Then, VOCs generally undergo substantial dilution and photochemical decay in the atmosphere (Limmer and Burken 2016). However, most organic contaminants such as petroleum hydrocarbons, PCBs, pesticides, organic solvents, and PAHs are known for their poor solubility. Most hydrophobic contaminants are uptaken by plants via

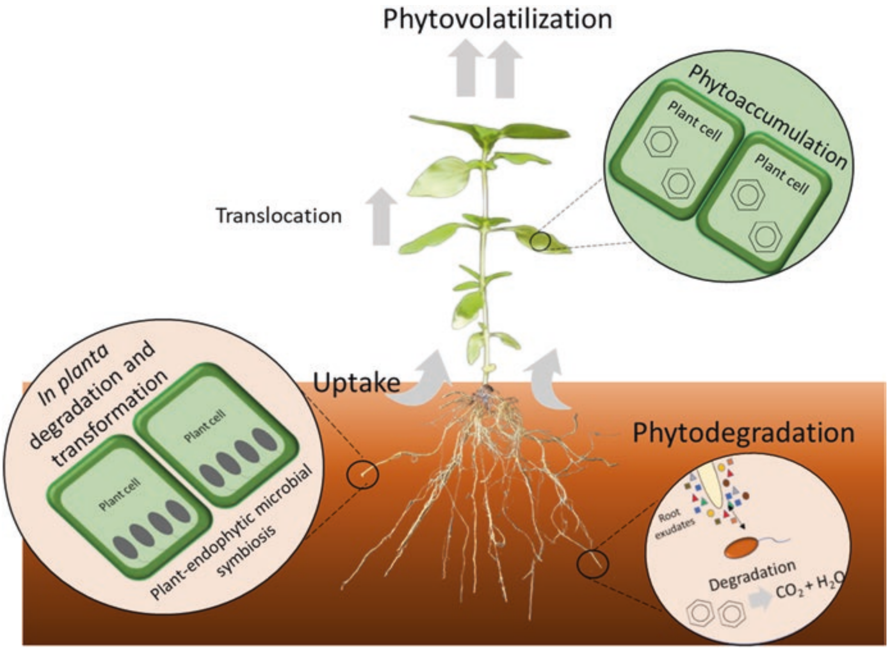


Fig. 11.2 Mechanism of phytoremediation of organic contaminants in the soil

passive transport as no specific active transporters have been identified to target organic contaminants unlike heavy metals (Ye et al. 1992; Shah and Daverey 2020). The partitioning coefficients of these chemicals and their solubility (or availability) in the water facilitate the crossing of pollutants to the outer cell membrane (Reichenauer and Germida 2008). Therefore, the removal of organic contaminants is mainly attributed to microbial degradation in the rhizosphere or so-called phytodegradation (Gao and Zhu 2004).

However, phytoremediation of organic contaminants is often limited by contaminant toxicity (Adam and Duncan 2003; Chouychai et al. 2007; Chowdhury et al. 2020). Organic pollutants inhibit root development reducing the total root contact with the soil and root exudation (Ahammed et al. 2013; Han et al. 2016). For example, petroleum hydrocarbons cover the surface of the roots, inhibit nutrient uptake, and increase the production of reactive oxygen species which may lead to cell death (Han et al. 2016). Furthermore, some organic contaminants such as PAHs have been reported to induce mutagenesis in plant cells (Ma et al. 2014). The subsequent reduction in plant biomass, the root biomass, in particular, lead to a decrease in the overall surface area of the rhizosphere which leads to reduced biodegradation rate of the contaminants. Therefore, selected plant species must tolerate the toxicity of the contaminants. Several plant species such as poplar, tall fescue, ryegrass, sorghum, alfalfa, vetiver grass, and maize have been suggested as suitable candidates for phytoremediation of organic contaminants (Palmroth et al. 2002; Wang et al. 2008; Datta et al. 2013; Dubrovskaya et al. 2017; Guo et al. 2017a; Zamani et al. 2018). Most of these plants belong to the *Poaceae* family with a fibrous root system. The fibrous root system is often preferred over tap root system as it has a larger root-soil interface due to its extensive root system (Rohrbacher and St-Arnaud 2016; Pokethitiyook 2017).

It has to be noted that the rhizosphere effect is primarily dependent on the quality and quantity of root exudates secreted by the plant species. Root exudation is the key mechanism involved in plant-microbial phytostimulation and their corresponding metabolic activities (Rohrbacher and St-Arnaud 2016). Hence, high root biomass and large root-soil interface does not always lead to enhanced rhizodegradation of organic contaminants. For example, Liste and Felgentreu (2006) investigated the phytoremediation potential of ryegrass, summer vetch, and white mustard in petroleum contaminated soil. They reported that ryegrass had the highest root biomass with the lowest petroleum hydrocarbon removal efficiency. However, summer vetch and white mustard enhanced the dissipation of TPH and microbial degradative activities with relatively lower root biomass. In the contaminated soil, root exudates serve as a powerful selection pressure in shaping the soil microbial communities (Berg and Smalla 2009; Chaparro et al. 2014). Every plant species has their specific root exudation pattern and recruit specific microbiota to dominate in the rhizosphere (Berg and Smalla 2009; Bourceret et al. 2017; Vergani et al. 2017). Studies on PAH and PCB contaminated soil indicated that the rhizosphere effect of a plant was stronger in shaping bacterial communities rather than pollutant concentration (Bourceret et al. 2015; Vergani et al. 2017). This indicates that plants do not select microbes for rhizoremediation efficiency but rather establish a strong relationship with the soil bacterial communities to adapt and counteract phytotoxicity of the polluted soil (Vergani et al. 2017). Therefore, in absence of effective contaminant biodegraders in the soil, the plants may only modify the diversity of rhizosphere microorganisms but may not enhance degradation (Cébron et al. 2011; Hou et al. 2015).

Rhizoremediation, also known as rhizospheric bioaugmentation, uses the synergy between plant and their associated rhizosphere microbes to degrade pollutants in soil. Rhizoremediation not only involves interaction between plant and their associated microorganisms but also introduces specific microbe or microbial consortiums with appropriate catabolic activities (Villacieros et al. 2005). Plants and microorganisms have coevolved to take advantage of their association over millions of years. Each plant species finely tune their root metabolites and select specific microbial communities to dominate in their rhizosphere (Berg and Smalla 2009). Although specific mechanisms involved in these complex plant-microbial interactions are still under investigation, several studies demonstrated that conjugation of plant and microorganisms can enhance bioremediation of organic contaminants (Hou et al. 2015; Xun et al. 2015; Murray et al. 2019). For instance, Hou et al. (2015) showed that conjugation of tall fescue with *Pseudomonas* sp. SB and *Klebsiella* sp. D5A enhanced the removal of petroleum hydrocarbons in aged petroleum contaminated soil.

11.3 Plant Root Exudation and Its Influence on Biodegradation

11.3.1 The Release of Root Exudates

Plants synthesize an enormous amount of organic compounds over the course of their life span. Diverse chemical compounds are produced which vary with their age, environmental condition, and plant species. It has been estimated that plants allocate approximately 10–20% of all photosynthetically fixed carbons into the rhizosphere (Dennis et al. 2010; Martin et al. 2014). These root exudates comprise chemical compounds that can be categorized into low molecular weight organic compounds (LMWOC) and high molecular weight organic compounds (HMWOC). In general, LMWOCs are water-soluble compounds that are present in the plant cytoplasm. These chemicals include amino acids, organic acids, sugars, and alcohols that are transported by passive transport. HMWOC includes root debris, soluble lysates, mucilage, proteins, and plant secondary metabolites (i.e., phenolics, flavonoids, and terpenoids). The generic chemical components of the root exudates and their functional role are summarized in Table 11.2.

The plant root exudation is not only dependent on environmental factors and the developmental stage of the plant but also affected by biological parameters. Some studies showed that plants allocate higher amount of C to roots when

Table 11.2 Components of root exudates and their functional role

Chemical groups	Specific compounds	Functions
Sugars	Arabinose, fructose, galactose, glucose, maltose, mannose, oligosaccharides, raffinose, rhamnose, ribose, sucrose, xylose, deoxyribose	Nutrient source Chemoattractant
Amino acids	a-Alanine, b-alanine, g-aminobutyric, a-aminoadipic, arginine, asparagine, aspartic, citrulline, cystathionine, cysteine, cystine, deoxymugineic, 3-epihydroxymugineic, glutamine, glutamic, glycine, histidine, homoserine, isoleucine, leucine, lysine, methionine, mugineic, ornithine, phenylalanine, praline, proline, serine, threonine, tryptophan, tyrosine, valine	Nutrient source Chemoattractant Nutrient acquisition
Organic acids	Acetic, aconitic, ascorbic, aldonic, butyric, citric, erythronic, formic, fumaric, glutaric, glycolic, lactic, glyoxilic, malic, malonic, oxalacetic, oxalic, propionic, pyruvic, succinic, syringic, tartaric, tetronic, valeric	Nutrient source Chemoattractant Nutrient acquisition
Fatty acids	Linoleic, linolenic, oleic, palmitic, stearic	Nutrient source Signaling molecule Antimicrobial
Phenolics	Benzoic, caffeic, cinnamic, p-coumaric, ferulic, hydroxybenzoic, p-piscidic, salicylic, syringic, vanillic	Nutrient source Chemoattractant Signaling molecule Microbial growth promoters
Growth factors and vitamins:	*p*-Amino benzoic acid, biotin, choline, *N*-methyl nicotinic acid, niacin, pantothenic, thiamine, riboflavin, pyridoxine, pantothenate	*Promoters of plant and microbial growth*
Others	*Nucleotides, flavonoids, alcohols, sterols, mucilages, terpenoids indole compounds, proteins, enzymes*	

Adapted from Badri and Vivanco (2009), Dennis et al. (2010), Haichar et al. (2014))

microorganisms are present in the medium (Canarini et al. 2019). It has been found that plants use root exudates as a chemoattractant and signaling molecules to promote colonization of beneficial microbes (Zhang et al. 2014; Feng et al. 2018). The legume-rhizobia interaction is one of the well-documented examples of root exudate mediated interaction between plants and microbes that showed high host specificity. Legumes synthesize and secrete various flavonoid compounds that induce nodule formation by *Rhizobium* and *Bradyrhizobium* species (Singh and Mukerji 2006). Increased production of amino acid and flavonoids were also observed when plants were exposed to certain microorganisms indicating their role as regulatory linkage between plant and microbial symbiosis (Phillips et al. 2004; Rêgo et al. 2014), although it is still unknown to what extent they influence each other.

11.3.2 *Influence of Root Exudates on Biodegradation*

Knowledge on how biodegradation is enhanced by the root exudates is still incomprehensive. However, the potential of root exudates to enhance the microbial degradation has been noted by several researchers (Miya and Firestone 2001; Yi and Crowley 2007; Zhu et al. 2009; Zhang et al. 2014; Yuan et al. 2015; Jia et al. 2016; Ely and Smets 2017; Yang 2018). It has been found that the contaminant concentration is negatively correlated with the concentration of root exudates (Sun et al. 2015) and the spatial distance from the plant root (Corgié et al. 2004; Rohrbacher and St-Arnaud 2016).

There are some proposed mechanisms on how root exudates may enhance the degradation of organic contaminants (Fig. 11.3). First of all, the root exudates serve as a viable substrate for rhizosphere microorganisms which results in increased microbial biomass, diversity, and activities (Miya and Firestone 2001; Técher et al. 2011; Guo et al. 2017b; Yang et al. 2021). For example, Miya and Firestone (2001) investigated the influence of slender oat (*Avena barbata*) root exudates and debris on phenanthrene degradation. They showed that plant root exudates and debris amended soil were occupied by larger phenanthrene degrading population than in unamended soil, leading to enhance phenanthrene biodegradation. Yang et al. (2021) also showed that cowpea and mung bean root exudates amendment lead to increased dehydrogenase and catechol 2,3 dioxygenase (C23O) activities with enhanced PAHs degradation. The root exudates of *Miscanthus* x *giganteus* and *Festuca arundinacea* L. promoted the growth of bacterial consortia and biodegradation of PAHs (Técher et al. 2011; Liu et al. 2015).

Secondly, the root exudates are composed of bioactive compounds that may increase the bioavailability of organic contaminants through contaminant desorption (Rohrbacher and St-Arnaud 2016). This phenomenon has been observed in root

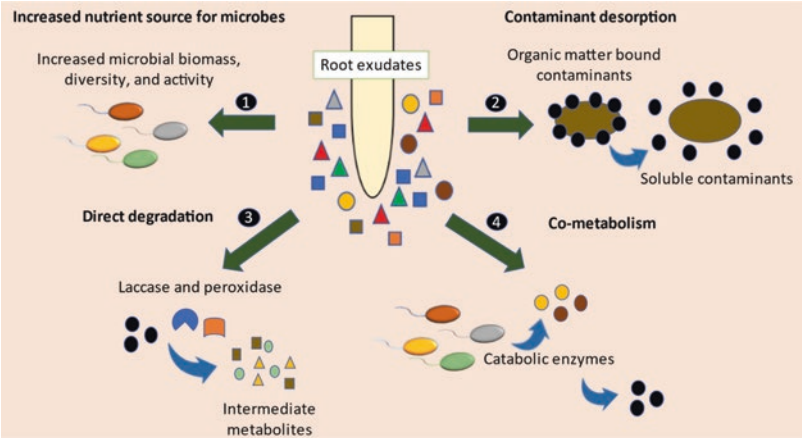


Fig. 11.3 Proposed mechanism of root exudates for enhancing degradation of organic contaminants

exudates of various plant species including celery, cordgrass, cowpea, mung bean, porcupine sedge, and purple prairie (Gao et al. 2010; LeFevre et al. 2013; Jia et al. 2016; Yang et al. 2021). Various studies showed that LMWOCs, particularly the organic acids, play a major role in portioning behavior of hydrophobic contaminants (Gao et al. 2010; LeFevre et al. 2013; Jia et al. 2016; Yang et al. 2021). The fate of organic contaminants depends on their solubility in soil water which is often indicated by the soil/water partitioning coefficient (K_d). In general, the contaminant mobility or solubility is inversely proportional to the K_d value. The higher the K_d value, the lower the solubility of contaminants. Most organic contaminants are generally non-polar molecules and, therefore, they do not form bonds with polar water molecules. This leads to the segregation of hydrophobic contaminants onto non-polar organic matters in the soil. Root exudates, especially the LMWOCs, can decrease the polarity of soil water. This inhibits contaminant sorption onto organic matters and enhances the desorption rate of the contaminants, thereby increasing the bioavailability of contaminants and subsequent biodegradation by soil microorganisms.

Thirdly, plants may secrete extracellular enzymes such as laccases and peroxidases, which directly degrade organic contaminants (Martin et al. 2014; Rohrbacher and St-Arnaud 2016; Dubrovskaya et al. 2017). For example, Dubrovskaya et al. (2017) demonstrated that peroxidases purified from alfalfa and sorghum root exudates oxidized PAHs in liquid media indicating the role of these plant extracellular enzymes in rhizosphere degradation of PAHs. However, direct degradation of organic contaminants by plant enzymes covers only minor portions of overall degradation and is therefore often regarded as negligible.

Finally, plant secondary metabolites may stimulate microbial metabolism through co-metabolic pathways, which is often regarded as the ‘secondary compound hypothesis’ (Donnelly et al. 1994; Singer et al. 2003; Musilova et al. 2016). The primarily biosynthetic pathway for aromatic compounds of a plant is known as the shikimate pathway. The shikimic acid (shikimate) serves as a precursor for benzoic and cinnamic acids. Derivatives of benzoic and cinnamic acids resemble the intermediate metabolites of aromatic contaminants and their structural analogy may induce upregulation of catabolic genes of microorganisms (Da Silva et al. 2006; Phillips et al. 2012; Pagé et al. 2015). The study by Pagé et al. (2015) showed that the addition of Salix purpurea root exudates upregulated the genes responsible for hydrocarbon degradation such as *alkB*, *npah*, *mmoX*, and *ppah*. In some cases, the plant metabolites may serve as an inducer of catabolic enzymes without being used as a carbon source (Gilbert and Crowley 1997; Toussaint et al. 2012; Musilova et al. 2016). For instance, Gilbert and Crowley (1997) reported that *Arthrobacter* sp. strain B1B was only able to degrade PCB when they were exposed to plant-derived terpenoids present in spearmint. Furthermore, flavonoids identified from *Arabidopsis* root exudates induced biphenyl degrading pathway of *Rhodococcus erythropolis* U23A, although the bacteria were not able to use flavonoids as a sole carbon source (Toussaint et al. 2012).

Plants continuously secrete myriads of chemicals into the soil and provide the optimal condition for microorganisms to degrade organic contaminants. Although phytostimulatory effects of root exudates were demonstrated by several researchers, very few studies attempted to link the chemical constituents to the observed effects. This limited the replicability of the results that have been observed previously, as root exudation is highly dependent on soil physicochemical properties as well as biological parameters. Therefore, it is clear that more research on root exudate composition and their potential effect on microbial degradation is required to further understand the plant-microbial interaction.

11.4 Plant Growth Promoting Microbes-Assisted Rhizoremediation

Plants are photoautotrophic organisms that have not evolved to metabolize toxic organic contaminants as their source of energy. Although some research demonstrated a plant's ability to secrete enzymes that may contribute to the transformation of organic contaminants, often their direct removal of contaminants is not regarded as insignificant (Rohrbacher and St-Arnaud 2016; Dubrovskaya et al. 2017). In the highly contaminated areas, where the concentration of organic contaminants is at a phytotoxic level, plants growth is often impaired leading to decreased phytoremediation efficiency in the contaminated soil (Ma et al. 2014; Wang et al. 2017).

Soil is generally defined as a nutrient poor medium where plants always thrive for nutrients. To obviate this problem, excessive use of chemical fertilizers and, to less extent, organic fertilizers are used to increase soil nitrogen and phosphorus content. This not only increases the cost of phytoremediation management but also increases the overall carbon footprint to the technology which is unfavorable. One potential method to resolve that has attracted attention from many researchers is the use of biological agents that are labeled as 'biofertilizers'.

Plants have developed a mutualistic symbiosis with soil microbiomes. Plant-associated microbiomes can be localized in three different ecosystems, the rhizosphere (nearby the roots), phyllosphere (on the leaves), and the endosphere (inside the plants) (Fig. 11.4). Some of those microbes have been shown to promote plant growth and improve tolerance to toxic contaminants (Lavania et al. 2006; Hou et al. 2015; Xun et al. 2015), which are referred to as plant growth promoting microorganisms (PGPM) or biofertilizers. Biofertilizers have been largely applied in agricultural fields to facilitate crop yield and to biocontrol pathogenic infection (Backer et al. 2018). Rhizospheric PGPM has been shown to solubilize nutrients in the soil for their host plants to uptake. Furthermore, PGPM has been shown to prevent pathogenic infection and reduce oxidative stress through hormonal and enzymatic regulation (Ahammed et al. 2013; Wang et al. 2017; Rezvani Borujeni et al. 2018). The benefits that PGPMs confer to their associated plants could be categorized into three main features: (i) increased plant growth, (ii) reduced stress, and (iii) enhanced soil fertility. In general, PGPMs that most effectively promote plant growth generally colonize in the plant rhizosphere or root endosphere (Martin et al. 2014; Lenoir

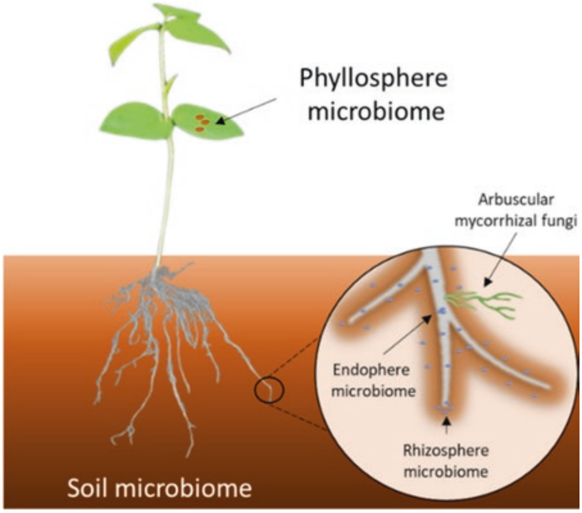


Fig. 11.4 The plant associated microbiome

et al. 2016; Musilova et al. 2016; Canarini et al. 2019). However, the use of PGPMs in the field of bioremediation is relatively new. Once microbes colonize in/onto plants, PGPMs tend to enhance remediation efficiencies of contaminated soil, which attracted many researchers to explore more to this synergistic interaction (Hou et al. 2015; Urana et al. 2019).

11.4.1 Arbuscular Mycorrhizal *Fungi (AMF)-Assisted Phytoremediation*

Arbuscular mycorrhizal fungi (AMF) are soil fungi that form a mutualistic symbiosis with the majority of higher plants. Soil contamination with hydrophobic organic contaminants generally leads to a reduction in water availability and root gas exchange to the plants. The prolonged exposure of plant roots to pollutants such as PAHs, hydrocarbons, and PCBs can lead to the accumulation of reactive oxygen species that cause injuries in root cells (Debiane et al. 2008; Xia et al. 2009; Ahammed et al. 2013). It has been shown that the colonization of AMF improves plant growth and health by alleviating oxidative stress by enhancing antioxidative activities (Xia et al. 2009; Ahammed et al. 2013). Furthermore, the AMF creates a mycelial network that acts as an extended root system allowing direct uptake and transfer of water and nutrients (Bolan 1991).

Some studies have demonstrated that phenolic compounds enhance the degradation of PAHs and other aromatic contaminants by soil microorganisms (Toyama et al. 2011; Liu et al. 2015; Musilova et al. 2016; Ely and Smets 2017; Yang et al. 2021). Secretion of these secondary metabolites may alter the biodegradation process by rhizosphere microorganisms through altering microbial diversity that prefers mycorrhizal exudates (Musilova et al. 2016). The mycorrhizal establishment on the host plant has been reported to enhance secretion of phenolics and flavonoids which may activate genes associated with contaminant degradation which may contribute to the overall biodegradation process (Lenoir et al. 2016). More particularly, plant phenolics have been shown to promote dioxygenase activities in indigenous microbial communities (Fletcher and Hegde 1995; Lee et al. 2008; Musilova et al. 2016). Other studies also reported that AMF could increase the soil dehydrogenase, peroxidase, catalase, and polyphenol oxidase which are catalytic oxidoreductase that is involved in the degradation of aromatic compounds such as PCBs and PAHs (Criquet et al. 2000; Yu et al. 2011; Lenoir et al. 2016).

11.4.2 Plant Growth-Promoting Bacteria (PGPB)-Assisted Phytoremediation

Plant growth-promoting bacteria (PGPB) are free living soil microbes that have abilities to promote plant growth in both direct and indirect means. The direct encouragement of plant health and growth by PGPBs can be achieved by facilitating nutrient uptake, a characteristic that is also referred as a biofertilizer. Other PGPBs can biocontrol pathogenic infection through competitive means, therefore indirectly improving plant growth and health (Glick 2012). A diverse bacterial group has been reported to have a wide spectrum of plant promoting abilities which includes *Acetobacter*, *Acinetobacter*, *Arthrobacter*, *Azospirillum*, *Azotobacter*, *Bacillus*, *Burkholderia*, *Caulobacter*, *Chromobacterium*, *Enterobacter*, *Erwinia*, *Flavobacterium,* *Herbaspirillum*, *Klebsiella*, *Micrococcus*, *Paenibacillus*, *Rhizobium*, *Pseudomonas*, *Serratia*, *Stenotrophomonas*, *Streptomyces*, *Variovorax*, and *Xanthomonas* species (Glick 2012; Alotaibi et al. 2021).

One of the most well-established groups of PGPBs is nitrogen-fixing bacteria. Nitrogen-fixing bacteria such as *Rhizobium* and *Bradyrhizobium* transform atmospheric nitrogen to viable forms balancing the C/N ratio of soil contaminated with organic contaminants (Radwan et al. 2007). Increased nitrogen source provides nutritional benefit to the host plants as well as other rhizosphere microorganisms, increasing their population and activities which encourage biodegradation of contaminants (Onwurah and Nwuke 2004; Delamuta et al. 2015). A study by Onwurah and Nwuke (2004) showed that N_2-fixing communities contribute to bioremediation of petroleum hydrocarbons by means of co-metabolic pathways and by increasing accessible nitrogen. Other PGPBs can solubilize inorganic phosphates by secretion of microbial metabolites (low molecular weight organic acids) and synthesis of different phosphatases (Glick 2012; Alori et al. 2017). Though the amount of phosphorus in the soil is generally known to be high (400–1200 mg kg^{-1}), most of these phosphorous are insoluble and therefore unavailable to the plants. Bacterial phosphatases hydrolyze these insoluble phosphoric esters to soluble forms, allowing plants to readily use them (Rodŕiguez and Fraga 1999). Some rhizosphere bacteria produce siderophores that play a critical role in plant iron uptake in iron deficient soil. Microbial siderophores are low molecular weight iron chelating agents that can bind to insoluble ferric ion (Fe^{+3}) forming Fe^{+3} – siderophore complex that can be readily uptake by the host plants. Siderophores not only promote iron uptake by plants but also function as a biocontrol agent for soil-borne pathogens by depriving iron available to certain rhizosphere pathogenic bacteria and fungi, hence lowering the chances of plant diseases.

Apart from enhancing nutrient availability, PGPBs can promote the growth and development of the associated plants by producing phytohormones such as indole-3-acetic acid (IAA), cytokinins, and gibberellins which influence plant hormonal regulation and promote cell division and cell enlargement (Hrynkiewicz and Baum 2012). In the contaminated soil, plants are continuously exposed to toxic pollutants that escalate the oxidative stress in the plants limiting plant growth and development (Debiane et al. 2008; Ahammed et al. 2013; Wang et al. 2017). In response, plants regulate their hormones to decrease the negative effects caused by environmental contaminants. IAA is a well-known plant growth regulator that influences plant cell division, elongation, and differentiation. The bacterial IAA can simulate plant root growth and root exudation (Golubev et al. 2011), which mediates the rhizosphere effect. Besides, IAA has also been suggested to yield a protective effect against oxidative stress by stimulating heme- oxygenase-1 and 1-aminocyclopropane-1-carboxylate (ACC) deaminase synthesis (Lecube et al. 2014).

Ethylene is one of the simplest forms of plant hormone that affects plant growth. In the contaminated soil, large amount of ethylene is produced, as a stress response, to a level that can be growth inhibitory (Glick et al. 1998; Rezvani Borujeni et al. 2018). Some rhizospheric PGPBs synthesize ACC deaminase that converts ACC, a direct precursor of ethylene, to ammonia and α-ketobutyrate which can be readily assimilated. Inoculation of PGPBs with ACC deaminase activity can lead to enhance biodegradation of organic contaminants such as PAHs (Benson et al. 2017; Rezvani Borujeni et al. 2018). The bacterial ACC deaminase counteract stress induced by contaminant toxicity and enhance plant root growth that leads increased root-soil interface consequently accelerated degradation (Rohrbacher and St-Arnaud 2016; Pokethitiyook 2017; Rezvani Borujeni et al. 2018).

Recent studies showed that some rhizospheric and endophytic PGPBs are capable of degrading organic contaminants (Muratova et al. 2005; Child et al. 2007; Teng et al. 2011). These microbes not only encourage plant root growth and root exudation but also contribute to biodegradation of toxic contaminants. The bioaugmented phytoremediation therefore seems to be more promising technique for remediation of organic contaminants compared to single treatment methods (bioaugmentation and phytoremediation). However, the capacity of PGPB to colonize on the plant rhizosphere and/or plant endosphere in a hostile environment characterized by pollution toxicity and vigorous competition from indigenous bacteria is the greatest hurdle for effective application of PGPB in the remediation sector. The PGPB-assisted phytoremediation has been shown to be particularly successful in petroleum contaminated soil. Some examples of successful bioaugmented phytoremediation in petroleum contaminated soil are shown in Table 11.3.

Table 11.3 Some examples of successful PGPB-assisted phytoremediation in soil contaminated with petroleum hydrocarbons

Plant used	PGPB	Bacterial characteristics	Reference
Alfalfa (*M. sativa* L.)	*Rhizobium meliloti* strain ACCC17519	Hydrocarbon degrading PGPB	Teng et al. (2011)
Barley (*H. sativum* L.)	*Mycobacterium* sp. strain KMS	Hydrocarbon degrading PGPB	Child et al. (2007)
Barley (*H. sativum* L.)	*P. fluorescens, P. aureofaciens*	Hydrocarbon degrading PGPB	Anokhina et al. (2004)
Italian ryegrass (*L. multiflorum*)	*P. putida* PCL1444	Naphthalene degrading PGPB	Kuiper et al. (2001)
Maize (Z. mays L.)	*Pseudomonas* sp. UG14Lr	Hydrocarbon degrading PGPB	Chouychai et al. (2012)
Maize (Z. mays L.)	*P. putida MUB1*	Hydrocarbon degrading PGPB	Chouychai et al. (2009)
Rice (*Oryza sativa* L.)	*Acinetobacteria* sp.	Hydrocarbon degrading PGPB	Li et al. (2008)
Ryegrass *(L. multiflorum L.)*	*Mycobacterium gilvum*	PAH degrading PGPB	Guo et al. (2018)
Ryegrass (*L. multiflorum*)	*Acinetobacter* sp.	PAH degrading PGPB	Yu et al. (2011)
Sorghum (*S. bicolor*)	*Sinorhizobium meliloti*	PAH degrader, IAA producer	Golubev et al. (2011)
Tall fescue (*F. arundinacea*)	*Pseudomonas sp. SB*	IAA, ACC deaminase, and siderophore producer	Liu et al. (2013)
Tall fescue (*F. arundinacea*)	*Klebsiella* sp. D5A and *Pseudomonas* sp. SB	IAA, ACC deaminase, and siderophore producer	Hou et al. (2015)
Wheat (*Triticum* spp.)	*Pseudomonas* sp.GF3	Phenanthrene degrading PGPB	Sheng and Gong (2006)
Wheat (*Triticum* spp.)	*Azospirillum brasilense SR80*	Hydrocarbon degrader, IAA producer	Muratova et al. (2005)
Winter rye (*Secale cereale L.*), alfalfa (*M. sativa L.*)	*Azospirillum brasilense* SR80	Hydrocarbon degrader, IAA producer	Muratova et al. (2010)

11.5 Future Perspectives

Rhizoremediation is a cost-effective and environmentally friendly technology for soil contaminated with organic contaminants. To implement successful rhizoremediation plan in the contaminated area, selection of plants that can well adapt to environmental contaminants are required. Currently, majority of research focus on AMF or PGPB-assisted phytoremediation, which could be enhanced selecting biosurfactant producing bacteria or consortia of microbes to increase bioavailability of the contaminants to promote dissipation of organic contaminants. Here, we suggested some topics that need to be further investigated to optimize and enhance the rhizoremediation technology.

1. Applying metagenomic-based techniques to better understand the plant microbial symbiosis during rhizoremediation of organic contaminants.
2. Finding novel consortia consisting PGPM, hydrocarbon degrading bacteria, and biosurfactant producing microorganisms to promote rhizoremediation of contaminated soil.
3. To investigate PGPM mediated shifts in root exudation of the host plants and their effect on biodegradation process.
4. Uncovering specific constituents of plant metabolites that lead to enhanced removal of organic contaminants.

References

Adam G, Duncan H (2003) The effect of diesel fuel on common Vetch (Vicia sativa L.) plants. Environ Geochem Health 25(1):123–130

Ahammed GJ, Ruan Y-P, Zhou J, Xia X-J, Shi K, Zhou Y-H et al (2013) Brassinosteroid alleviates polychlorinated biphenyls-induced oxidative stress by enhancing antioxidant enzymes activity in tomato. Chemosphere 90(11):2645–2653

Alori ET, Glick BR, Babalola OO (2017) Microbial phosphorus solubilization and its potential for use in sustainable agriculture, Front Microbiol 8(971)

Alotaibi F, Hijri M, St-Arnaud M (2021) Overview of approaches to improve rhizoremediation of petroleum hydrocarbon-contaminated soils. Appl Microbiol 1(2):329–351

Anokhina TO, Kochetkov VV, Zelenkova NF, Balakshina VV, Boronin AM (2004) Biodegradation of phenanthrene by pseudomonas bacteria bearing rhizospheric plasmids in model plant–microbial associations. Appl Biochem Microbiol 40(6):568–572

Backer R, Rokem JS, Ilangumaran G, Lamont J, Praslickova D, Ricci E et al (2018) Plant growth-promoting rhizobacteria: context, mechanisms of action, and roadmap to commercialization of biostimulants for sustainable agriculture. Front Plant Sci 9(1473)

Badri DV, Vivanco JM (2009) Regulation and function of root exudates. Plant Cell Environ 32(6):666–681

Balba MT, Al-Awadhi N, Al-Daher R (1998) Bioremediation of oil-contaminated soil: microbiological methods for feasibility assessment and field evaluation. J Microbiol Methods 32(2):155–164

Benson A, Ram G, John A, Melvin JM (2017) Inoculation of 1-aminocyclopropane-1-carboxylate deaminase–producing bacteria along with biosurfactant application enhances the phytoremediation efficiency of Medicago sativa in hydrocarbon-contaminated soils. Biorem J 21(1):20–29

Berg G, Smalla K (2009) Plant species and soil type cooperatively shape the structure and function of microbial communities in the rhizosphere. FEMS Microbiol Ecol 68(1):1–13

Bolan NS (1991) A critical review on the role of mycorrhizal fungi in the uptake of phosphorus by plants. Plant Soil 134(2):189–207

Bourceret A, Leyval C, de Fouquet C, Cébron A (2015) Mapping the centimeter-scale spatial variability of PAHs and microbial populations in the rhizosphere of two plants. PLoS One 10(11):e0142851

Bourceret A, Leyval C, Thomas F, Cébron A (2017) Rhizosphere effect is stronger than PAH concentration on shaping spatial bacterial assemblages along centimetre-scale depth gradients. Can J Microbiol 63(11):881–893

Burken JG, Schnoor JL (1998) Predictive relationships for uptake of organic contaminants by hybrid poplar trees. Environ Sci Technol 32(21):3379–3385

Canarini A, Kaiser C, Merchant A, Richter A, Wanek W (2019) Root Exudation of primary metabolites: Mechanisms and their roles in plant responses to environmental stimuli. Front Plant Sci 10(157)

Cébron A, Louvel B, Faure P, France-Lanord C, Chen Y, Murrell JC et al (2011) Root exudates modify bacterial diversity of phenanthrene degraders in PAH-polluted soil but not phenanthrene degradation rates. Environ Microbiol 13(3):722–736

Chaparro JM, Badri DV, Vivanco JM (2014) Rhizosphere microbiome assemblage is affected by plant development. ISME J 8(4):790–803

Child R, Miller CD, Liang Y, Narasimham G, Chatterton J, Harrison P et al (2007) Polycyclic aromatic hydrocarbon-degrading Mycobacterium isolates: their association with plant roots. Appl Microbiol Biotechnol 75(3):655–663

Chiou CT, McGroddy SE, Kile DE (1998) Partition characteristics of polycyclic aromatic hydrocarbons on soils and sediments. Environ Sci Technol 32(2):264–269

Chouychai W, Thongkukiatkul A, Upatham S, Lee H, Pokethitiyook P, Kruatrachue M (2007) Phytotoxicity assay of crop plants to phenanthrene and pyrene contaminants in acidic soil. Environ Toxicol 22:597–604

Chouychai W, Thongkukiatkul A, Upatham S, Lee H, Pokethitiyook P, Kruatrachue M (2009) Plant-enhanced phenanthrene and pyrene biodegradation in acidic soil. J Environ Biol 30(1):139–144

Chouychai W, Thongkukiatkul A, Upatham S, Pokethitiyook P, Kruatrachue M, Lee H (2012) Effect of corn plant on survival and phenanthrene degradation capacity of Pseudomonas sp. UG14Lr in two soils. Int J Phytoremediation 14(6):585–595

Chowdhury IF, Doran GS, Stodart BJ, Chen C, Wu H (2020) Trifluralin and atrazine sensitivity to selected cereal and legume crops. Agronomy 10(4)

Corgié SC, Beguiristain T, Leyval C (2004) Spatial distribution of bacterial communities and phenanthrene degradation in the rhizosphere of *Lolium perenne* L. Appl Environ Microbiol 70(6):3552–3557

Criquet S, Joner E, Leglize P, Leyval C (2000) Anthracene and mycorrhiza affect the activity of oxidoreductases in the roots and the rhizosphere of lucerne (*Medicago sativa* L.). Biotechnol Lett 22(21):1733–1737

Da Silva MLB, Kamath R, Alvarez PJJ (2006) Effect of simulated rhizodeposition on the relative abundance of polynuclear aromatic hydrocarbon catabolic genes in a contaminated soil. Environ Toxicol Chem 25(2):386–391

Datta R, Das P, Smith S, Punamiya P, Ramanathan DM, Reddy R et al (2013) Phytoremediation potential of vetiver grass *Chrysopogon zizanioides* (L.) for tetracycline. Int J Phytoremediation 15(4):343–351

Debiane D, Garçon G, Verdin A, Fontaine J, Durand R, Grandmougin-Ferjani A et al (2008) In vitro evaluation of the oxidative stress and genotoxic potentials of anthracene on mycorrhizal chicory roots. Environ Exp Bot 64(2):120–127

Delamuta JRM, Ribeiro RA, Ormeño-Orrillo E, Parma MM, Melo IS, Martínez-Romero E et al (2015) Bradyrhizobium tropiciagri sp. nov. and Bradyrhizobium embrapense sp. nov., nitrogen-fixing symbionts of tropical forage legumes. Int J Syst Evol Microbiol 65(Pt_12):4424–4433

Dennis PG, Miller AJ, Hirsch PR (2010) Are root exudates more important than other sources of rhizodeposits in structuring rhizosphere bacterial communities? FEMS Microbiol Ecol 72(3):313–327

Donnelly PK, Hegde RS, Fletcher JS (1994) Growth of PCB-degrading bacteria on compounds from photosynthetic plants. Chemosphere 28(5):981–988

Dubrovskaya E, Pozdnyakova N, Golubev S, Muratova A, Grinev V, Bondarenkova A et al (2017) Peroxidases from root exudates of Medicago sativa and Sorghum bicolor: catalytic properties and involvement in PAH degradation. Chemosphere 169:224–232

Ely CS, Smets BF (2017) Bacteria from wheat and cucurbit plant roots metabolize PAHs and aromatic root exudates: implications for rhizodegradation. Int J Phytoremediation 19(10):877–883

Feng H, Zhang N, Du W, Zhang H, Liu Y, Fu R et al (2018) Identification of chemotaxis compounds in root exudates and their sensing chemoreceptors in plant-growth-promoting rhizobacteria bacillus amyloliquefaciens SQR9. Mol Plant-Microbe Interact 31(10):995–1005

Fletcher JS, Hegde RS (1995) Release of phenols by perennial plant roots and their potential importance in bioremediation. Chemosphere 31(4):3009–3016

Gao Y, Zhu L (2004) Plant uptake, accumulation and translocation of phenanthrene and pyrene in soils. Chemosphere 55(9):1169–1178

Gao Y, Ren L, Ling W, Kang F, Zhu X, Sun B (2010) Effects of low-molecular-weight organic acids on sorption–desorption of phenanthrene in soils. Soil Sci Soc Am J 74(1):51–59

Gilbert ES, Crowley DE (1997) Plant compounds that induce polychlorinated biphenyl biodegradation by Arthrobacter sp. strain B1B. Appl Environ Microbiol 63(5):1933–1938

Glick BR (2012) Plant growth-promoting bacteria: mechanisms and applications. Scientifica 2012:963401

Glick BR, Penrose DM, Li J (1998) A model for the lowering of plant ethylene concentrations by plant growth-promoting bacteria. J Theor Biol 190(1):63–68

Golubev SN, Muratova AY, Wittenmayer L, Bondarenkova AD, Hirche F, Matora LY et al (2011) Rhizosphere indole-3-acetic acid as a mediator in the *Sorghum bicolor*–phenanthrene–Sinorhizobium meliloti interactions. Plant Physiol Biochem 49(6):600–608

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

Guo M, Gong Z, Miao R, Rookes J, Cahill D, Zhuang J (2017a) Microbial mechanisms controlling the rhizosphere effect of ryegrass on degradation of polycyclic aromatic hydrocarbons in an aged-contaminated agricultural soil. Soil Biol Biochem 113:130–142

Guo M, Gong Z, Miao R, Su D, Li X, Jia C et al (2017b) The influence of root exudates of maize and soybean on polycyclic aromatic hydrocarbons degradation and soil bacterial community structure. Ecol Eng 99:22–30

Guo M, Gong Z, Miao R, Jia C, Rookes J, Cahill D et al (2018) Enhanced polycyclic aromatic hydrocarbons degradation in rhizosphere soil planted with tall fescue: bacterial community and functional gene expression mechanisms. Chemosphere 212:15–23

Hafner WD, Hites RA (2003) Potential sources of pesticides, PCBs, and PAHs to the atmosphere of the great lakes. Environ Sci Technol 37(17):3764–3773

Haichar FZ, Santaella C, Heulin T, Achouak W (2014) Root exudates mediated interactions belowground. Soil Biol Biochem 77:69–80

Han G, Cui BX, Zhang XX, Li KR (2016) The effects of petroleum-contaminated soil on photosynthesis of Amorpha fruticosa seedlings. Int J Environ Sci Technol 13(10):2383–2392

Hou J, Liu W, Wang B, Wang Q, Luo Y, Franks AE (2015) PGPR enhanced phytoremediation of petroleum contaminated soil and rhizosphere microbial community response. Chemosphere 138:592–598

Hrynkiewicz K, Baum C (2012) The potential of rhizosphere microorganisms to promote the plant growth in disturbed soils. In: Malik A, Grohmann E (eds) Environmental protection strategies for sustainable development. Springer Netherlands, Dordrecht, pp 35–64

Jia H, Lu H, Dai M, Hong H, Liu J, Yan C (2016) Effect of root exudates on sorption, desorption, and transport of phenanthrene in mangrove sediments. Mar Pollut Bull 109(1):171–177

Kafilzadeh F, Khosrobak A, Jamali H (2016) Isolation and identification of phenanthrene degrading bacteria from the soil around oil company of Andimeshk and investigation of their growth kinetics. Polycycl Aromat Compd 36(1):58–71

Kuiper I, Bloemberg GV, Lugtenberg BJJ (2001) Selection of a plant-bacterium pair as a novel tool for rhizostimulation of polycyclic aromatic hydrocarbon-degrading bacteria. Mol Plant-Microbe Interact 14(10):1197–1205

Lavania M, Chauhan PS, Chauhan SVS, Singh HB, Nautiyal CS (2006) Induction of plant defense enzymes and phenolics by treatment with plant growth–promoting rhizobacteria *Serratia marcescens* NBRI1213. Curr Microbiol 52(5):363–368

Lecube ML, Noriega GO, Santa Cruz DM, Tomaro ML, Batlle A, Balestrasse KB (2014) Indole acetic acid is responsible for protection against oxidative stress caused by drought in soybean plants: the role of heme oxygenase induction. Redox Rep 19(6):242–250

Lee S-H, Lee W-S, Lee C-H, Kim J-G (2008) Degradation of phenanthrene and pyrene in rhizosphere of grasses and legumes. J Hazard Mater 153(1):892–898

LeFevre GH, Hozalski RM, Novak PJ (2013) Root exudate enhanced contaminant desorption: an abiotic contribution to the rhizosphere effect. Environ Sci Technol 47(20):11545–11553

Lenoir I, Lounes-Hadj Sahraoui A, Fontaine J (2016) Arbuscular mycorrhizal fungal-assisted phytoremediation of soil contaminated with persistent organic pollutants: a review. Eur J Soil Sci 67(5):624–640

Li JH, Gao Y, Wu SC, Cheung KC, Wang XR, Wong MH (2008) Physiological and biochemical responses of rice (Oryza sativa L.) to phenanthrene and pyrene. Int J Phytoremediation 10(2):106–118

Limmer M, Burken J (2016) Phytovolatilization of organic contaminants. Environ Sci Technol 50(13):6632–6643

Liste H-H, Felgentreu D (2006) Crop growth, culturable bacteria, and degradation of petrol hydrocarbons (PHCs) in a long-term contaminated field soil. Appl Soil Ecol 31(1):43–52

Liu W, Sun J, Ding L, Luo Y, Chen M, Tang C (2013) Rhizobacteria (Pseudomonas sp. SB) assist phytoremediation of oily-sludge-contaminated soil by tall fescue (Testuca arundinacea L.). Plant Soil 371(1):533–542

Liu W, Hou J, Wang Q, Yang H, Luo Y, Christie P (2015) Collection and analysis of root exudates of Festuca arundinacea L. and their role in facilitating the phytoremediation of petroleum-contaminated soil. Plant Soil 389(1):109–119

Lu C, Hong Y, Liu J, Gao Y, Ma Z, Yang B et al (2019) A PAH-degrading bacterial community enriched with contaminated agricultural soil and its utility for microbial bioremediation. Environ Pollut 251:773–782

Ma Y, Xie Z, Yang H, Möller A, Halsall C, Cai M et al (2013) Deposition of polycyclic aromatic hydrocarbons in the North Pacific and the Arctic. J Geophys Res Atmos 118(11):5822–5829

Ma J, Shen J, Liu Q, Fang F, Cai H, Guo C (2014) Risk assessment of petroleum-contaminated soil using soil enzyme activities and genotoxicity to Vicia faba. Ecotoxicology 23(4):665–673

Martin BC, George SJ, Price CA, Ryan MH, Tibbett M (2014) The role of root exuded low molecular weight organic anions in facilitating petroleum hydrocarbon degradation: current knowledge and future directions. Sci Total Environ 472:642–653

Miya RK, Firestone MK (2001) Enhanced phenanthrene biodegradation in soil by slender oat root exudates and root debris. J Environ Qual 30(6):1911–1918

Muratova AY, Turkovskaya OV, Antonyuk LP, Makarov OE, Pozdnyakova LI, Ignatov VV (2005) Oil-oxidizing potential of associative rhizobacteria of the genus Azospirillum. Microbiology 74(2):210–215

Muratova A, Pozdnyakova N, Golubev S, Wittenmayer L, Makarov O, Merbach W et al (2009) Oxidoreductase activity of sorghum root exudates in a phenanthrene-contaminated environment. Chemosphere 74(8):1031–1036

Muratova AY, Bondarenkova AD, Panchenko LV, Turkovskaya OV (2010) Use of integrated phytoremediation for cleaning-up of oil-sludge-contaminated soil. Appl Biochem Microbiol 46(8):789–794

Murray EW, Greenberg BM, Cryer K, Poltorak B, McKeown J, Spies J et al (2019) Kinetics of phytoremediation of petroleum hydrocarbon contaminated soil. Int J Phytoremediation 21(1):27–33

Musilova L, Ridl J, Polivkova M, Macek T, Uhlik O (2016) Effects of secondary plant metabolites on microbial populations: changes in community structure and metabolic activity in contaminated environments. Int J Mol Sci 17(8)

Onwurah IN, Nwuke C (2004) Enhanced bioremediation of crude oil-contaminated soil by a Pseudomonas species and mutually associated adapted Azotobacter vinelandii. J Chem Technol Biotechnol 79(5):491–498

Pagé AP, Yergeau É, Greer CW (2015) *Salix purpurea* stimulates the expression of specific bacterial xenobiotic degradation genes in a soil contaminated with hydrocarbons. PloS one 10(7):e0132062-e

Palmroth MRT, Pichtel J, Puhakka JA (2002) Phytoremediation of subarctic soil contaminated with diesel fuel. Bioresour Technol 84(3):221–228

Phillips DA, Fox TC, King MD, Bhuvaneswari TV, Teuber LR (2004) Microbial products trigger amino acid exudation from plant roots. Plant Physiol 136(1):2887–2894

Phillips LA, Greer CW, Farrell RE, Germida JJ (2012) Plant root exudates impact the hydrocarbon degradation potential of a weathered-hydrocarbon contaminated soil. Appl Soil Ecol 52:56–64

Pokethitiyook P (2017) Phytoremediation of petroleum-contaminated soil in association with soil bacteria. In: Ansari AA, Gill SS, Gill R, Lanza G, Newman L (eds) Phytoremediation: management of environmental contaminants, vol 5. Springer International Publishing, Cham, pp 77–99

Qu C, Albanese S, Lima A, Hope D, Pond P, Fortelli A et al (2019) The occurrence of OCPs, PCBs, and PAHs in the soil, air, and bulk deposition of the Naples metropolitan area, southern Italy: implications for sources and environmental processes. Environ Int 124:89–97

Radwan SS, Dashti N, El-Nemr I, Khanafer M (2007) Hydrocarbon utilization by nodule bacteria and plant growth-promoting rhizobacteria. Int J Phytoremediation 9(6):475–486

Rêgo MCF, Ilkiu-Borges F, MCCD F, Gonçalves LA, GBD S (2014) Morphoanatomical and biochemical changes in the roots of rice plants Induced by plant growth-promoting microorganisms. J Botany 2014:818797

Reichenauer TG, Germida JJ (2008) Phytoremediation of organic contaminants in soil and groundwater. ChemSusChem 1(8–9):708–717

Rezvani Borujeni S, Khavazi K, Asgharzadeh A, Rezvani BI (2018) Use of bacterial acc deaminase to increase oil (especially poly aromatic hydrocarbons) phytoremediation efficiency for maize (zea mays) seedlings. Int J Phytoremediation 20(5):476–482

Rodríguez H, Fraga R (1999) Phosphate solubilizing bacteria and their role in plant growth promotion. Biotechnol Adv 17(4):319–339

Rohrbacher F, St-Arnaud M (2016) Root exudation: the ecological driver of hydrocarbon rhizoremediation. Agronomy 6(1):19

Shah V, Daverey A (2020) Phytoremediation: a multidisciplinary approach to clean up heavy metal contaminated soil. Environ Technol Innov 18:100774

Sheng XF, Gong JX (2006) Increased degradation of phenanthrene in soil by Pseudomonas sp. GF3 in the presence of wheat. Soil Biol Biochem 38(9):2587–2592

Singer AC, Crowley DE, Thompson IP (2003) Secondary plant metabolites in phytoremediation and biotransformation. Trends Biotechnol 21(3):123–130

Singh G, Mukerji KG (2006) Root exudates as determinant of rhizospheric microbial biodiversity. In: Mukerji KG, Manoharachary C, Singh J (eds) Microbial activity in the rhizoshere. Springer/Berlin/Heidelberg, Berlin/Heidelberg, pp 39–53

Sowada J, Schmalenberger A, Ebner I, Luch A, Tralau T (2014) Degradation of benzo[a]pyrene by bacterial isolates from human skin. FEMS Microbiol Ecol 88(1):129–139

Sun R, Belcher RW, Liang J, Wang L, Thater B, Crowley DE et al (2015) Effects of cowpea (*Vigna unguiculata*) root mucilage on microbial community response and capacity for phenanthrene remediation. J Environ Sci 33:45–59

Técher D, Laval-Gilly P, Henry S, Bennasroune A, Formanek P, Martinez-Chois C et al (2011) Contribution of Miscanthus x giganteus root exudates to the biostimulation of PAH degradation: an in vitro study. Sci Total Environ 409(20):4489–4495

Teng Y, Shen Y, Luo Y, Sun X, Sun M, Fu D et al (2011) Influence of Rhizobium meliloti on phytoremediation of polycyclic aromatic hydrocarbons by alfalfa in an aged contaminated soil. J Hazard Mater 186(2):1271–1276

Toussaint J-P, Pham TTM, Barriault D, Sylvestre M (2012) Plant exudates promote PCB degradation by a rhodococcal rhizobacteria. Appl Microbiol Biotechnol 95(6):1589–1603

Toyama T, Furukawa T, Maeda N, Inoue D, Sei K, Mori K et al (2011) Accelerated biodegradation of pyrene and benzo[a]pyrene in the *Phragmites australis* rhizosphere by bacteria–root exudate interactions. Water Res 45(4):1629–1638

Urana R, Singh N, Sharma P (2019) Effects of PGPR on growth and photosynthetic pigment of *Trigonella foenum-graceum* and *Brassica juncea* in PAH-contaminated soil. SN Appl Sci 1(7):761

Vergani L, Mapelli F, Marasco R, Crotti E, Fusi M, Di Guardo A et al (2017) Bacteria associated to plants naturally selected in a historical PCB polluted soil show potential to sustain natural attenuation. Front Microbiol 8(1385)

Viguri J, Verde J, Irabien A (2002) Environmental assessment of polycyclic aromatic hydrocarbons (PAHs) in surface sediments of the Santander Bay. Northern Spain Chemosphere 48(2):157–165

Villacieros M, Whelan C, Mackova M, Molgaard J, Sánchez-Contreras M, Lloret J et al (2005) Polychlorinated biphenyl rhizoremediation by *Pseudomonas fluorescens* F113 derivatives, using a *Sinorhizobium meliloti* nod system to drive *bph* gene expression. Appl Environ Microbiol 71(5):2687–2694

Wang J, Zhang Z, Su Y, He W, He F, Song H (2008) Phytoremediation of petroleum polluted soil. Pet Sci 5(2):167–171

Wang X, Teng Y, Zhang N, Christie P, Li Z, Luo Y et al (2017) Rhizobial symbiosis alleviates polychlorinated biphenyls-induced systematic oxidative stress via brassinosteroids signaling in alfalfa. Sci Total Environ 592:68–77

Wu H, Sun B, Li J (2019) Polycyclic aromatic hydrocarbons in sediments/soils of the rapidly urbanized lower reaches of the river Chaohu, China. Int J Environ Res Public Health 16(13):2302

Xia X-J, Wang Y-J, Zhou Y-H, Tao Y, Mao W-H, Shi K et al (2009) Reactive oxygen species are involved in Brassinosteroid-induced stress tolerance in cucumber. Plant Physiol 150(2):801–814

Xu Y, Sun G-D, Jin J-H, Liu Y, Luo M, Zhong Z-P et al (2014) Successful bioremediation of an aged and heavily contaminated soil using a microbial/plant combination strategy. J Hazard Mater 264:430–438

Xun F, Xie B, Liu S, Guo C (2015) Effect of plant growth-promoting bacteria (PGPR) and arbuscular mycorrhizal fungi (AMF) inoculation on oats in saline-alkali soil contaminated by petroleum to enhance phytoremediation. Environ Sci Pollut Res 22(1):598–608

Yang KM (2018) The effect of root exudates on crude oil biodegrading bacteria [MSc dissertation]. Thailand: Mahidol University

Yang KM, Poolpak T, Pokethitiyook P, Kruatrachue M, Saengwilai P (2021) Responses of oil degrader enzyme activities, metabolism and degradation kinetics to bean root exudates during rhizoremediation of crude oil contaminated soil. Int J Phytoremediation:1–9

Ye Q, Puri RK, Kapila S, Yanders AF (1992) Studies on the transport and transformation of PCBs in plants. Chemosphere 25(7):1475–1479

Yi H, Crowley DE (2007) Biostimulation of PAH degradation with plants containing high concentrations of linoleic acid. Environ Sci Technol 41(12):4382–4388

Yu XZ, Wu SC, Wu FY, Wong MH (2011) Enhanced dissipation of PAHs from soil using mycorrhizal ryegrass and PAH-degrading bacteria. J Hazard Mater 186(2):1206–1217

Yuan J, Zhang N, Huang Q, Raza W, Li R, Vivanco JM et al (2015) Organic acids from root exudates of banana help root colonization of PGPR strain *Bacillus amyloliquefaciens* NJN-6. Sci Rep 5:13438

Zamani J, Hajabbasi MA, Mosaddeghi MR, Soleimani M, Shirvani M, Schulin R (2018) Experimentation on degradation o petroleum in contaminated soils in the root zone of maize (*Zea mays* L.) inoculated with Piriformospora Indica. Soil Sediment Contam Int J 27(1):13–30

Zhang N, Wang D, Liu Y, Li S, Shen Q, Zhang R (2014) Effects of different plant root exudates and their organic acid components on chemotaxis, biofilm formation and colonization by beneficial rhizosphere-associated bacterial strains. Plant Soil 374(1):689–700

Zhu Y, Zhang S, Huang H, Wen B (2009) Effects of maize root exudates and organic acids on the desorption of phenanthrene from soils. J Environ Sci 21(7):920–926

Chapter 12
Role of Microorganisms in the Remediation of Toxic Metals from Contaminated Soil

Amtul Bari Tabinda, Ajwa Tahir, Maryam Dogar, Abdullah Yasar, Rizwan Rasheed, and Mahnoor

Abstract Soil contamination with heavy metals is one of the major environmental concerns of time as it deteriorates human health and environmental quality to the worst. Toxic heavy metals become part of food chain and cause carcinogenic diseases in living organisms, i.e., plants, animals, and humans. Bioremediation is said to be a cost-effective and eco-friendly method of using living organism to eradicate impurities present in the soil. This chapter presents a brief overview of microbe-assisted remediation, the process in comparison to the physio-chemical remediation treatments, develops long-term benefits. Despite its multiple advantages, bioremediation does have some intrinsic limitations. It is observed that the limitations can be minimized by following proper management. This is why, the wide investigation efforts and hard work are required to discover and identify innovative microbial variety, their division, and functions in soil environments for metal sequestration, plant growth promotion, and reduction of metal toxicity. Thus, forming an optimal combination of soil + plant + microorganism via transgenic technology is a more advanced and emerging means for better future growth.

Keywords Microbe-assisted remediation · Soil microbes · Metals contamination · Soil reclamation · Soil pollution · Toxic heavy metals · Cost effective · Green technology

12.1 Introduction

Heavy metals are considered very toxic elements but their industrial and biological importance cannot be denied (Zhang et al. 2018). Soil pollution due to heavy metals is one of the major environmental concerns of time because it can deteriorate human

---

A. B. Tabinda (✉) · A. Tahir · M. Dogar · A. Yasar · R. Rasheed · Mahnoor
Sustainable Development Study Centre, GC University, Lahore, Pakistan
e-mail: amtulbaritabinda@gcu.edu.pk

L. Newman et al. (eds.), *Phytoremediation*, https://doi.org/10.1007/978-3-031-17988-4_12

condition and environmental quality to the worst (Afonso et al. 2020). Both natural and anthropogenic activities have significant part in release of heavy metals into the ecosystem. Owing to the massive use of heavy metals in advanced technology, the industrial revolution triggered the emission and release of heavy metals (Huang et al. 2017). Release of heavy metals because of mine production and manmade activities is huge as compared to the natural (Pierart et al. 2015). According to US Environmental Protection Agency, arsenic, chromium, cadmium, and lead are the top 20 hazardous substances (Chandrasekhar and Ray 2019). These toxic substances when accumulated in agricultural soil become part of food crops and vegetables and cause severe health issues to humans (Xiong et al. 2016). Accumulation of heavy metals in soil alters the pH, cation exchange capacity, electrical conductivity, and organic and inorganic ligands which ultimately deteriorate soil health. The residence time of Pb in soil has a period of 100–1000 years. Waste products also have a raised content of heavy metals in them, and these metals become more bioavailable in the environment (Tóth et al. 2016).

The sources of heavy metal ions are shown in Fig. 12.1.

As compared to the metal concentration in water, heavy metal accumulation in the soil exhibits a high level whereas in water concentration is being diluted and transported to other places (Baldantoni et al. 2016).

Accumulation of heavy metals in soil alters the pH, cation exchange capacity, electrical conductivity, and organic and inorganic ligands which ultimately deteriorate soil health. The residence time of Pb in soil has a period of 100–1000 years. Waste products also have a high content of heavy metals in them, and these metals become more bioavailable in the environment (Tóth et al. 2016). Heavy metals' accumulation in plants changes the physiological, biochemical, and metabolic processes and reduces biomass production. Heavy metals found in water bioaccumulate in fish bodies and become part of the food chain (Yang et al. 2019). Since heavy metals are highly resistant and non-biodegradable compounds, they move into the whole food web. Tannery industries discharge their effluents without any treatment, elevate the heavy metal concentration in surrounding areas (Sharma et al. 2021a). Heavy metals are very harmful to humans and cause carcinogenic diseases. Human survival and development are very challenged in heavy metal contaminated soil (Kumar et al. 2021).

12.1.1 Human Health and Heavy Metals

Intaking contaminated food that includes various concentrations of heavy metals or metalloids is deemed to be the foremost route (approximately 90%) of human contact in contrast with external exposure or inhalation (Sharma et al. 2021b). Our soil is considered to be the immediate route for the pollution, and accumulation of heavy metals or metalloids in fruits, vegetables, and other crops through the process is known as root uptake (Pierart et al. 2015). The crops are farmed in areas polluted with heavy metals or metalloids. The plants absorb and uptake the metals or

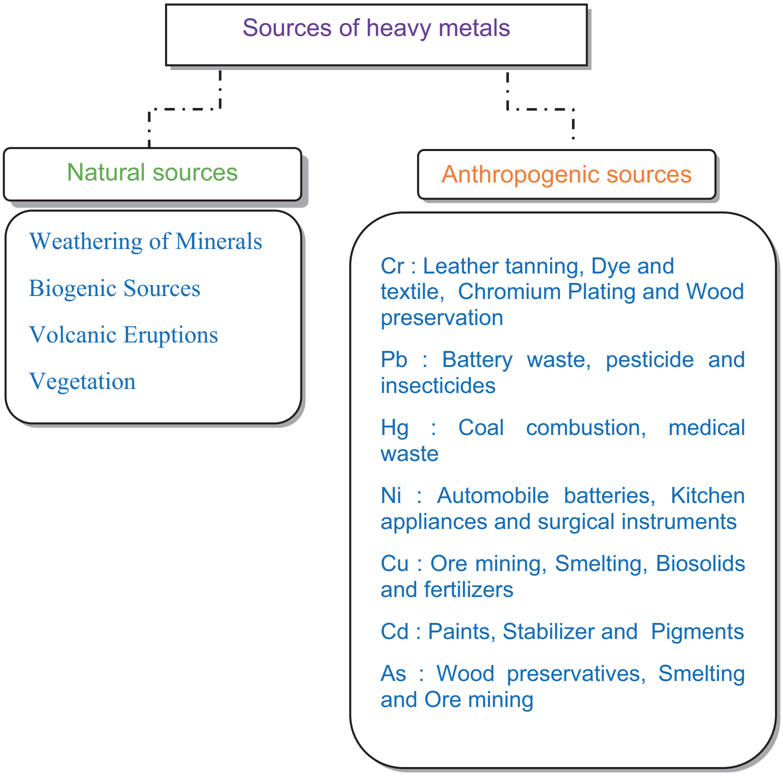


Fig. 12.1 Source of heavy metals

metalloids (if contaminant bioavailability is ideal) when the concentrations are higher than the permitted thresholds and subsequently stimulate significant public health consequences (Thakur et al. 2019). Too much heavy metals or metalloid levels in the plant body is a reason for causing numerous physical, structural, and biochemical toxicities (Kamarudzaman et al. 2015). These develop toxicity in the plant body by unbalancing mineral and water uptake and transportation, changing nitrogen absorption, deteriorating the working of ATPase, lowering photosynthesis rate, altering with plant growth and development, malfunctioning of plan's photosynthetic apparatus), and allowing the closure of stomata (Khalid et al. 2017). Heavy metals or metalloids can develop imperceptible signs of damage in plants including searing of roots, diseases like chlorosis, necrosis, and leaf turning (Chandran et al. 2020). High-level accumulation of heavy metals or metalloids in inner parts of plants can elevate the generation of reactive oxygen species, modification of cycles, and abnormalities associated with chromosomes (Kassaye et al. 2017).

Prolonged consumption of heavy metals or metalloids polluted food can develop a constant accumulation of noxious metals in the human body leading towards several kidneys and liver-related issues and distortion of other physio or biochemical processes (Abinandan et al. 2019). The linkage between soil and microbes allows the plants to develop well. It also shields them from the harmful impacts of heavy metals or metalloids (Sharma et al. 2021a, b). Biomagnification and bioaccumulation induce a higher contact for certain organisms than their particular concentration in nature (Vermote et al. 2018). Heavy metals or metalloids also develop noxious impacts on human beings even at minor levels. This is subjected to the lack of an appropriate protection system in the body to alleviate the noxious impacts of such contaminants and to get rid of them from the body (Gan et al. 2018). Intaking the heavy metals or metalloids polluted vegetables/fruits/crops can lead to the reduction of essential nutrients in the body that ultimately triggers many health-related problems such as growth impedance, disabilities, undernourishment, weakened psychosocial abilities, gastrointestinal malignancy, and immunological failings (Gul et al. 2020).

Heavy metals or metalloids can provoke oxidative stress in the body as a result of excessive production of reactive oxygen species that destroy the cell's intrinsic defense mechanisms and ultimately leads to cell damage or even death (Gyamfi et al. 2019). Furthermore, heavy metals or metalloids can replace vital metals in enzymes, therefore disturbing their working (Amare et al. 2018). Heavy metals or metalloids (lead and cadmium) are believed to provoke carcinogenesis, teratogenesis, and mutagenesis. Elevated concentration of lead and cadmium in the plant's edible portions is one of the major causes of upper gastrointestinal cancer (Jiang et al. 2020). Additionally, lead is also stated to initiate inappropriate HB synthesis, renal infections, and tumors raised BP, and malfunctioning of the reproductive system (Ullah et al. 2019). This is a reason; a considerable amount of attention is offered globally on the subjects of food safety and risk evaluation.

Precipitation, adding chelating agents, and land excavation are some of the techniques useful to eliminate the heavy metals. Biological methods are introduced for the decontamination of metals that are eco-friendly and sustainable. These techniques are economically viable and do not cause secondary pollution (Wu et al. 2021). Phytoremediation is based on the reclamation of metal-poisoned soil with the aid of plants (Kumar et al. 2019). It is regarded as one of the suitable methods as plants have the potential to stabilize, transfer, and extract various metals with the process of phytostabilization and phytoaccumulation. Hyper accumulator plants improve the activity of antioxidant enzymes and enhance the production of osmoregulatory chemicals that helps plants (Mahdavian et al. 2017).

12.2 Microbial Remediation

Over time, microbes have evolved their defensive mechanisms to survive in the toxic environment (Jain et al. 2012). Microbes enhanced the remediation via absorption, oxidation, and precipitation. Growth-promoting microbes protect the plants from the lethal effects of metal pollutants. The rhizosphere is rich with microorganisms, and their activity may transform and degrade the toxic heavy metals (Infante et al. 2014). Microbes are well known for their use in remediation and their potential to act as biosorbents. Microbial remediation has gained more attention due to its low cost, high efficiency for metal recovery, and less chemical and biological waste production, and no nutrient requirements (Gupta et al. 2016). Microorganisms reside in the rhizosphere and help plants in their growth thus referred as plant growth-promoting rhizobacteria. PGPR comprises various groups of free-living organisms including bacteria, fungi, and yeast that improve plant development. Different microbes used for remediation of heavy metals are presented in Table 12.1.

Table 12.1 Various microbes used for heavy metals removal

Microbes	Species	Heavy metal	References
Bacteria	*Azotobacter chroococcum*		Singh et al. (2019)
	Bacillus cereus	Co, Mn, Ni	
	Bacillus circulans	Cr	Srinath et al. (2002)
	Bacillus megaterium	Cr, Ni, Pb	Esringü et al. (2014)
	Bacillus sphaericus	Cr, Ni	Aryal (2015)
	Bacillus subtilis	Co, Cr, Cu, Hg, Mn, Ni, Pb	Banerjee et al. (2015)
	Cellulosimicrobium sp	Cr	Bharagava and Mishra (2018)
	Bacillus thuringiensis	Ni	Jiang et al. (2015)
	Brassica oxyrrhina	Cu, Zn	Ma et al. (2016)
	E. coli AS21	Ni	Chaudhary et al. (2017)
	Geobacillus toebii	Cd	Özdemir et al. (2013)
	Geobacillus thermoleovorans	Cd	Özdemir et al. (2012)
	Pseudomonas aeruginosa	Cd	Tang et al. (2018)
	Zoogloea ramigera	Cu	Yahaya and Don (2014)
Fungi	*Aspergillus niger*	Cd, Co, Cu, Zn	Sharma et al. (2018)
	Aspergillus tereus	Cr	Shokoohi et al. (2020)
	Aspergillus awamori	Cd	El-Sayed (2015)
	Aspergillus ussamii		
	Penicillium simplicissimum	Cd, Ni, Pb, Zn	Chen et al. (2019)
	Rhizopus delemar	Cd, Cu, Zn	Gola et al. (2016)
	Candida utilis		Gupta et al. (2016)
Yeast	*Candida blankii*		Patel et al. (2009)
	Hansenula anomala		Goyal et al. (2003)
	Rhodotorula mucilaginosa		Ollivier et al. (2011)
	Rhodotorula taiwanensis		Singh et al. (2021)
	Saccharomyces cerevisiae	Cu, Pb	Amirnia et al. (2015)
	Yarrowia lipolytica	Cd, Hg	Soares and Soares (2012)

12.2.1 Biological Remediation with Bacteria

Microorganisms change the physical and chemical properties of heavy metal pollutants, thereby reducing toxicity. Leaching is an effective technique for metal removal in a low-grade mineral environment (Galal et al. 2017). The biosorptive ability of microbes depends on permanent and experimental conditions and varies among microbes. Bacteria are established as valuable biosorbents because of their ability and resistance to grow (Srivastava et al. 2019). *Bacillus pumilus, Brevibacterium iodonium, Pseudomonas aeruginosa,* and *Alcaligenes faecalis* have shown exceptional remediation potential for Cd and Pb. In 96 h, *Brevibacterium iodonium* removed more than 87% of Pb and *A. faecalis* took about 72 h for the removal of Cd. Singh et al. (2013) used *Bacillus cereus* to detoxify chromium and it showed 72% removal capacity for 1000 mg/L of chromate at initial pH of 8.0. *Bacillus cereus* was effective at a wide range of temperatures with an optimum temperature of 30 °C. Bacillus, *Enterobacter, Flavobacterium,* and *Micrococcus sp.* are great biosorbents due to the active sites present on the cell wall and the high surface-to-volume ratio. PGPR comprises various groups of free-living organisms that improve plant development. They help in N_2 fixation, siderophores production, and transformation of elements (Srivastava et al. 2019). In mixed culture, the persistence of bacteria increased (Mosa et al. 2016). Thus, consortium culture is more applicable and superior for pilot-scale projects. *Acinobacter sp.* and *Arthrobacter sp.* when used in consortium increased the Cr reduction up to 78%. A huge quantity of Pb was removed with the use of *Micrococcus luteus. Desulfovibrio desulfuricans* studied by Kim et al. (2015) have shown excellent removal ability for Cu, Cr (VI), and Ni of 98.2%, 99.8%, and 90.1%, respectively. Bacterial consortia remarked outstanding results for metals like Pb, Cu, Cr, Co, and Zn in less than 2 h.

12.2.1.1 Endophytic Bacteria Used for Phytoremediation

Endophytic bacteria live in the tissues just underneath the layer of epidermal cells. Here they make colonies and create a variety of distinct connections with the host species involving symbiotic, communalistic, mutualistic, and trophobiotic relations (Porteous-Moore et al. 2006). These bacteria are present in large quantity in significant variety of plants. Also, they are capable to colonize a specific host as well as maximum concentrations accumulated in the roots and decrease from stems to leaves of the plant (Schulz and Boyle 2006). Commonly, a huge number of endophytes belong to the epiphytic bacterial populations inhabiting within the plant's rhizosphere or phyllosphere. However, a few can be transferred through the plant seeds or injured foliar tissues (Ryan et al. 2008). The long-term co-progression of endophytic bacteria and plants develops a special biota that allows plants to fit/endure equally in biotic and abiotic stress situations and improve the natural ecological systems (Bacon and Hinton 2007).

In order to tolerate and avoid the metal ions stress, endophytic bacteria specifically develop many processes, due to which they relieve the harmfulness of the metals. These processes and systems incorporate the outflow of metal ions outside to the premises of the cell, modification of metal ions to a less harmful state, metal ions sequestration, precipitation, adsorption, or desorption of metals (Luo et al. 2011). Recent research regarding the hyperaccumulator plants described that combining soils and seedlings through metal-resilient endophytic bacteria enhanced the development of plants and augmented the phytoremediation in both natural and artificial metal polluted soil specimens via increasing mineral acquisition, cell elongation, metal stabilization, and mitigation of metal stress in plants (Rajkumar et al. 2013).

Correspondingly, the plant growth-promoting endophytic bacteria (PGPE) are identified for playing effective part for the improvement of fertility and assimilable vital nutrients present in soil (Doty 2008), They also synthesize 1-aminocyclopropane-1-carboxylic acid (ACC) deaminase and lessens the ailment intensity by overpowering pathogens (Zhang et al. 2011). Moreover, bioaugmentation with such bacteria having many plants growth encouraging behaviors (such as tolerance against metals, decontamination, modification, and sequestration) can reduce the harmfulness and modify the phyto-availability of heavy metals in polluted soils (Phetcharat and Duangpaeng 2012). This makes them an ideal option for microbes-supported remediation analyses (Rajkumar et al. 2009).

- **Culture-Dependent Analysis**

Processes employed for separation of endophytic bacteria have evaluated with time and tested widely (Visioli et al. 2014). To ensure the growth of isolated bacteria in the plant, two approaches are currently used: (1) surface purification of plant tissues and then separation of the endophytic bacteria employing suitable growing media and (2) microbial recognition and identification with the help of molecular techniques (for instance, amplification of microbial DNA) (Glick 2004). To locate the valuable endophytic inoculums, detection of bacterial endophytes is important. Studies regarding the recognition of bacterial endophytes are primarily dependent on traditional techniques supporting morphologic, physiological, and biochemical traits. For instance, Gram stain reaction, anaerobic or aerobic development, pH limits, temperature thresholds, and several nutritive necessities can be included in the list (Ahmad et al. 2008).

- **Culture-Independent Analysis**

Culture-independent techniques offer elevated magnification proficiency which identifies bacterial varieties overlooked with conventional plating of bacterial communities. However, they are usually reliant on PCR (polymerase chain reaction) or further molecular methods. Once the DNA of bacteria is isolated, primers are employed to crossbreed those DNA spots and particularly augment the 16S ribosomal DNA genes in bacteria (Weisburg et al. 1991). The 16S rDNA comprises extremely locked domains of sequence interspersed with extremely mutable areas all over the DNA structure. Sequencing is used to examine the duplicated 16S rDNA. The rDNA categorization of the unidentified bacteria is paired to direct DNA sequences in an archive provided by the Bioinformatics Bacterial Identification (BIBI) or the National Centre for Biotechnology Information (NCBI) (Zhu et al. 2014).

Lately, fingerprints of genomic DNA supporting an elevated extent of taxonomical classification are frequently utilized to classify bacteria (Maropola et al. 2015). Terminal restriction fragment length polymorphism (TRFLP) is a technique in which restriction enzymes are utilized to cut genomic DNA in numerous sections split through gel electrophoresis to produce the bacterial DNA fingerprints. The resemblance of electrophoretic forms from quoted bacteria is employed for categorization (Sessitsch et al. 2002).

Rep-polymerase chain reaction is another method that allows the PCR amplification of concerned DNA by isolating and dividing the DNA into two distinct strands and nurturing them with DNA polymerase. This yields DNA sections of various sizes. Electrophoresis gel splits the DNA sections and generates a DNA fingerprint that ultimately used in categorization (Ma et al. 2015). Furthermore, several molecular techniques are regularly employed to analyze the changes in the endophytic population, including the denaturing gradient and temperature gradient (Wei et al. 2014).

Additionally, amplifying primers can be utilized to assess the expertise of the endophytic population to take part in operational activities contained by host (Shin et al. 2012). For example, nitrogen fixation genes are included in microbial fixation of nitrogen; on the other hand, the b-thermostable b-glucosidase gene is especially utilized to research the rhizobium potential (Babu et al. 2013). Moreover, further molecular ecological techniques frequently applied are epi-fluorescence microscopy methods. They make it viable to illustrate in situ microbial communities in their native environments (Aravind et al. 2010).

12.2.2 Biological Remediation with Fungi

Due to the excellent metal uptake and recovery capacities of fungi, they are marked as exceptional biosorbent (Fu et al. 2014). *Aspergillus sp.* removed 85% Cr from the tannery wastewater in a bioreactor system at the pH of 6 whereas 65% Cr was removed from the tannery effluent. Organic pollutants tend to stop microbial survival (Srivastava and Thakur 2006).

Coprinopsis atramentaria is indicated as an efficient accumulator due to its ability to remove 76% of Cd and 94.7% of Pb at concentration of 1 mg/L and 800 mg/L, correspondingly. This is documented as mycoremediation (Lakkireddy and Kües 2017). *Aspergillus niger, pencillium chrysogenum, Rhizopus oryzae,* and *Saccharomyces cerevisiae* were used to convert the toxic Cr into less toxic Cr (III). Chatterjee et al. (2012) observed Ni and Cu removal at optimum pH of 3–5. The initial concentration of metal ions affected the process and tried to slow down the removal rate. Removal efficiency for Zn and Pb was also studied by Luna et al. (2016).

12.3 Microbes-Assisted Remediation Mechanisms

12.3.1 Biomining

Biomining is used for both biooxidation and bioleaching. Bioleaching helps the heavy metal in mobilization by biological dissolution (Bojórquez et al. 2016). Heavy metals are dissolved by the secretions such as organic acids of low molecular weights, formed by the microbes. Soil particles connected to the heavy metals are also absorbed by microbial secretions (Rahman and Sathasivam 2015). The leaching rate increases in the presence of nutrients and reduces its efficiency when nutrients are not available because microbes require nutrients and energy for secretions. In the presence of glucose, leaching rate increases up to 36% as compared to 9% in nutrients-free environment (Marchenko et al. 2015). Citrobacter produces inorganic phosphate that forms an insoluble metal coat and traps toxic heavy metals. Microorganisms change the valence metals by redox reaction and change the mobility of toxic heavy metals. For example, Pb^{2+} is reduced to Pb^0 by dead *Bacillus licheniformis* R08. *Coryne bacterium* reduces the toxic Cr^{3+} into poorly water-soluble and less toxic and Cr^{3+} (Goyal et al. 2003).

12.3.2 Biosorption

Microbes can harness heavy metals in two ways: absorption and adsorption. In terms of their working principle, both are different techniques (Gan et al. 2012). In adsorption, individual molecules assemble at the surface of the adsorbent whereas in absorption, the liquid or fluid material is completely soaked by the absorbent (Danis et al. 2008). Heavy metal ions gather on the cell surface and ultimately absorb into the cell surface (Wuana and Okieimen 2011). The cell wall and mucous layer support the absorption and adsorption very smoothly. Functional groups like nitrogen, sulphur, phosphorous, and oxygen of cell walls make complex metal ions (Asrari 2014). Negatively charged carboxyl anionic and phosphoric acid anions are present on the microbial cell wall surface. In addition, the cationic group of heavy metal relates with the cell wall and passes the cell membrane (Brunetti et al. 2012). Adsorption does not depend on energy, so it is a primary method that is being used by the microbes. Absorption occurs in living cells due to their energy dependency (Singh et al. 2017). It is found that microbes easily adsorb the large molecules of heavy metals. *Bacillus* reach the adsorption equilibrium within the first 10 minutes and adsorb, i.e., 60% for Cu^{2+} in the first minute. Absorption is an inefficient and time-consuming technique. With the addition of EDTA or lemon oil, efficiency of absorption can be enhanced up to 31.5% (Gan et al. 2017). In non-living brown algae, ion exchange to cell surface also makes complexation by binding the heavy metal ions. In the absorption of Cu^{2+}, 70% of K^+ and 60% of Mg^{2+} are released by the yeast rapidly and slowly, respectively. The release of fewer cations is the main limitation of this remediation method.

12.3.3 Plant and Microbes-Assisted Remediation

Mycorrhizal fungi and many other microorganisms improve the conditions in the rhizosphere and assist the plants to absorb these metal ions at maximum. Mycorrhizal plants improve the percentage removal of Cd up to 131% for the concentration of 100 mg/kg. Mycelia of mycorrhizal fungi spread the root surface area and the ability to absorb heavy metals improves after the inoculation of mycorrhiza (Bissonnette et al. 2010). The host plants are capable of developing resistance against the heavy metal ions with the help of Endophytic mycorrhiza. The symbiotic association of plants and endophytic mycorrhiza surges through iron carriers, the production of chelating agents, organic acids, and acidification (Singh et al. 2019). In a very toxic environment, the fungal cell wall produces a mucous that combines with the organic acid ions and reduces the mobility of heavy metals. The protective mechanism of mycorrhiza inhibits the transfer of heavy metals to plants. Inoculation of fungi changes the composition and number of roots and affects the oxidation of heavy metals rhizosphere area (Ma et al. 2011).

12.4 Factors Contribute to the Microbial Degradation of Heavy Metal Pollution

12.4.1 Ambient Temperature

Microorganisms' growth is temperature-dependent, and any change in ambient temperature can affect the rate of heavy remediation (Fang et al. 2011). Optimum temperature is not the same and specific for all the microorganisms. There are medium-temperature bacteria and thermophilic bacteria including *Thiobacillus acidophilus, Thiobacillus ferrooxidans, Thiobacillus tepidarius*, Sulfolobus solfataricus, and *Acidianus brierleyi,* respectively (Rodríguez-Tirado et al. 2012). Park et al. (2016) stated in their research that even for the same microbes, optimum temperature is different for different heavy metals. *Bacillus licheniformis* and *Bacillus jeotgali* studied the adsorption capacity of Cd^{2+}, Zn^{2+}, and Cr^{2+} (Zouboulis et al. 2004). The most appropriate temperature range for microbes is 25–35 °C (Gan et al. 2012). *Bacillus jeotgali* showed maximum adsorption at 35 °C and 30 °C for Cd^{2+} and Zn^{2+}, respectively (Goyal et al. 2003).

12.4.2 pH

Although optimum pH is different for different microorganisms, it plays a very important role in microbial degradation (Wei and Zhou 2006). If pH is not stable and appropriate, it can cause adverse effects on the growth of microorganisms. The activity of enzymes in microorganisms is linked with pH, and any slight change can alter the rate of microbial remediation (Rahman 2020). The pH affects the microorganism‘s surface charge, which impacts its adsorption of heavy metal ions (Mohsenzadeh et al. 2010). pH also has the potential to disturb the hydration and mobility of heavy metals present in soil ecosystem. Wierzba (2015) and Rodríguez-Tirado et al. (2012) both performed respective studies and determined that increase in pH ultimately increases the removal rate of heavy metals above that limit, microorganism's ability to remove the heavy metal decreases with an increase in pH. Adsorption capacity for Pb at pH of 2.0 is 10 mg/g whereas at pH of 5.5, it grows seven times, i.e., 70 mg/g. The same condition is reported for Zn^{2+} as well. This is the optimum pH, and increasing the pH further decreases the pH to the previous level, i.e., 2.0. The optimum pH range for bacteria is 5.5–6.5. However, some of the bacteria have an exceptional trend by showing maximum removal at pH 7 (Tarekegn et al. 2020). The pH range for aerobic and anaerobic microorganisms can be different. In addition, metal ions form hydroxide precipitates into the soil; hence at high pH, they are less prone to microbial removal (Abioye et al. 2018).

12.4.3 Substrate Species

Soil type, soil additives, and heavy metals are three mainstream factors to consider while working on substrate species. Different soil properties can significantly affect the adsorption capacity (Banik et al. 2018). For example, the adsorption capacity of black soil is very less as compared to that of beach tidal soil. Yellow mud has the least ability for the adsorption of soil. Retention of heavy metals and their adsorption rate determines the microbial removal (Hu et al. 2010). The ability of microorganisms for remediation also depends on the species of heavy metals. Heavy metals that dissolve easily, i.e., Ni and Zn, have less retention time as compared to Pb and Cr with more retention time and less solubility.

The substrate generation time of sulfur with *Thiobacillus ferrooxidans* is comparatively high, i.e., 10–25 h, whereas for Fe as a substrate, it is 6–15 h only. Accumulation of various heavy metals at the same time also hinders the microorganisms' functionality. For example, Cd^{2+}, Zn^{2+}, and Pb^{2+} have more bioavailability as individual metals. Adsorption of Cd is 11.2 mg/g, whereas in combined presence of Zn and Pb, it reduced to 3.15 mg/g. Parallel changes have been detected for Pb and Zn. Adsorption of Pb is 2.25 mg/g and 19.5 mg/g that of Zn which reduces to 0.915 mg/g and 8.08 mg/g, respectively (Park et al. 2016).

Soil additives are used to enhance the heavy metal removal by microorganisms. The leaching of heavy metals can vary in their response to the change in the concentration of additives. Leaching rate for Zn and Cu increases in a lower concentration of respective metals but decreases when the concentration of both heavy metals is more than 20 g/L (Tyagi et al. 2014). Combinations of additives are also used so that a high removal rate can be obtained. $FeSO_4$–$7H_2O$ is considered an effective additive for metal removal (Jin et al. 2018).

12.4.4 Substrate Concentration

The concentration of heavy metals is directly related to the adsorption ability of microorganisms (Laurenti et al. 2013). Langmuir model and Freundlich model are used to describe the accumulative features of a biosorbent. The first one states the adsorption of single-layer surfaces which is comprehensible, whereas Freundlich model is useful for the adsorption equilibrium. Freundlich model is widely used because of its simplicity. Ehrlich has shown concentration of heavy metal ions adsorption according to microorganisms (Karci et al. 2014). Brunetti et al. (2012) recommended that with the increase of concentration of heavy metals, adsorption also increases and then becomes constant at equilibrium.

12.4.5 Composite Reclamation

The composite reclamation is based on the use of electric-microbial combination and microbial-plant combination (Park et al. 2016). Mycorrhizal fungi are used in this technology to attain maximum removal of metals. Bacteria and DC power plant is also used for restoration purposes. The composite reclamation technique is used in soil flushing and washing (Lakkireddy and Kües 2017).

The microbial-plant remediation technology is very resolute for heavy metal ions removal. Ryegrass, Bacteroides, and sulfuric acid when used in combination enhanced the Cu removal. Rather than the use of microbial reclamation or plant-assisted remediation, the composite recovery method is very effective. Festuca and mycorrhizal fungi have a removal efficiency of 64–72%. When *Polygonum aviculare L.* and mycorrhizal fungi are used in a combination, it shows an increase of 54% in contrast to control. DC electric field and electrodes help the microorganisms in their movement and metal degradation, respectively. In this way, these combinations assist and the removal rate increase from 10% to 88% (Sharma et al. 2018).

Various environmental conditions control efficiency and wide application of composite technology including temperature, soil moisture, high cost, and nutrients (Azubuike et al. 2016).

12.5 Bioremediation- A Sustainable Approach for Environmental Restoration

In order to have a sustainable ecosystem, it is important to address contamination of natural ecosystems due to anthropogenic activities using green technologies. Microbe-assisted bioremediation is being called an economical technology within the realms of integrated environmental remediation efforts that restores the polluted site back to its actual form (Pande et al. 2020). Following are some of the major consideration that should be considered for the process of bioremediation:

I. Human health.
II. Environmental conservation.
III. The cost of remediation process.

Just like any other remediation technology, the reduction of toxicity associated with the environmental contaminant is a major aim of bioremediation. Bioremediation solutions are used to address the problems related to the chronic toxicity by minimizing the effects of contaminants in polluted sites (Philp et al. 2005). Over the time, the quality of degradation and remediation of environmental pollution have improved a lot because of the metabolic potential of microbes. Microorganisms not only help in the restoration of contaminated ecosystems by cleaning up waste in an eco-friendly and safe way but also produce safe end products (Pande et al. 2020).

The microorganism-assisted remediation has been found to be successful when applied to restore the agricultural lands, lagoons, water streams, ground water, sludge, oil spills, petroleum, and hydrocarbon contaminated sites (Arora 2018). Bioremediation is not only environmentally safe but also provide benefits to the environment (Glass 2000). The number of environmental benefits is as follows:

- Conservation of biodiversity.
- Various sources of energy and aesthetics.
- Soil restoration and protection.
- Sequestration of carbon.
- Watershed management.
- Stability and sustainability (Dickinson et al. 2009).

Microbe-assisted bioremediation has made its name as a sustainable soil decontamination technology because of decreased soil disruption, low maintenance, and affordable costs (Balseiro-Romero et al. 2017). The studies conducted in recent times have revealed that microbes play an essential part in bioremediation technology. Few species of microbes which includes filamentous fungi, plant growth-promoting bacteria (PGPB), and biodegradative bacteria are found to be useful in phytoremediation in several ways like changed rhizospheric environment, increased production of biomass and bioavailability or/and stabilization of heavy metals, and reduced toxicity (Wang et al. 2017).

This is why they are said to be used for soil amelioration. Some polysaccharides secreted by microbes are able to bind with soil particles easily; as a result, the generation of soil aggregates is improved. For example, glomalin and other glycoproteins which are secreted by arbuscular mycorrhizal fungi (AMF) increase the particle aggregation and aggregating stabilization against water and wind erosion which tends to improve soil structure. Microbes are also capable of producing organic compounds that changes the pH and capability of oxidation-reduction of the respective soil ecosystem in order to solubilize and/or stabilize heavy metals. Moreover, few of the soil bacteria are capable of biodegrading toxic organic compounds which are produced as a result of processing of the minerals (Wang et al. 2017).

12.6 Economic Perspective

Growing population and expanding economies are actively contributing to the heavy metal pollution. The conventional technologies are not only laborious but also very expensive (Ali et al. 2017). Phytoremediation is a plant-based technology assisted by microbes which is not only environmentally friendly but also cost effective. The study suggests that global market of this technology is around 34–54 billion US$ and is rapidly growing in developed countries. A review by Pilon-Smits (2005) revealed that the real market for this treatment consists of $100–150 million in the world. It generates revenue by the production of non-consumable agricultural products, biofuels, or wood. Moreover, the production of metal rich biochar provides an additional economic perspective in phytoremediation as its application as a fertilizer. From 2017 to 2015, the global market scenario of bioremediation technology shows an increasing trend with the compound annual growth rate of 8.3% (Arora 2018).

The process of bioremediation is moderately economical as compared to physiochemical remediation techniques. All these types of bioremediations usually make use of natural procedures and decontaminate the metal-polluted areas in site without any sort of excavation or physical removal; as a result, the cost of site clean-up ends up getting reduced significantly. Other than that, in some cases, bioremediation is capable of removing the heavy metal(loid)s without any involvement of humans, and it results in significant reduced cost. Once established in the field, this treatment can operate with least maintenance; this is why it costs almost tenfold lesser as compared to the engineering-oriented methods (Marques et al. 2009). Similarly, the cost for post-cleanup is less for bioremediation treatment since it generates minimum site disruptions in comparison with traditional and conventional clean-up methods.

The cost evaluation for varying remedial approaches also requires the costs of operations and maintenance (O&M) and the cost of monitoring over the lifetime of the decontamination project along with the initial capital costs. Initial capital costs include previous evaluation and investigations, soil preparation, any nursery tools, and equipment or water irrigation systems. Operational costs mainly include cost of labor, material, any large machinery of needed, and all the secondary cost like subsidiary and indirect costs that are associated with the primary operational costs (Wan et al. 2016). Such a life-cycle cost analysis helps the involved stakeholders to assess not only the overall costs of various options available, but also make them familiarize with the rate and timing of spending. It is observed that some of the remedies may require larger up-front financial investments but have lesser life-cycle costs. On the other hand, some of them may have relatively low upfront costs, but increased operation and maintenance costs as compared to other options (Krug et al. 2009). It is noted that in order to reduce the cost further, improvement in the mechanization level of bioremediation and accurate prediction or prevention of the unexpected and untimely outcome are recommended (Wan et al. 2016).

Comparison of different soil clean-up methods in terms of cost and time required is shown in Table 12.2.

Microbes facilitated bioremediation costs less per volume of soil to treat as compared to other methods of mechanical bioremediation like ultraviolet oxidation, absorption by activated carbon, and electron beam destruction. For example, it would cost $2 to decontaminate the 2-liter bottle of soil contaminated with trinitrotoluene (TNT) using activated carbon absorption. It would cost more using ultraviolet oxidation and electron beam destruction which is $6 and $10, respectively. The cost is found to be growing exponentially in case of complete soil of larger areas are saturated with TNT. However, microbes facilitated bioremediation amount to as less as only $1.28 (Meagher and Heaton 2005). Salt et al. (1995) reported that the bioremediation costs for sandy loam soil per acre is expected to be €55,000 to €92,500 which is almost 4–7 times less in comparison to that of soil excavation (€370,000). Similar results were found for lead (Pb) pollution. Pb is one of the most common and difficult pollutants to remove. It costs only $27,000 to reduce lead levels in soil from 1.4 to 0.4 g/kg over a 10-year period which is much lower as compared to the most popular decontamination techniques like soil leaching $790,000 and excavation and land filling $1,620,000 (Meagher and Heaton 2005).

In another study (Cunningham and Ow 1996), the cost of bioremediation of 12-acre soil contaminated by Pb over the estimated period of 30 years was calculated to be €185,000, which is lot less as compared to costs that are required in soil capping and washing, excavation and disposal, etc. An overview of the costs of all these various methods is illustrated in Fig. 12.2.

Table 12.2 Comparison of cost and time required for various soil clean-up methods (Khalid et al. 2017)

	Techniques	Cost	Time required
Physical remediation	Soil replacement	Costly because of large working volume	Comparatively very less
	Soil isolation	Costly as soil clean up requires further engineering measures	Comparatively very less
	Vitrification	High cost due to energy requirement	Comparatively very less
	Electrokinetic remediation	Economically effective	Comparatively very less
Chemical remediation	Immobilization	Relatively low cost	Less to medium
	Soil washing	Cost-effective	Less to medium
Biological remediation	Phytovolatilization	Economical	Very high
	Phytostabilization	Economical	Very high
	Phytoextraction	Highly economical	Very high
	Chelate-associated phytoextraction	Costly	Very high but less than phytoextraction alone
	Microbial-assisted phytoextraction	Economical	Very high but less than phytoextraction alone

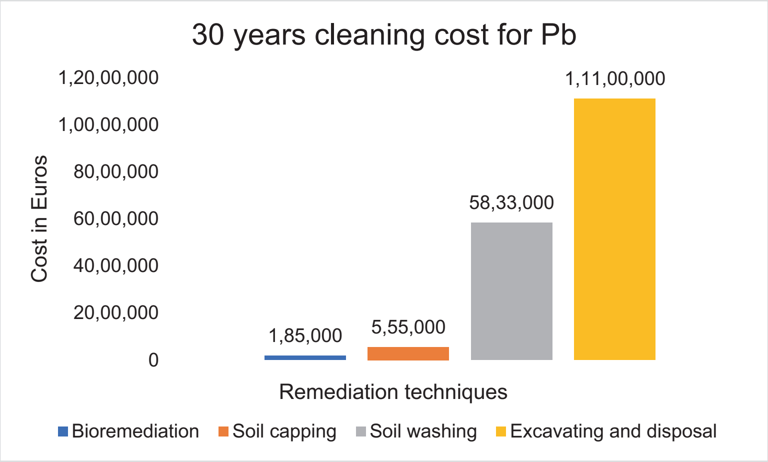


Fig. 12.2 Cleaning cost for Pb contaminated soil with various techniques

Schnoor (1997) calculated the difference in cost for various remediation techniques that are being used for the removal of heavy metals from contaminated sites and reported bioremediation to be the most cost effective. The cost was found to be US$10–35 which is low as compared to other methods' cost that ranges from US$20 to US$1500 for processes like stabilization, soil venting and washing, solvent extraction and incineration, etc. The comparison of cost is shown in Fig. 12.3.

In another study, the estimated cost was found to be €140–230 for remediating one acre of Pb contaminated soil, which is 50–65% less as compared to traditional treatments that were calculated to be €460 (Blaylock et al. 1997). In a study conducted by US EPA (2004), bioremediation costs per ton of soil was calculated to be about US$25–100 which is really less in case of using treatments like vitrification process 300–500 US$/ton and 75–210 US$/ton for flushing. The expenses of remediation treatment highly differ as it depends on the type of treatment being used and the concentration of contaminant in soil, types and properties of soil, on-site circumstances, etc. A comparison of cost has been shown in Table 12.3.

Table 12.3 presents costs for different treatments in order to remediate soil polluted with water-soluble and volatile contaminants (Cunningham et al. 1995).

Government intervention is important in order to implement the economic activities of bioremediation. It will allow the formation of regulations that would be helpful in creating development opportunities. Microbes-assisted bioremediation should be taken as an example for the integrated approach in development framework that has goals of preservation of the environment as well as providing employment. This stands true particularly for the developing countries. These countries generally lack well-established and definite environmental legislation policy and economic framework that might require modifications. Nonetheless, educating and creating social awareness of the benefits of bioremediation have to

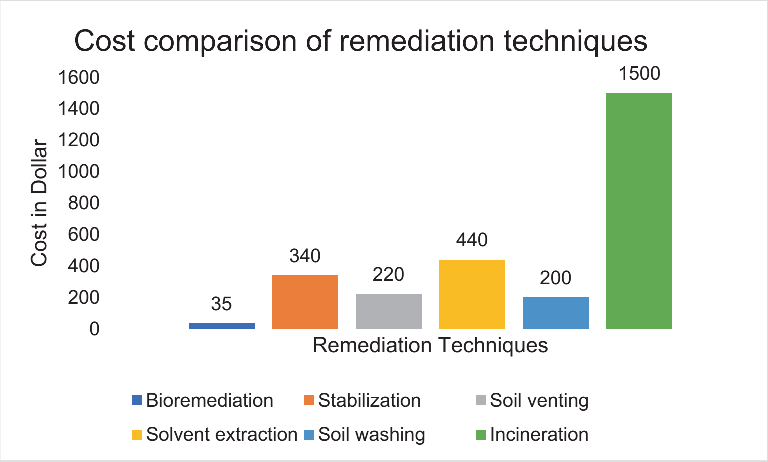


Fig. 12.3 Cost comparison of various techniques used for remediation

Table 12.3 Remediation costs for a soil contaminated with volatile or water-soluble pollutants (Cunningham et al. 1995)

Type of treatment	Price per cubic meter of soil (in $)
Physicochemical remediation	10–100
Landfilling or low temperature thermal treatment	60–300
Special landfill arrangements or high temperature thermal treatments	70–200
Bioremediation	0.02–1.00

be greatly stressed upon, especially to stakeholders and decision makers (Pandey and Souza-Alonso 2019).

12.6.1 Market Niches for Secondary Products

The secondary products also play their role when it comes to making profits and developing economic opportunities through bioremediation. There are several market fields where it has a massive potential to create market niche for itself. It is because plants can be used in several ways during and after their remediation process cycle is complete. The usage of the obtained biomass of a complete bioremediation cycle has the potential of turning it into a profit-making operation by using it as the source of energy. However, the plants are harvested after the remediation of heavy metals. This incineration process can be used as source of energy generation. Making use of the polluted plant biomass, once the bioremediation cycle is complete, as a source of energy is one of the most safe and economical approach. The combustion and process of gasification are essential methods during the production of the electric and thermal energies from the plant biomass after its life cycle (Khalid et al. 2017).

Some of the other market opportunities are enlisted below:

- Aromatic essential oils.
- Biofortification.
- Biochar.
- Wood products.
- Energy/biodiesel.
- Ornamental and decorative purposes.
- Pulp-paper business.
- Phyto-mining (Pandey and Souza-Alonso 2019).

Bioremediation is said to be an economical and eco-friendly safe method of utilizing living organism to eradicate pollutants from soil (Padmavathiamma and Li 2007; Prasad 2003). As mentioned before, the process is relatively cheaper as compared to the other remediation treatments. Still, a thorough economic analysis for this process is not available. Most bioremediation studies are focused on the biological, biochemical, and agronomic processes (Ali et al. 2013).

A complete economic stance, rather than simple and minimal assessments of the expense pluses of bioremediation over other techniques, has not been investigated. This is why, a kind of method is required that may efficiently allocate remediation funds is need of an hour. After a comprehensive and thorough evaluation and assessment of pollutants has been performed, the decision-making on the use of remediation choices is a critical measure (Scholz and Schnabel 2006). Many treatment technologies for soil clean-up are available, but their clean-up costs are often very high (Karachaliou and Kaliampakos 2011). Many methodological studies had designed to establish patterns, standards, and techniques so that cost-effectiveness and economic feasibility can be understand thoroughly (Scholz and Schnabel 2006). Nonetheless, literature is not sufficient enough because it yields and produces limited basic parameters (Lemming et al. 2010). The accurate decision-making can only be attained as a result of enhanced real-world experience and knowledge (Demougeot-Renard and De Fouquet 2004).

12.7 Public Perception of Bioremediation

Keeping in mind the social dimension point of view of sustainability, involvement of general public during the decision-making process before implementation of new restoration projects should be given due importance. Moreover, they should be encouraged to actively participate and remain engaged. This is because they will get advantages from the environmental reclamation of the contaminated areas. It is generally observed that management or restoration actions in remediation are usually better implemented when there is a meaningful involvement of the members of society (Le Maitre et al. 2011). Knowledge about the ecological and societal consequences of pollution and its possible remediation would result in investments from public or private. The lack of knowledge within society, economic benefits in traditional remediation treatment processes, and preference to short-term gains can be limiting the applications of bioremediation. This is why the advice given by Le Maitre et al. (2011) related to public involvement should be employed to engage society in a cost-benefit negotiation in order to earn their trust and support for such investments.

The harmful and toxic impacts of pollutants on plants, animals, and individual health have resulted in noticeable increase in public attention and acceptance towards technologies to remediate polluted areas. The study conducted by Weir and Doty 2016 through the use of surveys indicated a high level of social acceptability of bioremediation in parks. It suggests focusing on explaining environmental benefits of phytoremediation to encourage more usage and acceptance in masses. It is important to highlight a wonderful observation made by Licht and Isebrands (2005), they indicated that there is a crucial belief in environmental justice that should be kept in mind by all those working on bioremediation. It simply means the fair and just treatment for all people through environmental laws and policies irrespective of their culture, race, income, etc. This emphasizes on how no man should bear negative environmental consequence as a result of remediation and restoration treatment.

12.8 Applicability of Bioremediation Techniques for Decontamination of High Metal and Multi-metal Contamination in Soil

Bioremediation can be used to decontaminate the multi-metal contaminated soils as some hyperaccumulators are capable of growing well and accumulating high content of toxic metals. Nonetheless, most of the hyperaccumulator plants usually accumulate only a specific metal, and are not useful when it comes to their application in the field under multi-metal contaminated soil conditions. As most of the plants and microbes will not survive well under high heavy metal(loid) concentration in soil, so bioremediation is restricted to low or moderately contaminated sites. Bioremediation is effective only for contaminated sites in which heavy metals are easily moveable in soil. Their extraction is frequently limited when the metals are highly immobile in soils like the heavy metalloids one, e.g., Cr and Pb. However, using the chelating agents tend to enhance the ability of microbes to remediate multi-metal contaminated sites (Khalid et al. 2017).

12.9 Challenges and Future Prospect

The soil decontamination has become a demanding task because of the financial and technical implications and intricacies. As mentioned earlier, bioremediation of soils polluted with heavy metal(loid)s shows greater benefits in terms of safety of environment, large-scale field application, public acceptance, and finances as compared to physiochemical treatments**.** Despite its multiple advantages, bioremediation does have some intrinsic limitations. Some of the limitations are extreme or highly varying climate conditions, seasonal variations, soil toxicity level, limited metabolic detoxifying capacity, etc. Another major challenge is the possibility of mixing of pollutants into the food chain because of how long the process of remediation is (Witters et al. 2012). How effective the bioremediation process is generally depends on the interaction of microbes-plants, soil, and contaminants. In case of high level of pollutants, many of the plants fail to gain significant biomass (Harvey et al. 2002; Chaudhry et al. 2005).

The poor nutrient nature of soil causes the remediation procedure of polluted site to be slowed and limited. Soil microorganisms are supposed to show welcoming impact on plant growth and health through their mutualistic relationship among them. The presence of multiple contaminants may pose extreme challenges to the survival, function, and activity of the microbial community in soils (Shi et al. 2002). Within the physicochemical and biological properties of rhizosphere soil environment, even a minor change can cause a biotic or abiotic stress which can have substantial effect on plant–microbe mutualistic interaction.

Moreover, the characterization of microbes that is compatible with plants is a time-taking process. It consists of analyzing more than thousands of isolates, and later identifying the specific biomarkers that may facilitate to choose the most appropriate plant–microbe interaction for the specific bioremediation (Rajkumar et al. 2012). The studies that are focused on plant species that are potentially appropriate for microbe-assisted bioremediation are extensively studied in scientific literature. Still, the absolute knowledge and understanding regarding the biological processes that are related to the re-introduction of indigenous microorganism and plants and their ability to degrade heavy metals is still quite limited for the application of these bioremediation treatments on a larger scale in a field context.

In spite of the fact that large-scale field application of bioremediation tends to have practical and technical challenges, it is observed that these limitations can be minimized by following proper management. This is why, the wide research endeavors are required to find and identify novel microbial diversity, distribution, and functions in both the autochthonous and allochthonous soil environments for metal sequestration, plant growth promotion, and reduction of metal toxicity. The foremost approach is the development of the more organized and structured process on less-contaminated industrial or urban sites in order to reduce soil metal pollutant and to promote soil fertility and health. A second approach is to make use of the bioremediation on the low-contaminated sites only when the highly-polluted soils have been excavated from there. The third way is to use the transgenic technology in order for improving bioremediation efficiency and effectiveness as well as large-scale field application. The pursuit of latest candidate genes that is adaptive for metal hyper-tolerance or hyperaccumulation is one of the important research avenues. There is a need to make use of genetic engineering, in order to explore several heavy metal(loid)s resistant genes that can be introduced into contaminated sites.

12.10 Conclusion

It is a dire need of time to adapt the less expensive and clean process for degrading the pollutants present in the ecosystem. For this purpose, it is very essential to fulfill the demand for organisms that are capable of performing remediation. Bioremediation is a very safe technology but requires extensive knowledge for interaction among environmental pollutants and microbes. Bioremediation can be performed without any major disruption, and in the long run, it provides both economic and environmental advantages. Biological treatments alone are not sufficient enough to treat the sites at maximum rate and due to dissimilar growth requirements, there are biased opinions associated with it. Consultants, government officials, investors, and the public want demand for applicable and immediate remediation of heavy metal pollutants.

The aim of forthcoming studies should be based on the priority guidelines and regulations proposed by the Environmental Protection Agency (EPA). Regional EPA should formulate a protocol with policies and strategies on the use of bioremediation techniques and priority areas, cost-effectiveness, and comparison of execution. To ensure the safety of the ecosystem, EPA should propose extraction procedures, and fencing of a contaminated site to inhibit the animal interaction with the contaminated land. A bacterium is one of the most promising microorganisms which need to be investigated more for inclusive results and complete comprehension. Though few studies have been performed, it still needs to be explored for heavy metal extraction. Genomic metabolism data can optimize the bioremediation for future prospects. The forthcoming research should be based on the co-inoculation of arbuscular mycorrhizal fungi and plant growth-promoting rhizobacteria, identification of mechanisms involved in microbe, and plant interaction effectiveness of viable synthesis of bioinoculants. Therefore, making the use of transgenic technology to develop an optimum combination of soil + plant + microorganism is an optimistic way forward towards the future development.

References

Abinandan S, Subashchandrabose SR, Venkateswarlu K, Perera IA, Megharaj M (2019) Acid-tolerant microalgae can withstand higher concentrations of invasive cadmium and produce sustainable biomass and biodiesel at pH 3.5. Bioresour Technol 281:469–473

Abioye OP, Oyewole OA, Oyeleke SB, Adeyemi MO, Orukotan AA (2018) Biosorption of lead, chromium and cadmium in tannery effluent using indigenous microorganisms

Afonso TF, Demarco CF, Pieniz S, Quadro MS, Camargo FA, Andreazza R (2020) Bioprospection of indigenous flora grown in copper mining tailing area for phytoremediation of metals. J Environ Manag 256:109953

Ahmad F, Ahmad I, Khan MS (2008) Screening of free-living rhizospheric bacteria for their multiple plant growth promoting activities. Microbiol Res 163(2):173–181

Ali H, Khan E, Sajad MA (2013) Phytoremediation of heavy metals—concepts and applications. Chemosphere 91(7):869–881

Ali A, Guo D, Mahar A, Ping W, Wahid F, Shen F, Li R, Zhang Z (2017) Phytoextraction and the economic perspective of phytomining of heavy metals. Solid Earth Discuss:1–40

Amare E, Kebede F, Berihu T, Mulat W (2018) Field-based investigation on phytoremediation potentials of *Lemna minor* and *Azolla filiculoides* in tropical, semiarid regions: case of Ethiopia. Int J Phytoremediation 20(10):965–972

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

Aravind R, Eapen SJ, Kumar A, Dinu A, Ramana KV (2010) Screening of endophytic bacteria and evaluation of selected isolates for suppression of burrowing nematode (Radopholus similis Thorne) using three varieties of black pepper (Piper nigrum L.). Crop Prot 29(4):318–324

Arora NK (2018) Bioremediation: a green approach for restoration of polluted ecosystems

Aryal M (2015) Removal and recovery of nickel ions from aqueous solutions using *Bacillus sphaericus* biomass. Int J Environ Res 9(4):1147–1156

Asrari E (2014) Heavy metals in contaminated soils: a review of sources, chemistry, risks and best available strategies for remediation. In: Heavy metal contamination of water and soil, Taylor & Francis Group, London, pp 33–82

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(11):1–8

Babu AG, Kim JD, Oh BT (2013) Enhancement of heavy metal phytoremediation by *Alnus firma* with endophytic *Bacillus thuringiensis* GDB-1. J Hazard Mater 250:477–483

Bacon CW, Hinton DM (2007) Bacterial endophytes: the endophytic niche, its occupants, and its utility. In: Plant-associated bacteria. Springer, Dordrecht, pp 155–194

Baldantoni D, Morra L, Zaccardelli M, Alfani A (2016) Cadmium accumulation in leaves of leafy vegetables. Ecotoxicol Environ Saf 123:89–94

Balseiro-Romero M, Gkorezis P, Kidd PS, Van Hamme J, Weyens N, Monterroso C, Vangronsveld J (2017) Use of plant growth promoting bacterial strains to improve Cytisus striatus and Lupinus luteus development for potential application in phytoremediation. Sci Total Environ 581:676–688

Banerjee S, Gothalwal R, Sahu PK, Sao S (2015) Microbial observation in bioaccumulation of heavy metals from the ash dyke of thermal power plants of Chhattisgarh, India. Adv Biosci Biotechnol 6(02):131

Banik A, Pandya P, Patel B, Rathod C, Dangar M (2018) Characterization of halotolerant, pigmented, plant growth promoting bacteria of groundnut rhizosphere and its in-vitro evaluation of plant-microbe protocooperation to withstand salinity and metal stress. Sci Total Environ 630:231–242

Bharagava RN, Mishra S (2018) Hexavalent chromium reduction potential of Cellulosimicrobium sp. isolated from common effluent treatment plant of tannery industries. Ecotoxicol Environ Saf 147:102–109

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(1):55–67

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(3):860–865

Bojórquez C, Frías Espericueta MG, Voltolina D (2016) Removal of cadmium and lead by adapted strains of Pseudomonas aeruginosa and Enterobacter cloacae. Rev Int Contam Ambient 32(4):407–412

Brunetti G, Farrag K, Soler-Rovira P, Ferrara M, Nigro F, Senesi N (2012) The effect of compost and Bacillus licheniformis on the phytoextraction of Cr, Cu, Pb and Zn by three brassicaceae species from contaminated soils in the Apulia region, Southern Italy. Geoderma 170:322–330

Chatterjee AK, Sarkar RK, Chattopadhyay AP, Aich P, Chakraborty R, Basu T (2012) A simple robust method for synthesis of metallic copper nanoparticles of high antibacterial potency againstE. coli. Nanotechnology 23(8):085103. https://doi.org/10.1088/0957-4484/23/8/085103

Chandran H, Meena M, Sharma K (2020) Microbial biodiversity and bioremediation assessment through omics approaches. Front Environ Chem 1:9

Chandrasekhar C, Ray JG (2019) Lead accumulation, growth responses and biochemical changes of three plant species exposed to soil amended with different concentrations of lead nitrate. Ecotoxicol Environ Saf 171:26–36

Chaudhary A, Shirodkar S, Sharma A (2017) Characterization of nickel tolerant bacteria isolated from heavy metal polluted glass industry for its potential role in bioremediation. Soil Sediment Contam Int J 26(2):184–194

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 (15 pp). Environ Sci Pollut Res 12(1):34–48

Chen SH, Cheow YL, Ng SL, Ting AS (2019) Mechanisms for metal removal established via electron microscopy and spectroscopy: a case study on metal tolerant fungi *Penicillium simplicissimum*. J Hazard Mater 362:394–402

Cunningham SD, Berti WR, Huang JW (1995) Phytoremediation of contaminated soils. Trends Biotechnol 13(9):393–397

Cunningham SD, Ow DW (1996) Promises and Prospects of Phytoremediation. Plant Physiol 110(3):715–719. https://doi.org/10.1104/pp.110.3.715

Danis U, Nuhoglu A, Demirbas A (2008) Ferrous ion-oxidizing in *Thiobacillus ferrooxidans* batch cultures: influence of pH, temperature and initial concentration of Fe2+. Fresenius Environ Bull 17(3):371–377

Demougeot-Renard H, De Fouquet C (2004) Geostatistical approach for assessing soil volumes requiring remediation: validation using lead-polluted soils underlying a former smelting works. Environ Sci Technol 38(19):5120–5126

Dickinson NM, Baker AJ, Doronila A, Laidlaw S, Reeves RD (2009) Phytoremediation of inorganics: realism and synergies. Int J Phytoremediation 11(2):97–114

Doty SL (2008) Enhancing phytoremediation through the use of transgenics and endophytes. New Phytol 179(2):318–333

El-Sayed MT (2015) An investigation on tolerance and biosorption potential of Aspergillus awamori ZU JQ 965830.1 TO Cd (II). Ann Microbiol 65(1):69–83

EPA, A (2004) Risk assessment guidance for superfund. Volume I: Human health evaluation manual (Part E, supplemental guidance for dermal risk assessment) (Vol. 5). EPA/540/R/99. Available at: http://www.epa.gov/oswer/riskassessment/ragse/

Esringü A, Turan M, Güneş A, Karaman MR (2014) Roles of Bacillus megaterium in remediation of boron, lead, and cadmium from contaminated soil. Commun Soil Sci Plant Anal 45(13):1741–1759

Fang L, Zhou C, Cai P, Chen W, Rong X, Dai K, Liang W, Gu JD, Huang Q (2011) Binding characteristics of copper and cadmium by cyanobacterium Spirulina platensis. J Hazard Mater 190(1–3):810–815

Fu F, Dionysiou DD, Liu, H. (2014) The use of zero-valent iron for groundwater remediation and wastewater treatment: A review. J Hazard Mater 267:194–205. https://doi.org/10.1016/j.jhazmat.2013.12.062

Galal TM, Gharib FA, Ghazi SM, Mansour KH (2017) Phytostabilization of heavy metals by the emergent macrophyte Vossia cuspidata (Roxb.) Griff: A phytoremediation approach. Int J Phytoremediation 19(11):992–999

Gan Y, Wang L, Yang G, Dai J, Wang R, Wang W (2017) Multiple factors impact the contents of heavy metals in vegetables in high natural background area of China. Chemosphere 184: 1388–1395. https://doi.org/10.1016/j.chemosphere.2017.06.072

Gan W, He Y, Zhang X, Shan Y, Zheng L, Lin Y (2012) Speciation analysis of heavy metals in soils polluted by electroplating and effect of washing to the removal of the pollutants. J Ecol Rural Environ 28(1):82–87

Gan Y, Miao Y, Wang L, Yang G, Li YC, Wang W, Dai J (2018) Source contribution analysis and collaborative assessment of heavy metals in vegetable-growing soils. J Agric Food Chem 66(42):10943–10951

Glass DJ (2000) Economic Potential of Phytoremediation In: Raskin I, and Ensley BD Eds., Phytoremediation of Toxic Metals: Using Plants to Clean up the Environment, John Wiley & Sons Inc, New York, pp.15–31

Glick BR (2004) Bacterial ACC deaminase and the alleviation of plant stress. Advances in applied microbiology 56:291–312

Gola D, Dey P, Bhattacharya A, Mishra A, Malik A, Namburath M, Ahammad SZ (2016) Multiple heavy metal removal using an entomopathogenic fungi *Beauveria bassiana*. Bioresour Technol 218:388–396

Goyal N, Jain SC, Banerjee UC (2003) Comparative studies on the microbial adsorption of heavy metals. Adv Environ Res 7(2):311–319

Gul I, Manzoor M, Kallerhoff J, Arshad M (2020) Enhanced phytoremediation of lead by soil applied organic and inorganic amendments: Pb phytoavailability, accumulation and metal recovery. Chemosphere 258:127405

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(4):364–372

Gyamfi E, Appiah-Adjei EK, Adjei KA (2019) Potential heavy metal pollution of soil and water resources from artisanal mining in Kokoteasua, Ghana. Groundw Sustain Dev 8:450–456

Harvey PJ, Campanella BF, Castro PM, Harms H, Lichtfouse E, Schäffner AR, Smrcek S, Werck-Reichhart D (2002) Phytoremediation of polyaromatic hydrocarbons, anilines and phenols. Environ Sci Pollut Res 9(1):29–47

Hu N, Luo Y, Song J, Wu L, Zhang H (2010) Influences of soil organic matter, pH and temperature on Pb sorption by four soils in Yangtze River Delta. Acta Pedol Sin 47(2):246–252

Huang D, Gong X, Liu Y, Zeng G, Lai C, Bashir H, Zhou L, Wang D, Xu P, Cheng M, Wan J (2017) Effects of calcium at toxic concentrations of cadmium in plants. Planta 245(5):863–873

Infante JC, De Arco RD, Angulo ME (2014) Removal of lead, mercury and nickel using the yeast Saccharomyces cerevisiae. Revista MVZ Córdoba 19(2):4141–4149

Jain AN, Udayashankara TH, Lokesh KS (2012) Review on bioremediation of heavy metals with microbial isolates and amendments on soil residue. Int J Sci Res 6:2319–7064

Jiang J, Liu H, Li Q, Gao N, Yao Y, Xu H (2015) Combined remediation of Cd–phenanthrene co-contaminated soil by *Pleurotus cornucopiae* and Bacillus thuringiensis FQ1 and the antioxidant responses in *Pleurotus cornucopiae*. Ecotoxicol Environ Saf 120:386–393

Jiang HH, Cai LM, Wen HH, Hu GC, Chen LG, Luo J (2020) An integrated approach to quantifying ecological and human health risks from different sources of soil heavy metals. Sci Total Environ 701:134466

Jin Y, Luan Y, Ning Y, Wang L (2018) Effects and mechanisms of microbial remediation of heavy metals in soil: a critical review. Appl Sci 8(8):1336

Kamarudzaman AN, Chay TC, Amir A, Talib SA (2015) Biosorption of Mn (II) ions from aqueous solution by Pleurotus spent mushroom compost in a fixed-bed column. Procedia Soc Behav Sci 195:2709–2716

Karachaliou T, Kaliampakos D (2011) ORFA: introducing a method for maximizing social profit from soil remediation funds. J Soils Sediments 11(2):260–270

Karci A, Arslan-Alaton I, Bekbolet M, Ozhan G, Alpertunga B (2014) H2O2/UV-C and photo-Fenton treatment of a nonylphenol polyethoxylate in synthetic freshwater: follow-up of degradation products, acute toxicity and genotoxicity. Chem Eng J 241:43–51

Kassaye G, Gabbiye N, Alemu A (2017) Phytoremediation of chromium from tannery wastewater using local plant species. Water Pract Technol 12(4):894–901

Khalid S, Shahid M, Niazi NK, Murtaza B, Bibi I, Dumat C (2017) A comparison of technologies for remediation of heavy metal contaminated soils. J Geochem Explor 182:247–268

Krug TA, Wolfe C, Norris RD, Winstead CJ (2009) Cost analysis of in situ perchlorate bioremediation technologies. In: In situ bioremediation of perchlorate in groundwater. Springer, New York, pp 199–218

Kim RY, Yoon JK, Kim TS, Yang J E, Owens G, Kim KR (2015) Bioavailability of heavy metals in soils: definitions and practical implementation—a critical review. Environ Geochem Health 37(6):1041–1061. https://doi.org/10.1007/s10653-015-9695-y

Kumar V, Sharma A, Kaur P, Sidhu GP, Bali AS, Bhardwaj R, Thukral AK, Cerda A (2019) Pollution assessment of heavy metals in soils of India and ecological risk assessment: a state-of-the-art. Chemosphere 216:449–462

Kumar A, Hussain T, Susmita C, Maurya DK, Danish M, Farooqui SA (2021) Microbial remediation and detoxification of heavy metals by plants and microbes. In: The future of effluent treatment plants. Elsevier, Amsterdam, pp 589–614

Lakkireddy K, Kües U (2017) Bulk isolation of basidiospores from wild mushrooms by electrostatic attraction with low risk of microbial contaminations. AMB Express 7(1):1–22

Laurenti M, Garcia Blanco F, Lopez-Cabarcos E, Rubio-Retama J (2013) Detection of heavy metal ions using a water-soluble conjugated polymer based on thiophene and meso-2, 3-dimercaptosuccinic acid. Polym Int 62(5):811–816

Le Maitre DC, Gaertner M, Marchante E, Ens EJ, Holmes PM, Pauchard A, O’Farrell PJ, Rogers AM, Blanchard R, Blignaut J, Richardson DM (2011) Impacts of invasive Australian acacias: implications for management and restoration. Divers Distrib 17(5):1015–1029

Lemming G, Hauschild MZ, Bjerg PL (2010) Life cycle assessment of soil and groundwater remediation technologies: literature review. Int J Life Cycle Assess 15(1):115–127

Licht LA, Isebrands JG (2005) Linking phytoremediated pollutant removal to biomass economic opportunities. Biomass Bioenergy 28(2):203–218

Luo SL, Chen L, Chen JL, Xiao X, Xu TY, Wan Y, Rao C, Liu CB, Liu YT, Lai C, Zeng GM (2011) Analysis and characterization of cultivable heavy metal-resistant bacterial endophytes isolated from Cd-hyperaccumulator Solanum nigrum L. and their potential use for phytoremediation. Chemosphere 85(7):1130–1138

Luna JM, Rufino RD, Sarubbo LA (2016) Biosurfactant from Candida sphaerica UCP0995 exhibiting heavy metal remediation properties. Process Saf Environ Prot 102:558–566. https://doi.org/10.1016/j.psep.2016.05.010

Ma Y, Prasad MN, Rajkumar M, Freitas HJ (2011) Plant growth promoting rhizobacteria and endophytes accelerate phytoremediation of metalliferous soils. Biotechnol Adv 29(2):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

Ma Y, Rajkumar M, Zhang C, Freitas H (2016) Inoculation of Brassica oxyrrhina with plant growth promoting bacteria for the improvement of heavy metal phytoremediation under drought conditions. J Hazard Mater 320:36–44

Mahdavian K, Ghaderian SM, Torkzadeh-Mahani M (2017) Accumulation and phytoremediation of Pb, Zn, and Ag by plants growing on Koshk lead–zinc mining area. Iran J Soils Sediments 17(5):1310–1320

Marchenko AM, Pshinko GN, Demchenko VY, Goncharuk VV (2015) Leaching heavy metal from deposits of heavy metals with bacteria oxidizing elemental sulphur. J Water Chem Technol 37(6):311–316

Maropola MK, Ramond JB, Trindade M (2015) Impact of metagenomic DNA extraction procedures on the identifiable endophytic bacterial diversity in Sorghum bicolor (L. Moench). J Microbiol Methods 112:104–117

Marques AP, Rangel AO, Castro PM (2009) Remediation of heavy metal contaminated soils: phytoremediation as a potentially promising clean-up technology. Crit Rev Environ Sci Technol 39(8):622–654

Meagher RB, Heaton AC (2005) Strategies for the engineered phytoremediation of toxic element pollution: mercury and arsenic. J Ind Microbiol Biotechnol 32(11–12):502–513

Medfu Tarekegn M, Zewdu Salilih F, Ishetu AI (2020) Microbes used as a tool for bioremediation of heavy metal from the environment. Cogent Food Agric 6(1):1783174. https://doi.org/10.1080/23311932.2020.1783174

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. https://doi.org/10.3389/fpls.2016.00303

Mohsenzadeh F, Nasseri S, Mesdaghinia A, Nabizadeh R, Zafari D, Khodakaramian G, Chehregani A (2010) Phytoremediation of petroleum-polluted soils: application of Polygonum aviculare and its root-associated (penetrated) fungal strains for bioremediation of petroleum-polluted soils. Ecotoxicol Environ Saf 73(4):613–619

Moore FP, Barac T, Borremans B, Oeyen L, Vangronsveld J, Van der Lelie D, 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 29(7):539–556

Ollivier PR, Bahrou AS, Church TM, Hanson TE (2011) Aeration controls the reduction and methylation of tellurium by the aerobic, tellurite-resistant marine yeast Rhodotorula mucilaginosa. Appl Environ Microbiol 77(13):4610–4617

Özdemir S, Kilinc E, Poli A, Nicolaus B, Güven K (2012) Cd, Cu, Ni, Mn and Zn resistance and bioaccumulation by thermophilic bacteria, Geobacillus toebii subsp. decanicus and Geobacillus thermoleovorans subsp. stromboliensis. World J Microbiol Biotechnol 28(1):155–163

Özdemir S, Kılınç E, Poli A, Nicolaus B (2013) Biosorption of heavy metals (Cd2+, Cu2+, Co2+, and Mn2+) by thermophilic bacteria, Geobacillus thermantarcticus and Anoxybacillus amylolyticus: equilibrium and kinetic studies. Biorem J 17(2):86–96

Padmavathiamma PK, Li LY (2007) Phytoremediation technology: hyper-accumulation metals in plants. Water Air Soil Pollut 184(1):105–126

Pande V, Pandey SC, Sati D, Pande V, Samant M (2020) Bioremediation: an emerging effective approach towards environment restoration. Environ Sustain 3(1):91–103

Pandey VC, Souza-Alonso P (2019) Market opportunities: in sustainable phytoremediation. In: Phytomanagement of polluted sites. Elsevier, Amsterdam, pp 51–82

Park JH, Lee SJ, Lee ME, Chung JW (2016) Comparison of heavy metal immobilization in contaminated soils amended with peat moss and peat moss-derived biochar. Environ Sci: Processes Impacts 18(4):514–520

Patel MJ, Tipre DR, Dave SR (2009) Isolation and identification of a Candida digboiensis strain from an extreme acid mine drainage of the Lignite Mine, Gujarat. J Basic Microbiol 49(6):564–571

Phetcharat P, Duangpaeng A (2012) Screening of endophytic bacteria from organic rice tissue for indole acetic acid production. Procedia Eng 32:177–183

Philp JC, Bamforth SM, Singleton I, Atlas RM (2005) Environmental pollution and restoration: a role for bioremediation. In: Bioremediation: applied microbial solutions for real-world environmental cleanup, pp 1–48

Prasad MNV, 2003 Metal Hyperaccumulation in Plants-Biodiversity Prospecting for Phytoremediation Technology. Electron J Biotechnol 6:1–25. http://doi.org/10.2225/vol6-issue3-fulltext-6

Pierart A, Shahid M, Séjalon-Delmas N, Dumat C (2015) Antimony bioavailability: knowledge and research perspectives for sustainable agricultures. J Hazard Mater 289:219–234

Pilon-Smits E (2005) Phytoremediation. Annu Rev Plant Biol 56(1):15–39. https://doi.org/10.1146/annurev.arplant.56.032604.144214

Rahman Z (2020) An overview on heavy metal resistant microorganisms for simultaneous treatment of multiple chemical pollutants at co-contaminated sites, and their multipurpose application. J Hazard Mater 396:122682

Rahman M, Sathasivam KV (2015) Heavy metal adsorption onto Kappaphycus sp. from aqueous solutions: the use of error functions for validation of isotherm and kinetics models. Biomed Res Int 2015

Rajkumar M, Ae N, Freitas H (2009) Endophytic bacteria and their potential to enhance heavy metal phytoextraction. Chemosphere 77(2):153–160

Rajkumar M, Sandhya S, Prasad MN, Freitas H (2012) Perspectives of plant-associated microbes in heavy metal phytoremediation. Biotechnol Adv 30(6):1562–1574

Rajkumar M, Prasad MN, Swaminathan S, Freitas H (2013) Climate change driven plant–metal–microbe interactions. Environ Int 53:74–86

Rodríguez-Tirado V, Green-Ruiz C, Gómez-Gil B (2012) Cu and Pb biosorption on Bacillus thioparans strain U3 in aqueous solution: kinetic and equilibrium studies. Chem Eng J 181:352–359

Ryan RP, Germaine K, Franks A, Ryan DJ, Dowling DN (2008) Bacterial endophytes: recent developments and applications. FEMS Microbiol Lett 278(1):1–9

Salt DE, Blaylock M, Kumar NP, Dushenkov V, Ensley BD, Chet I, Raskin I (1995) Phytoremediation: a novel strategy for the removal of toxic metals from the environment using plants. Bio/Technology 13(5):468–474

Schnoor JL (1997) Phytoremediation. Technology evaluation report TE-98-01. Ground-Water Remediation Technologies Analysis Center, Pittsburgh

Schulz BJ, Boyle C (2006) What are Endophytes? Soil Biology 1–13. https://doi.org/10.1007/3-540-33526-9_1

Scholz RW, Schnabel U (2006) Decision making under uncertainty in case of soil remediation. J Environ Manag 80(2):132–147

Sessitsch A, Reiter B, Pfeifer U, Wilhelm E (2002) Cultivation-independent population analysis of bacterial endophytes in three potato varieties based on eubacterial and Actinomycetes-specific PCR of 16S rRNA genes. FEMS Microbiol Ecol 39(1):23–32

Sharma S, Tiwari S, Hasan A, Saxena V, Pandey LM (2018) Recent advances in conventional and contemporary methods for remediation of heavy metal-contaminated soils. 3 Biotech 8(4):1–8

Sharma P, Kumar S, Pandey A (2021a) Bioremediated techniques for remediation of metal pollutants using metagenomics approaches: a review. J Environ Chem Eng 9:105684

Sharma P, Tripathi S, Chandra R (2021b) Highly efficient phytoremediation potential of metal and metalloids from the pulp paper industry waste employing Eclipta alba (L) and Alternanthera philoxeroide (L): biosorption and pollution reduction. Bioresour Technol 319:124147

Shi W, Becker J, Bischoff M, Turco RF, Konopka AE (2002) Association of microbial community composition and activity with lead, chromium, and hydrocarbon contamination. Appl Environ Microbiol 68(8):3859–3866

Shin MN, Shim J, You Y, Myung H, Bang KS, Cho M, Kamala-Kannan S, Oh BT (2012) Characterization of lead resistant endophytic Bacillus sp. MN3-4 and its potential for promoting lead accumulation in metal hyperaccumulator Alnus firma. J Hazard Mater 199:314–320

Shokoohi R, Salari M, Molla Mahmoudi M, Azizi S, Ghiasian SA, Faradmal J, Faraji H (2020) The sorption of cationic and anionic heavy metal species on the biosorbent of Aspergillus terreus: isotherm, kinetics studies. Environ Prog Sustain Energy 39(2):e13309

Singh AK, Bhatt BP, Sundaram PK, Gupta AK, Singh D (2013) Planting geometry to optimize growth and productivity in faba bean (*Vicia faba L.) and soil fertility. J Environ Biol 34(1):117–122*

Singh S, Kumar V, Upadhyay N, Singh J, Singla S, Datta S (2017) Efficient biodegradation of acephate by Pseudomonas pseudalcaligenes PS-5 in the presence and absence of heavy metal ions [Cu (II) and Fe (III)], and humic acid. 3 Biotech 7(4):1-0

Singh S, Kumar V, Sidhu GK, Datta S, Dhanjal DS, Koul B, Janeja HS, Singh J (2019) Plant growth promoting rhizobacteria from heavy metal contaminated soil promote growth attributes of Pisum sativum L. Biocatal Agric Biotechnol 17:665–671

Singh M, Singh D, Rai PK, Suyal DC, Saurabh S, Soni R, Giri K, Yadav AN (2021) Fungi in remediation of hazardous wastes: current status and future outlook. In: Recent trends in mycological research. Springer, Cham, pp 195–224

Srinath T, Verma T, Ramteke PW, Garg SK (2002) Chromium (VI) biosorption and bioaccumulation by chromate resistant bacteria. Chemosphere 48(4):427–435

Srivastava S, Thakur IS (2006) Biosorption Potency of Aspergillus niger for Removal of Chromium (VI). Curr Microbiology 53(3):232–237. https://doi.org/10.1007/s00284-006-0103-9

Srivastava V, Tanmay S, Suresh Kumar M (2019) Fate of the persistent organic pollutant (POP) Hexachlorocyclohexane (HCH) and remediation challenges. Int Biodeterior Biodegradation 140 (2019):43–56

Soares EV, Soares HM (2012) Bioremediation of industrial effluents containing heavy metals using brewing cells of Saccharomyces cerevisiae as a green technology: a review. Environ Sci Pollut Res 19(4):1066–1083

Tang X, Zeng G, Fan C, Zhou M, Tang L, Zhu J, Wan J, Huang D, Chen M, Xu P, Zhang C (2018) Chromosomal expression of CadR on Pseudomonas aeruginosa for the removal of Cd (II) from aqueous solutions. Sci Total Environ 636:1355–1361

Thakur M, Medintz IL, Walper SA (2019) Enzymatic bioremediation of organophosphate compounds—progress and remaining challenges. Front Bioeng Biotechnol 7:289

Tóth G, Hermann T, Da Silva MR, Montanarella L (2016) Heavy metals in agricultural soils of the European Union with implications for food safety. Environ Int 88:299–309

Tyagi S, Kumar V, Singh J, Teotia P, Bisht S, Sharma S (2014) Bioremediation of pulp and paper mill effluent by dominant aboriginal microbes and their consortium. Int J Environ Res 8(3):561–568

Ullah R, Hadi F, Ahmad S, Jan AU, Rongliang Q (2019) Phytoremediation of lead and chromium contaminated soil improves with the endogenous phenolics and proline production in Parthenium, Cannabis, Euphorbia, and Rumex species. Water Air Soil Pollut 230(2):40

Vermote L, Verce M, De Vuyst L, Weckx S (2018) Amplicon and shotgun metagenomic sequencing indicates that microbial ecosystems present in cheese brines reflect environmental inoculation during the cheese production process. Int Dairy J 87:44–53

Visioli G, D'Egidio S, Vamerali T, Mattarozzi M, Sanangelantoni AM (2014) Culturable endophytic bacteria enhance Ni translocation in the hyperaccumulator Noccaea caerulescens. Chemosphere 117:538–544

Wan X, Lei M, Chen T (2016) Cost–benefit calculation of phytoremediation technology for heavy-metal-contaminated soil. Sci Total Environ 563–564:796–802. https://doi.org/10.1016/j.scitotenv.2015.12.080

Wang L, Ji B, Hu Y, Liu R, Sun W (2017) A review on in situ phytoremediation of mine tailings. Chemosphere 184:594–600

Wei S, Zhou QX (2006) Phytoremediation of cadmium-contaminated soils by Rorippa globosa using two-phase planting (5 pp). Environ Sci Pollut Res 13(3):151–155

Wei Y, Hou H, ShangGuan Y, Li J, Li F (2014) Genetic diversity of endophytic bacteria of the manganese-hyperaccumulating plant Phytolacca americana growing at a manganese mine. Eur J Soil Biol 62:15–21

Weisburg WG, Barns SM, Pelletier DA, Lane DJ (1991) 16S ribosomal DNA amplification for phylogenetic study. J Bacteriol 173(2):697–703

Wierzba S (2015) Biosorption of lead (II), zinc (II) and nickel (II) from industrial wastewater by Stenotrophomonas maltophilia and Bacillus subtilis. Pol J Chem Technol 17(1)

Witters N, Mendelsohn RO, Van Slycken S, Weyens N, Schreurs E, Meers E, Tack F, Carleer R, Vangronsveld J (2012) Phytoremediation, a sustainable remediation technology? Conclusions from a case study. I: Energy production and carbon dioxide abatement. Biomass Bioenergy 39:454–469

Wu D, Yu X, Lai M, Feng J, Dong X, Peng W, Su S, Zhang X, Wan L, Jacobs DF, Zeng S (2021) Diversified effects of co-planting landscape plants on heavy metals pollution remediation in urban soil amended with sewage sludge. J Hazard Mater 403:123855

Wuana RA, Okieimen FE (2011) Heavy metals in contaminated soils: a review of sources, chemistry, risks and best available strategies for remediation. Int Sch Res Notices: pp 1–20

Xiong T, Austruy A, Pierart A, Shahid M, Schreck E, Mombo S, Dumat C (2016) Kinetic study of phytotoxicity induced by foliar lead uptake for vegetables exposed to fine particles and implications for sustainable urban agriculture. J Environ Sci 46:16–27

Yahaya YA, Don MM (2014) Pycnoporus sanguineus as potential biosorbent for heavy metal removal from aqueous solution: a review. J Phys Sci 25(1):1

Yang Y, Zeng Z, Zeng G, Huang D, Xiao R, Zhang C, Zhou C, Xiong W, Wang W, Cheng M, Xue W (2019) Ti3C2 Mxene/porous g-C3N4 interfacial Schottky junction for boosting spatial charge separation in photocatalytic H2O2 production. Appl Catal B Environ 258:117956

Zhang YF, He LY, Chen ZJ, Wang QY, Qian M, Sheng XF (2011) Characterization of ACC deaminase-producing endophytic bacteria isolated from copper-tolerant plants and their potential in promoting the growth and copper accumulation of Brassica napus. Chemosphere 83(1):57–62

Zhang X, Li M, Yang H, Li X, Cui Z (2018) Physiological responses of Suaeda glauca and Arabidopsis thaliana in phytoremediation of heavy metals. J Environ Manag 223:132–139

Zhu LJ, Guan DX, Luo J, Rathinasabapathi B, Ma LQ (2014) Characterization of arsenic-resistant endophytic bacteria from hyperaccumulators Pteris vittata and Pteris multifida. Chemosphere 113:9–16

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(8):909–916

Part V

Phytoremediation of Organic and Inorganic Contaminants and Organic-Inorganic Mixtures

Chapter 13
Prospects for the Use of *Sorghum Bicolor* for Phytoremediation of Soils Contaminated with Heavy Metals in Temperate Climates

S. V. Gorelova, A. P. Kolbas, A. Yu. Muratova, M. V. Frontasyeva, I. Zinicovscaia, and O. I. Okina

Abstract The chapter provides information on a strategy for remediation of soils contaminated with potential toxic trace elements (PTTE) using high biomass plants including the following steps:

1. Evaluation of the initial level of pollution and environmental risks
2. Selection of plant/microorganisms/amendments candidates and suitable options
3. Implementation of the selected remediation strategy in the field condition (pilot)
4. Biomass valorization and developing the remediation strategy and implementation in the large scale

The possibility of using *Sorghum bicolor cv. Sucro* and *Biomass* for phytoremediation of urban soils of sanitary protection zones of enterprises and highways was investigated in a model experiment. The influence of polluted soils with different elements on growth, physiological adaptation of plants to oxidative stress, and biomass formation has been assessed. The stimulating effect of soil polluted with PTTE

S. V. Gorelova (✉)
Tula State University, Natural Science Institute, Tula, Russia

A. P. Kolbas
Brest State A. Pushkin University, Brest, Belarus

Institute of Nature Management of the National Academy of Sciences of Belarus, Minsk, Belarus

A. Y. Muratova
Institute of Biochemistry and Physiology of Plants and Microorganisms, Russian Academy of Sciences, Saratov, Russia

M. V. Frontasyeva · I. Zinicovscaia
Joint Institute for Nuclear Research, Dubna, Moscow, Russia

O. I. Okina
Geological Institute of the Russian Academy of Sciences, Moscow, Russia

L. Newman et al. (eds.), *Phytoremediation*, https://doi.org/10.1007/978-3-031-17988-4_13

on the growth and formation of biomass of the studied sorghum varieties was revealed. It was found that sorghum well adapts to the conditions of moderate polyelement pollution: the content of the components of the antioxidant system (carotenoids, ascorbic acid, glutathione, and phenolic compounds) in both studied varieties grown on urban soils with polyelement anomalies was higher than on the soils of the background zone.

The bioaccumulation of elements from soils of experimental zones in a model experiment of two *Sorghum bicolor* cultivars was assessed using a complex of physico-chemical methods of analysis (AAS, INAA and ICP MS). It was found that the sorghum root system absorbs a large amount of Fe (3460–96,100 mg/kg), Mn (289–1780 mg/kg), V (3.5–45.5 mg/kg) and Cr (4.3–16 mg/kg dry weigth) from soils. Differences between cultivars were revealed in the accumulation of such elements as Pb, Cu, As and Ba (*Sorghum bicolor cv. Sucro* accumulates more elements). The barrier role of the root system in relation to these elements and a decrease in their uptake by the shoots was investigated. The main mechanism for extracting the listed elements from soils is rhizofiltration. It is shown that sorghum is promising for phytoextraction of zinc from soils when the permissible concentrations are exceeded.

The rhizosphere microflora of sorghum grown on soils with multielement anomalies has been studied. The characteristics of the isolated microorganism strains suggested that the rhizosphere of *S. bicolor cv. Biomass* had greater microbial diversity in comparison with rhizosphere of *S. bicolor cv. Sucro*. It was found that the rhizosphere of sorghum *Sucro* was characterized by an increased number of microorganisms in highly contaminated highway soils; therefore, this variety may be more promising for phytoremediation of sanitary protection zones of highways. As a result of the research, 47 heavy-metal-resistant microbial isolates were collected. In the future, a promising inoculant will be selected to improve the growth of sorghum plants in heavy metal contaminated soils and to increase the efficiency of phytoremediation.

Calculation of the removal of elements from soils showed that due to its significant biomass, sorghum is efficiently used for phytoextraction of Pb and Cu (variety Sucro) and V, Cr, Co, Mn, Zn and As (variety Biomass). Both studied sorghum varieties actively absorb iron by roots and phytoextract some amount in shoots. All the above facts, as well as the ability to valorize the resulting biomass, make it possible to recommend sorghum for remediation of urban soils with polyelement contamination.

Keywords Potential toxic trace elements (PTTE) · Soil pollution · High biomass plants · *Sorghum bicolor* · Soil bioremediation · Heavy metals · Adaptation to stress · Bioaccumulation · Rhizosphere microflora · Resistance to PTTE

13.1 Introduction. High Biomass Plants in Soil Phytoremediation. Features of Use

Plants that are selected for soil phytoremediation are usually characterized by high accumulative abilities for heavy metals or organic pollutants.

However, most of them, being hyperaccumulators, do not differ in high biomass, and when conducting phytoremediation measures, it is important to take into account the adaptive abilities of plants and the total number of toxic components that a plant can accumulate in itself (phytoextraction) or convert into insoluble forms per unit of biomass from unit area.

A multidisciplinary approach is warranted to make phytoextraction a feasible commercial technology to remediate Me-contaminated soils (Pilon-Smits 2005; Vangronsveld et al. 1996, 2009; Mench et al. 2018). Options for the appraisal of phytoextraction depend on several initial settings, some being related to legislation. They are as follows: (1) the initial concentrations of matrix contaminants, the magnitude of their labile pools that interact with biota and risks these pose for relevant pollutant linkages, (2) remediation objectives based on proposed end use, and (3) site management constraints.

Based on our results and other research studies carried out on TSU, BRSU, and BIOGECO platforms, a management plan is suggested in the purpose of full-cycle phytoremediation of Me-contaminated sites using sustainable aided phytoextraction strategy tandem with high biomass production, including the following steps (Fig. 13.1):

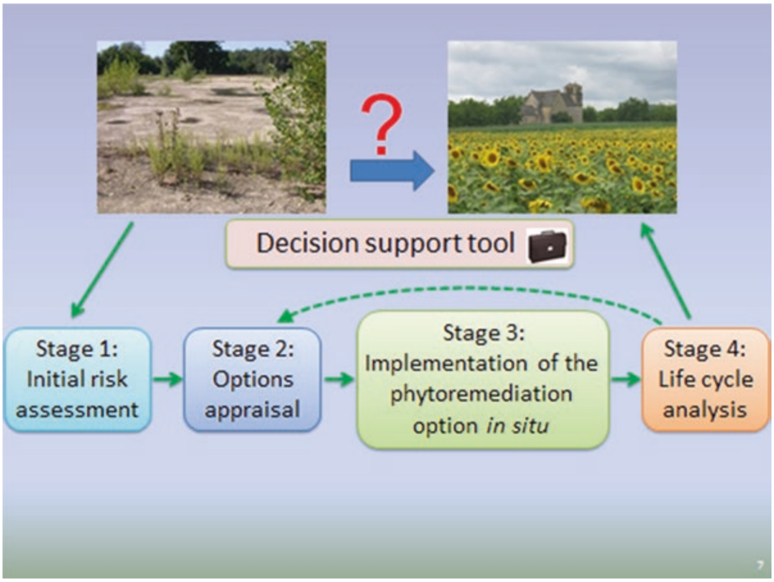


Fig. 13.1 Bioremediation of Me-contaminated soils

1. Evaluation of the initial level of pollution and environmental risks. First, the site's suitability for phytoextraction should be evaluated by field observations and laboratory studies. Soil samples should be analyzed to determine not only the magnitude of metal contamination, but also other physico-chemical parameters influencing the behavior of metal in the soil and soil solution, chemical forms in which metals are present for determining whether decreasing metal concentrations to target cleanup criteria by means of phytoextraction can be a realistic option (Kolbas et al. 2014). Bioassays using phyto- or zooindicators can be applied to determine the bioavailable fraction of contaminant. The biocenotic research of plant and animal communities living in the contaminated area is necessary to carry out for a subsequent long-term monitoring. It is also recommended to study the genetic structure of populations.
2. Selection of plant/microorganisms/amendments candidates and suitable options. The site-specific capacities of various plant species/cultivars/mutants/clones to survive, accumulate, and tolerate metals should likewise be tested under laboratory conditions using bioassay and/or fading techniques. Next, the most indicative plant parameters must be measured: biochemical, chemical, morphological, and physiological traits. The defined limits of plant tolerance allow us to determine the range of contamination, where phytoextraction can be most effective and to model the trace elements (TE) transfer from soils and roots to harvestable parts. With the help of amendments, we can regulate bioavailable fractions in soil (increase or decrease depending on objectives). In parallel, the improving role of bacteria and mycorrhizae can be tested (Hagerberg et al. 2011; Mench et al. 2018; Kolbas et al. 2015). Based on the gathered information, as well as on the local climatic conditions, a suitable plant/microorganisms/amendments combination may then be selected.
3. Implementation of the selected remediation strategy in the field condition (pilot). Before starting the implementation of phytoremediation option, a planning is needed, because many operations have to start much earlier than the planting (e.g., amendment addition, seed inoculation and seedling cultivation). The plant mortality and productivity of various parts (vegetative and generative) influence plant density. In view of allelopathic and pathogenic relations, intercropping and/or crop rotation can be successfully used (Fig. 13.2). During the field experience, the plant status must be constantly monitored, and if necessary, fertilization, irrigation (especially in the first stages of development), and other agricultural practices must be adapted (Faessler et al. 2010; Kidd et al. 2015). It is necessary to apply mechanical means for plot isolation and protection (fencing and netting) against wild animals (with both objectives to protect animal to toxic feed resources and to preserve the plant harvest). Time and type of harvest and separation of the collected parts depend on the pollutant content and type of subsequent valorization. If in the future the green parts of plants will be used, the harvest of non-senescent biomass is recommended to avoid reincorporation of contaminated plant parts (especially leaves) into the soil. It is also recommended

Fig. 13.2 Three-years' crop rotation: i.e., sunflower, tobacco, and vetiver in field plots at a former wood preservation site (BIOGECO platform, M. Mench, France)

to cultivate intermediate crops after harvest – so-called winter crop cover in temperate climate.

4. Biomass valorization and developing the remediation strategy and implementation in the large scale. The choice of conversion process for plant material depends on its type and contaminant content. If it is oil-based substrate with low metal contents, the most cost-effective manner is the production of biodiesel (sunflower and tobacco), bioethanol (tobacco), or essential oils (vetiver). Sugary seeds and shoot (sorghum) can be used to produce bioethanol. The seeds with negligible Me content were recommended also for animal feed. The main part of the green mass of plants may be susceptible to various conversion processes, depending on the level of contamination and local conversion chains: (1) composting to fertilize TE-deficient soil (low Me-level); (2) vacuum and oxidative pyrolysis; (3) liquid extraction; (4) synthesis of hydrogen fuel, biofuel and bioplastic; (5) biogas and activated carbons; (6) hydrothermal oxidation (Carrier et al. 2011) and (7) gasification.

Heavily contaminated material is sometime subjected to incineration or ashing with subsequent use of thermal energy. The resulting post-combustion ash can be used in the production of nutrient additives for the plants or buried in special landfills. Financial returns and other economical aspects are needed to be revised at this stage.

The monitoring of soil and biota, during (once in 3–5 years) and after the application of aided phytoextraction, is recommended for assessing the status of ecosystems and clarifying the real duration of phytoremediation. To date, commercial phytoextraction has been constrained by the expectation that site remediation should be achieved in a time comparable to other clean-up technologies. After a pilot testing, this low-cost technology should be used for the in situ remediation of large areas of contaminated land.

Potentially two strategies are used: (1) phytoextraction using hyperaccumulator plants with high concentrations of PTTE in harvestable plant parts but usually low biomass and (2) phytoextraction using secondary accumulator plants with high biomass and moderate PTTE concentrations in aerial plant parts. Starting from the discovery of hyperaccumulators (Brooks et al. 1977), which are able to concentrate high levels of specific PTTE in the aboveground biomass, there is now great interest in crop species, which may solve the bottleneck of the low biomass of hyperaccumulators. The use of hyperaccumulators is limited also by their low biodiversity, e.g., there are few reports of possible Me-accumulators, even though such plants have been reported in Zaire, central Africa and China, they usually demand specific climatic conditions (Baker et al. 2000; Reeves 2006; Sheoran et al. 2009).

These hyperaccumulators thrive when some PTTE contents (e.g., Cd, Ni, As, and Zn) are high, and it is likely that such PTTE levels in plant parts provide protection against herbivory or microbial attack (Boyd 2007). In several cases, the high Cu levels in plants from central Africa could be attributed to dust that could be removed by washing (Faucon et al. 2007). In addition, agronomic cultivation techniques are still in development for these plants.

Regarding secondary Cu-accumulators, the desirable characteristics for these plant species are (1) relatively fast growth and high biomass; (2) extended root system for exploring large soil volumes; (3) good tolerance to high concentrations of PTTE in plant tissues; (4) high translocation factor (TF); (5) adaptability to specific environments/sites; and (6) easy agricultural management (Vamerali et al. 2010). But usually points 3 and 4 are difficult to combine, so preference is given to tolerant plants with excluder traits. Metal(loid) removal by plants arises from two factors: (I) PTTE concentration in dry plant tissue (Gabrielli dos Santos et al. 2010) and (II) the amount of harvested biomass (Vangronsveld et al. 1996, 2009).

Moreover, some authors point to the leading role of the second factor. Therefore, working with plants with high biomass are becoming increasingly important (Sonowal et al. 2018). Among these plants, a significant group consists of C4 plants.

C4 plants are plants with a special type of photosynthesis characterized by high productivity and drought tolerance, that is especially important for urban and industrial soils with polyelemental anomalies which, in addition to direct toxic effects, cause physiological drought in the plants grown on them.

The deposition of carbon dioxide in the composition of the four-carbon compounds malate or aspartate allows these plants to keep stomata closed during a hot period or lack of moisture and to carry out photosynthesis even in the absence of gas exchange, when the stomata are closed. Intensive photosynthesis, which is carried out in the cells of the lining of the conductive beam with a low risk of photorespiration, allows plants to quickly transport the formed organic compounds into the cells of the phloem and transport through the plant.

Even with a small amount of toxic components carried per unit of biomass, due to the intense photosynthesis, C-4 plants form a large biological harvest in comparison of the C-3 type of photosynthesis plants, which allows one to consider them as phytoremediants under the absence of hyperaccumulative properties.

Sunflower is widely used for phytoremediation in temperate climates (Faessler et al. 2010; Kidd et al. 2015; Mench et al. 2018). Phytoextraction combined with oilseeds production for biofuel may represent a sustainable option (Vangronsveld et al. 1996). Several crops producing oilseeds, i.e., rapeseed (*Brassica napus* L.), Indian mustard (*Brassica juncea* (L.) Czern.), sunflower (*Helianthus annuus* L.), and common flax (*Linum usitatissimum* L.), can be cultivated on TE contaminated soils (Meers et al. 2005; Vangronsveld et al. 1996). Sunflower accumulates moderate TE concentrations, but due to its high biomass production, it has been used to phytoextract Zn, Pb, Cd, Cu, and radionuclides (Madejon et al. 2003; Marchiol et al. 2007; Vangronsveld et al. 1996, 2009; Nehnevajova et al. 2007; Mench et al. 2018) (Table 13.1).

Sorghum can be included in a sustainable crop rotation for promoting soil development processes, nutrient cycles, microbial community, and soil ecosystem functions with either or no acceptable residual pollutant linkages.

Sorghum previously used in both the fading experiment (Fig. 13.3), and the field-trial in 2010–2018 (Fig. 13.4) showed a moderate resistance to PTTEs. Due to these qualities, sorghum can be effectively used as a bioindicator and bioremediator of low contaminated soils. In our investigation two commercial sorghum cultivars (Sucro and Biomas) were tested. A comparison of the copper accumulation by sorghum relative to other biomass crops is shown in Table 13.2. Sorghum was selected also for biomass and bioethanol production (Sathya et al. 2016). Sorghum was previously used in both the fading experiments (Fig. 13.3), and the field trial in 2010–2018 (Fig. 13.4) showed a moderate resistance to PTTEs. Due to these qualities, sorghum can be effectively used as a bioindicator and bioremediator of low contaminated soils.

13.2 The Physiological Characteristics of Sorghum Growing on Soils Contaminated with Heavy Metals. Adaptation to Stress

The first step in our research was the study of the soils of a model urban ecosystem that has multielement soil anomalies in sanitary protection zones of industrial enterprises and roads.

Sampling and soil preparation were carried out in accordance with GOST R 53123-2008. The sampling depth was 0–25 cm (GOST 28168-89). Sample preparation and analysis was carried out on the basis of the chemical analytical laboratory of the Geological Institute of the Russian Academy of Sciences by X-ray fluorescence analysis using a Bruker ASX instrument.

Assessment of the level of chemical pollution of soils as an indicator of adverse effects on public health and the state of biota was carried out according to the following indicators: concentration coefficient of the chemical substance (Kc), which

Table 13.1 Phytoextraction of Cu depending on plant species in field trials and some pot experiments, with and without addition of chemical chelators in the soil

Plant species	Total soil Cu (mg kg^{-1})	Shoot Cu^{c} (mg kg^{-1} DW)	Shoot yield (Mg ha^{-1})	Cu removal (g ha^{-1} y^{-1})	References
B. juncea^{b}	516–570	20	7.3	146	Kayser et al. (2000)
B. napus	970			71	Claus et al. (2007)
B. rapa^{a,b}	162.6	11.28 37.8^{b}		Cu accumulated (%) 0.054 0.185^{b}	Kos and Lestan (2004)
G. max^{a}	94.4	11.6			Murakami and Ae (2009)
H. annuus(cultivars)	163–1170	10–51	0.2–7.0	10–58	Kolbas et al. (2011)
N. tabacum^{b}	516–570	38	12.6	474	Kayser et al. (2000)
S. bicolor^{b}	1527	28 49		50–820 644–3215	Marchiol et al. (2007)
S. bicolor	1491	4.6–11.7			Murillo et al. (1999)
T. caerulescens^{b}	460–529	53	0.9	50	Keller et al. (2003)
Z. mays^{a}	94.4	16.5			Murakami and Ae (2009)
Z. mays^{b}	516–570	10	15.6	163	Kayser et al. (2000)
Z. mays^{b}	460–529	8	14.2	108	Keller et al. (2003)
Z. mays^{b}	970			117	Claus et al. (2007)

B. juncea: Brassica juncea (L.) Czern., *B. napus: Brassica napus* L., *B. rapa*: *Brassica rapa* L., *G. max*: *Glycine max* (L.) Merr., *H. annuus: Helianthus annuus* L., *N. tabacum: Nicotiana tabacum* L., *S. bicolor: Sorghum bicolor* (L.) Moench, *T. caerulescens: Thlaspi caerulescens* J.&C. Presl., *Z. mays: Zea mays* L.

[a] Pot experiment

[b] Aided phytoextraction using chemical chelators

[c] Phytotoxic ranges for most plants (in mg Cu kg^{-1}): 15–30 (MacNicol and Beckett 1985), 25–40 (Chaney 1989), 10–70 (Gupta and Gupta 1998).

is determined by the ratio of the actual content of the analyte substance in the soil (Ci) in mg/kg of soil to the regional background (Cbg). Assessment of the degree of danger of soil pollution by the total pollution index Zc was carried out according to the accepted rating scale (Saet et al. 1990).

The results of the investigations showed that more than 40% of the territory of the selected ecosystem was characterized by excess of maximum permissible levels (MPC) of the set of heavy metals. The main element pollutants of urban (Tula city)

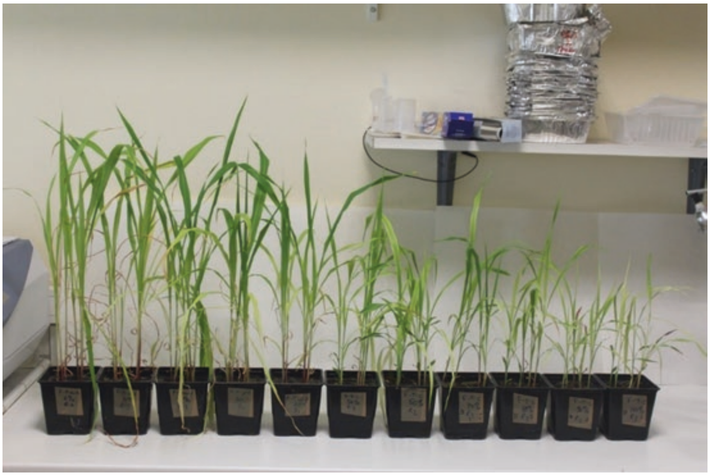


Fig. 13.3 Testing for sorghum resistance to copper in the laboratory conditions (fading technique)

Fig. 13.4 Field experiment BRSU platform (sorghum)

soils were as follows: Mn (in sampling point 1 up to 50% of soil exceeded MPC), Fe (high gross concentration all over), Cu (24% of soils exceeded MPC up to 3–6 times), Zn (28% of soils showed excess of MPC by 15–62%), As (38% of soils exceeded of MPC by 36–62%) and Pb (12% soils exceeded of MPC by 10–50%). The total index for grading soil contamination identified 20 areas of moderately hazardous category (28% of soils) and 4 of extremely dangerous category (6% of soils) (Gorbunov et al. 2020). In the most polluted areas, the analysis of atmospheric air was carried out as well. The high content of Fe in the form of oxides and sulfates which exceeded the MPC average concentrations of Fe in the air by several

Table 13.2 Contamination of urban soils used in the study

Sample point **Elements, mg/kg**	**Background**	**Kosogorsky metallurgical plant**	**Tulachermet**	**Lenina avenue**
Soil type	Clay loam	Clay loam	Sandy loam	Clay loam
pH	6.20	7.26	7.35	7.29
Mn	1300	**5700**	**1100**	**1600**
Fe	15600	**78100**	**120600**	**37400**
V	57	55	**136**	61
Cr	**55**[3]	**60**	**91**	**76**
Ni	25	31	**55**	41
Cu	19	51	**75**	**378**
Zn	47	**310**	**161**	**186**
Pb	18	**72**	26	59
As	5	**6**	**6.4**	**7.3**
petroleum products, g/kg	1.5 ± 0,6	2.6 ± 0,4	**4.1 ± 1.0**	2.5 ± 0.7

Exceeding MPC marked in red (GN, 2006, 2009)

hundreds times was revealed at all sampling sites. The copper concentration was higher than the maximum single MPC by 56% of the surveyed zones and exceeded the daily average by 1.5…3.3 times and maximum single – in 3…9 times. Pb content exceeded the average daily MPC rate at sampling site close to Kosogorsky Metallurgical Plants.

To test the resistance of sorghum to the effects of complex soil pollution with heavy metals and to assess the bioaccumulation of toxic elements, soil samples were taken from three experimental sanitary protection zones of industrial enterprises and city highways: point I – JSC “Kosogorsky Metallurgical Plant” (KMP) (ferromanganese production); point II – complex of enterprises of JSC JV “Tulachermet” and “Vanadium” (TCh) (production of pig iron, vanadium, and chromium) and point III – sanitary protective zone of a large highway – Lenina Avenue (LP), characterized by a high level of danger in the complex of heavy metals (Gorelova et al. 2020) (Table 13.2).

The KMP soil was characterized by a high content of Fe (78100 mg/kg), exceeding the MPC for Mn (by 3.8–4.4 times) and Zn (by 41%); Tulachermet soil was characterized by a very high content of Fe (120600 mg/kg), exceeding the MPC (APC) for V-Mn (by 40–50% for V and 10% for Mn), Ni (by 110–175%), Cu (by 127%), Zn (by 29–192%), As (by 115–220%), and oil products (by four times); the soil of Lenin avenue was characterized by a high content of Fe (37,400 mg/kg), exceeding the permissible concentrations of Mn (by 6%) and Cu (by 186%). In the soils from the territory of the L.N. Tolstoy "Yasnaya Polyana" (the background soils) the excess of MPC and APC for normalized elements was not noted.

The second step of the research was the laying of the model experiment on the soils of experimental zones to identify the physiological resistance of sorghum to complex pollution of urban soils. The soils for the model experiment were placed in plastic containers with drainage that did not have a drain for water. Sowing of seeds and observation of plants was carried out in laboratory conditions at a temperature of 21–23 °C using natural light. The energy of seed germination was determined on the third day after sowing and germination on the seventh day. A spectrophotometric method was used to determine the quantitative content of pigments in plants. Calculation of the quantitative content of chlorophylls and carotenoids was carried out according to the formulas of Lichtentaller and Welburn (1983), followed by conversion to g of fresh weight. The content of secondary metabolites, phenolic compounds, which play the role of antioxidants in oxidative stress caused by a high content of heavy metals, was determined by standart method (Zaprometov 1971).

Germination is an important indicator that further determines the biomass yield per unit area and the removal of toxic elements from soils. Sorghum grain biomass was characterized by low germination energy and germination. Seeds of this variety reacted to polyelement soil contamination.

Their germination energy and germination on the soils of the experimental zones ranged from 7% to 30%. This fact should be taken into account when calculating the seeding rate during phytoremediation of soils with polyelement anomalies. Sucro grain Sucro was characterized by normal germination energy and germination rate of 60–80%.

A decrease in the sowing quality of Sucro sorghum seeds on the soils of the metallurgical industry and Lenina Avenue was noted: the germination energy on KMP soils and the highway decreased by 12–34% with respect to the control; germination on KMP soils decreased by 25% with respect to control.

A study of the biometric parameters of sorghum revealed a significant increase in the shoot length of sorghum Biomass from 40% to 65% on contaminated soils relative to the control. The shoots of Biomass sorghum on the soils of KMP and Lenin Avenue reached a length of 164 cm (when grown in containers for one plant without thickening the crops). Sorghum Sucro at the end of the growing season in the model experiment reached 135 cm, while an increase in shoot length by 65–77% with respect to the control was observed in the contaminated soils of the SPZ (Figs. 13.5 and 13.6). This fact allows us to make an assumption that the removal of toxic elements in terms of shoot biomass per unit will be higher on contaminated soils, which corresponds to the tasks of phytoremediation.

Pollutants entering the plant organism induce a complex change in physiological and biochemical processes at the molecular, subcellular, and cellular tissue levels. One of the most serious consequences of stress for plants is damage of the photosynthetic apparatus, manifested by a change in the ratio of pigments and their quantitative content and leading to disruption of the photosynthesis and metabolism as a whole. Pigments under stress are not only directly affected by the components of technogenic emissions (resulting from the dissolution of oxides of acid and salt, they destroy pigments), but also due to the intensification of heavy photochemical processes by the action of heavy metals, which can be caused by the formation of

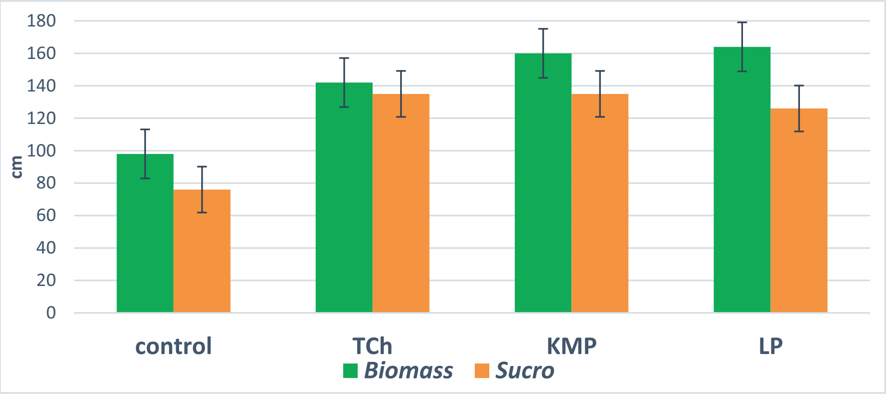


Fig. 13.5 Sorghum height in the model experiment on soils of sanitary protective zones of metallurgical enterprises and highways

Fig. 13.6 Sorghum Sucro (**a**) (when thickening crops) and Biomass (**b**) (end of vegetation) growing on soils contaminated with a complex of heavy metals from left to right: control; (TCh; KMP; LP). Plant nutrition area: 0.0113 m^2

reactive oxygen species (ROS), leading to the development of oxidative stress (Tihonov 1999).

In photosynthetic cells, chloroplasts are powerful ROS producers (Mittler 2002; Foyer and Noctor 2005). ROS damage cell membranes, destroy pigment systems, inhibit the photosynthetic apparatus, and ultimately lead to a decrease in plant productivity, leading to a decrease in biomass. In this regard, the study of the quantitative content of pigments is important when studying the adaptive characteristics of plants in response to stress.

We studied the content of photosynthetic sorghum pigments of two varieties *Sorghum bicolor cv. Sucro* and *Sorghum bicolor cv. Biomass* in a model experiment on the soils of the sanitary protection zones of an urban ecosystem characterized by polyelement anomalies. In the course of the research, it was found that the sorgum biomass on Tulachermet soils showed a decrease in the quantitative content of chlorophyll a by 20–35% compared with the control; however, the content of chlorophyll b on the soils of KMP and Lenin Avenue increased (Fig. 13.7).

For the successful operation of pigment systems, a certain ratio of pigments is necessary. The ratio of chlorophyll a to chlorophyll b in sorghum Biomas and Sucro was optimal on the soils of Tulachermet and Lenin Avenue. On the soils of Tulachermet, the content of carotenoids in the leaves of sorghum Biomass also slightly increased; in all other cases, a decrease in the content of carotenoids in this variety compared to the control was observed.

Sorghum bicolor Sucro was distinguished by the stability of the photosynthetic apparatus on soils with polyelement anomalies. On the soils of the experimental zones, the content of all components of the pigment systems in the leaves of sorghum Sucro increased. The content of chlorophyll significantly increased in the leaves of sorghum growing on the soils of the sanitary protective zone (SPZ) of highways (up to 38% compared to control); the chlorophyll b content in plants on

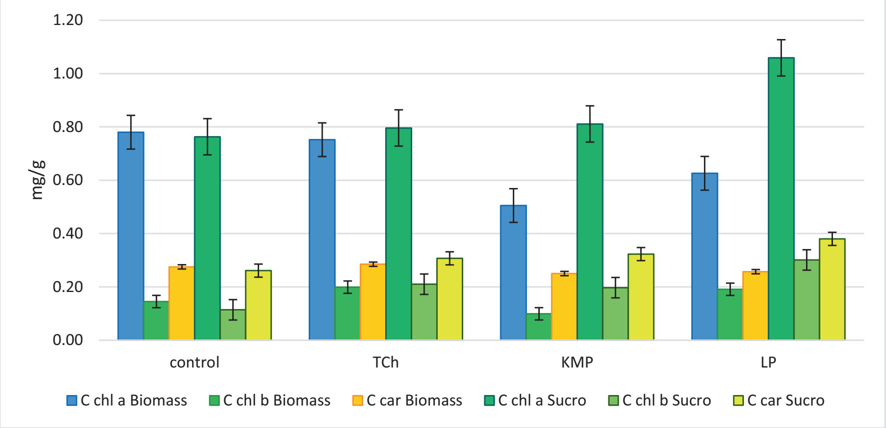


Fig. 13.7 Content of photosynthetic pigments in the leaves of *sorghum bicolor* grown on soils contaminated with heavy metals

the soil of the SPZ of metallurgical enterprises was higher than in the control by 72–84%; on the soils of the SPZ of motorways 2.6 times. *Sorghum bicolor* Sucro was also characterized by an increase in the content of components of the antioxidant system of carotenoids from 16% to 46% under conditions of polymetallic stress (Fig. 13.4). Stress factors can cause damage activate protective and adaptive reactions, as a result the plants adapt to adverse environmental conditions. The results allow us to conclude that the pigment apparatus of the sorghum studied varieties is adapted to the conditions of polymetallic soil contamination.

One of the most important mechanisms of plant resistance to the action of stressors of various origins is the activation of phenolic metabolism (Zagoskina 2018; Takahama and Oniki 2000).

The functions of phenolic compounds, which are one of the most common representatives of secondary metabolism in plants, are extremely diverse.

Phenolic compounds are participants in redox processes during respiration and photosynthesis, uncouple oxidative phosphorylation, stimulate cell division, and affect plant growth and development.

The amount of phenolic compounds synthesized in plants depends on their physiological state and habitat conditions (Zaprometov 1974). According to published data, the accumulation of phenolic compounds under the influence of adverse and stressful environmental conditions can ensure the stability of the species. This is due, first of all, to the fact that phenolic compounds exhibit antioxidant properties, which consist in their ability to bind heavy metal ions into stable complexes, thereby depriving them of the last catalytic effect, and also serve as acceptors of free radicals (Zaprometov 1996; Zagoskina 2018).

We have studied the content of phenolic compounds as components of the antioxidant system of sorghum under the influence of soils with complex pollution with heavy metals. A significant increase in the content of phenolic compounds in the studied varieties of sorghum was established. So in the shoots of sorghum Biomass on the soils of sanitary protection zones of metallurgical enterprises, the content of phenolic compounds was more than 5–14% relative to the control. In the shoots of sorghum Sucro, the content of phenolic compounds increased from 77% to 98% with respect to the control samples (Fig. 13.8).

The revealed features of the phenolic metabolism of sorghum when exposed to heavy soil metals indicate good adaptive abilities of the studied varieties. Sorghum varieties Sucro showed the most advanced devices.

In general, the identified physiological characteristics of sorghum revealed a further study of culture as a possible phytoremediator of technologically contaminated complex of heavy metals urbanozems of central Russia and the Republic of Belarus.

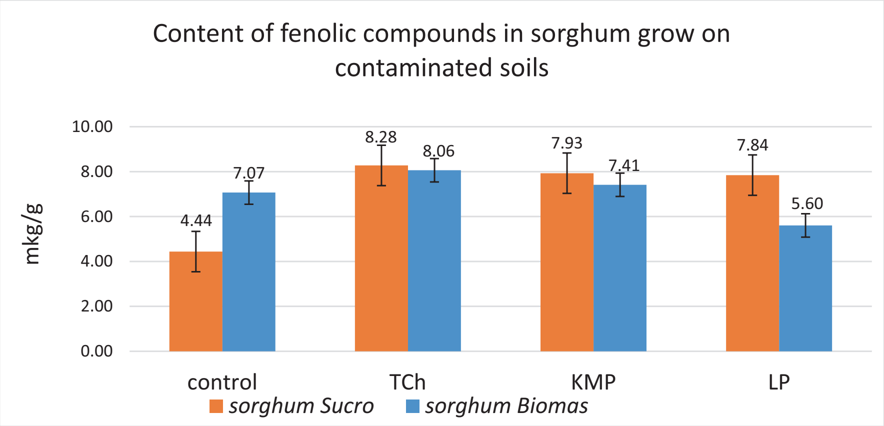


Fig. 13.8 The content of phenolic compounds in sorghum shoots on soils contaminated with a complex of heavy metals

13.3 Features of Bioaccumulation of Toxic Elements from Soils Contaminated with Heavy Metals in Conditions of Model Experiment

During the research, the accumulative ability of toxic elements from urbanozem with multielement anomalies by two varieties of grain sorghum was studied. The characteristics of the soils of the model lands on which the plants were grown are shown in Table 13.1. The growing season of the plants during the experiment was 3.5 months (Fig. 13.6). Samples were grown in plastic cache-pots in laboratory conditions. Watering was carried out with distilled water as the top layer of the soil was drying up. Plants were harvested after vegetation, the root system was separated from the shoots and weighed separately. The organs of sorghum were washed in running water, then twice in distilled water. They were dried at a temperature of 60 °C, weighed again to determine the solids content, packed, and labeled. In the chemical laboratory of the Frank Laboratory of Neutron Physics of the Joint Institute for Nuclear Research (FLNP JINR) and the chemical analytical laboratory of the GIN RAS, samples were prepared for elemental analysis.

Instrumental neutron activation analysis of plant material was carried out at the fast-pulsed reactor IBR-2 in FLNP JINR using activation with epithermal neutrons along with the full energy spectrum.

For the determination of elements with long-lived isotopes, samples were packed in aluminum foil. Containers with samples were irradiated for 3 days in a channel with the cadmium screen (epithermal neutron activation analysis). Then, irradiation samples were repacked in clean polyethylene containers for measurement of induced activity. Induced gamma activity was measured twice: in 4–5 days after irradiation (for determination of As, Br, K, La, Na, Mo, Sm, U, and W) and in

20 days (for determination of Ba, Ce, Co, Cr, Cs, Fe, Hf, Ni, Rb, Sb, Sc, Sr, Ta, Tb, Th, Yb, and Zn). The time of measurement was 30 and 90 min, respectively.

For the determination of elements with short-lived isotopes (Al, Ca, Cl, I, Mg, Mn и V), samples of about 0.3 g were packed in polyethylene and irradiated for 3–5 min. Induced gamma activity was measured directly after irradiation for 15 min. After appropriate decay times, gamma spectra of induced activity were obtained using three spectrometers based on HPGe detectors with an efficiency of 40–55% and resolution of 1.8–2.0 keV for total-absorption peak 1332 keV of the isotope ^{60}Co and Canberra spectrometric electronics. For quality control, the following reference materials were used: IAEA-336 (Lichen), NIST SRM 1572 (Citrus Leaves) and NIST SRM 1575 (Pine Needles) (Gorbunov et al. 2015).

The analysis of the spectra was performed using the Genie2000 software from Canberra, with the verification of the peak fit in an interactive mode, while the calculation of concentration was carried out using software "Concentration" developed in FLNP.

The content of elements in samples was determined by using an iCE 3400 AAS Atomic Absorption Spectrometer with electrothermal (graphite furnace) atomization (Thermo Fisher Scientific, Waltham, MA, USA). The calibration solutions were prepared from AAS standard solutions with metal ion concentrations of 1 g/L (Merck, Germany).

Moreover, the content of Al, As, Ba, Be, Cd, Ce, Co, Cr, Cu, Er, Eu, Gd, Hf, La, Mn, Mo, Nb, Nd, Ni, Pb, Pr, Rb, Sb, Sc, Se, Sm, Sn, Sr, Ta, Tb, Tl, Tm, Ti, Th, U, V, Yb, W, Zn and Zr in experimental samples was determined using inductively coupled plasma mass spectrometry. For the determination of Fe and Mg, flame atomic absorption spectrometry was used.

Mass spectrometric analysis was carried out using a mass spectrometer Element2 (Thermo Fisher Scientific of GmbH, Germany) adding indium as internal standard. The concentration of indium in the analyzed solutions was 1 μg/L. The mathematical correction of spectral interference due to the formation of oxides and hydroxides was done using previously experimentally determined coefficients. Before measurements, the instrument was adjusted in such a way as to achieve sensitivity of at least 1,000,000 cps when analyzing an indium solution with a concentration of 1 μg/L. To calibrate the instrument, multielement standard solutions ICP-MS-68A Solution B, ICP-MS-E, ICP-MS-B (High-Purity Standards, USA) were used. The main instrumental measurement requirements are shown in Table 13.3.

For atomic absorption analysis, a KVANT-2 spectrometer (KORTEK, Russia) was used. The measurements were performed in an air-acetylene flame using absorption lines 248.3 nm for Fe and 285.2 for Mg. Nonselective absorption was corrected automatically using a deuterium lamp. The device was adjusted before the measurement of each element until the maximum sensitivity was obtained. The instrument was calibrated using the multi-element standard solution ICP-MS-68A Solution A (High-Purity Standards, USA).

A microwave oven (MARS5, CEM Corporation, USA) and XP-1500 Teflon vessels were used for mineralization. The vessels were preliminarily kept with 10.0 ml of an aqueous solution of nitric acid (1:1) at 160 °C, then cooled and rinsed with

Table 13.3 Operating conditions of measurement of microelements concentrations in plants

Plasma power	1150 Watt
Consumption of plasma-supporting gas	Argon, 16 L/min
Consumption of cooling gas	Argon, 0.90 L/min
Cone	Nickel
Scanning pattern	EScan, 3 runs/3 passes
Detector mode	Combined
Number of measurements per peak	20
Time of one measurement	0.01 s –LR; 0.02 s –MR; 0.05 s –HR
Integration type	Average
LR (low resolution)	^{9}Be, ^{85}Rb, ^{90}Zr, ^{93}Nb, ^{95}Mo, ^{98}Mo, ^{112}Cd, ^{114}Cd, ^{118}Sn, ^{121}Sb, ^{123}Sb, ^{138}Ba, ^{139}La, ^{140}Ce, ^{141}Pr, ^{143}Nd, ^{146}Nd, ^{147}Sm, ^{152}Sm, ^{151}Eu, ^{153}Eu, ^{157}Gd, ^{160}Gd, ^{159}Tb, ^{166}Er, ^{167}Er, ^{169}Tm, ^{171}Yb, ^{172}Yb, ^{177}Hf, ^{178}Hf, ^{181}Ta, ^{182}W, ^{184}W, ^{203}Tl, ^{205}Tl, ^{206}Pb, ^{208}Pb, ^{232}Th, ^{238}U
MR (middle resolution)	^{27}Al, ^{45}Sc, ^{47}Ti, ^{51}V, ^{52}Cr, ^{53}Cr, ^{55}Mn, ^{59}Co, ^{60}Ni, ^{63}Cu, ^{65}Cu, ^{64}Zn, ^{66}Zn, ^{88}Sr
HR (high resolution)	^{75}As, ^{77}Se

deionized water (18.2 MΩ.cm, Milli-Q, ADVANTAGE A10, Millipore Corporation, France). A sample of 0.5 g was placed in a vessel in which nitric acid was added and kept at room temperature for 48 hours. Then, hydrogen peroxide was added, and after the end of the violent reaction, decomposition was carried out in a microwave oven at 180 °C. The resulting solution was analyzed after dilution with deionized water.

Each plant sample was analyzed twice; the content of the element in the sample was calculated as the average of two independent results.

Simultaneously with plants, the analysis of "blank" samples and reference materials of phytogenous origin, certified for trace element composition was performed. As reference materials, Elodea EK-1, birch leaf LB-1, and grass mixture Tr-1 (Institute of Geochemistry SB RAS, Russia) were used. For every 10 analyzed samples, one blank sample and one standard sample were analyzed.

The results of the analysis of standards (mean and standard deviation from the results of two independent determinations) show good agreement of determined and certified concentrations was observed for all elements except for Hf, Ta in EK-1 and LB-1 and Nb, Zr in LB-1. For these elements in the standard materials are given indicative, not certified values, that can explain the resulting discrepancies.

The laboratories, in which measurements were performed, are accredited by the Federal Agency for Technical Regulation and Metrology, all listed equipment has passed the procedure of annual verification of the engineering status.

Statistical analysis of AAS, INAA, and ICP-MS results was performed using Excel and Statistical software.

Content of *V* in roots of sorghum was on the level of 6.5–272 mg/kg dry weight (DW), which is 10–240 times higher than in the overground parts of the plant (Table 13.4). On the soil with high V content (PAO Tulachermet), the accumulation of elements by the sorghum root system increased sharply, while in the shoots, the element content was in a low range: 0.52–1.03 mg/kg DW. The sorghum root system is an active barrier, preventing the penetration of V from the soil into photosynthetic organs. The transfer factor of the element from roots to shoots was 0.001–0.05. Apparently, the element does not cross the endodermal barrier. A possible way of soil remediation from an element using sorghum of the studied cultivars of sorghum is rhizofiltration.

The content of *Pb* in the shoots of sorghum Sucro was 0.5–2.4 mg/kg DW, and in the roots, it was 3.5–9.7 mg/kg of DW (Table 13.4). However, even at the low content of this element in the shoots, its removal from the soil by shoots of sorghum was 1.4–2.9 g/ha with the maximum value for soils of highway sanitary protection zone. Removal by the root system was much higher and amounted to 6.7–21.1 g/ha. This fact should be taken into account at plants harvest and in the course of execution of phytoremediation measures. The content of Pb in shoots of sorghum Biomass was lower and amounted to 0.08–0.13 mg/kg DW. These values are significantly lower than the Reference plants (Markert 1992).

For most plants, the critical level of copper content is 10–20 mg/kg DW (Bityuckij 2011). The content of *Cu* in the shoots of sorghum Sucro in the range of 5.8–7.8 mg/kg DW was below critical values, the content in the roots was 13.7–31.7 mg/kg DW and was maximum on the soils of PJSC “KMZ” and Lenin Avenue. The values of Cu accumulation by shoots of sorghum Sucro in our experiment are in agreement

Table 13.4 Accumulation of toxicants of 1–3 class of hazard in organs of grain sorghum (AAS, ICP MS), mg/kg DW

Sorghum var.	Collection site	Organ	*Pb*	*Cd*	*Cu*	*V*
Sucro	Background	Shoot	2.43 ± 0.07	0.35 ± 0.01	5.87 ± 0.18	0.95 ± 0.03
		Roots	3.46 ± 0.10	0.091 ± 0.003	13.73 ± 0.41	13.4 ± 0.4
	Tulachermet	Shoot	0.53 ± 0.02	0.14 ± 0.004	5.56 ± 0.17	0.52 ± 0.02
		Roots	4.79 ± 0.14	0.06 ± 0.002	14.74 ± 0.44	*272 ± 8*
	Kosogorsky Metallurgical Plant	Shoot	0.26 ± 0.01	0.25 ± 0.007	5.92 ± 0.17	0.69 ± 0.02
		Roots	9.72 ± 0.29	0.23 ± 0.007	31.73 ± 0.95	17.02 ± 0.05
	Lenin Avenue	Shoot	0.55 ± 0.02	0.21 ± 0.006	7.79 ± 0.23	1.03 ± 0.03
		Roots	6.59 ± 0.19	0.15 ± 0.004	29.9 ± 0.97	21.7 ± 0.6
Biomass	Background	Shoots	0.12 ± 0.01	0.26 ± 0.008	10.5 ± 00.3	0.112 ± 0.003
	Tulachermet	Shoots	0.082 ± 0.002	0.04 ± 0.001	2.72 ± 00.08	0.111 ± 0.003
	Kosogorsky Metallurgical Plant	Shoots	0.091 ± 0.003	0.04 ± 0.001	2.03 ± 00.06	0.72 ± 0.02
	Lenin Avenue	Shoots	0.132 ± 0.004	0.003 ± 0.001	3.82 ± 00.11	0.073 ± 0.002
Reference plant, Markert 1992			*1*	*0.05*	*10*	*0.5*

with the values resented in the work of Murillo et al. 1999: 4.6–11.7 mg/kg DW. However, in grain sorghum Biomass, the content of the element on contaminated soils was lower and varied in the range of 2.03–3.82 mg/kg DW. Since the transfer factor of lead from roots to shoots is very low in comparison with the transfer of copper, which is significantly higher (0.18–0.42), it can be concluded that copper is less toxic for plants than lead. This is explained by copper physiological function: copper constitutes an integral part of many enzymatic systems.

The *Cd* content in the shoots of *Sorghum bicolor* was in the range of 0.06–0.35 mg/kg DW, in the roots, the cadmium content was lower and constituted 0.09–0.23 mg/kg DW (Table 13.4). At the same time, the content of the element was higher in the shoots of plants grown on the soils of the background zone. It is possible indeed, that, in the case of multielement soils contamination, Cd competes for protein carriers with other elements and is absorbed worse. Cadmium is not a pollutant in the soils of the model experiment and of the model region; therefore, its content in the organs of the studied plants is rather stable and does not exceed critical values.

The *Cr* content in sorghum roots varied in the range of 4.3–16 mg/kg DW (Table 13.5). These values exceeded the limits of toxic concentrations for plants. However, the active detoxification mechanisms in the roots of this cereal prevented the development of toxic effects in photosynthetic shoots. The high content of the element in the root system did not affect in any way the growth parameters and the formation of plant biomass at multi-elemental soil pollution. The element content in the shoots of sorghum varied in the range of 0.47–0.82 mg/kg dry weight and was within the normal average values (Kabata-Pendias and Pendias 2001).

The critical concentrations of manganese in plants vary from 220 to 5300 mg/kg DW (Bityuckij 2011). Bioaccumulation of *Mn* by roots of Sucro sorghum ranged from 118 to 1780 mg/kg DW; shoots accumulated an element of 16–122 mg/kg DW. Mn accumulation was maximal on Tulachermet soils. The transfer factor of the element from roots to shoots was 0.07–0.42 and was maximal for plants grown on the soil of the background zone, i.e., the transfer of an element to shoots on soils with polyelement anomalies decreases. Most of the manganese accumulates in the roots.

Bioaccumulation of *Mn* in sorghum Biomass varied in the range of 33–122 mg/kg DW for stems and 177–1440 mg/kg DW for roots. These values are close to the values of the accumulation of the element sorghum, cv Sucro. The concentration coefficient of the element by sorghum roots relative to RP on soils with polyelement anomalies was 1.3–7.2 and was maximum for the most contaminated soils of the KMP. The element content in shoots of both varieties did not exceed the value established for RP.

Bioaccumulation of *Fe*, the content of which was high in all soils of the model experiment (Table 13.2), by sorghum shoots was 183–1400 mg/kg DW. The roots accumulated the element in values 7–62 times higher than the toxicity limits for plants: the content of the element in the root system was 3160–96,100 mg/kg DW. Since such high concentrations of the element in the roots did not affect the growth of shoots, the threshold of toxic values for the sorghum root system is higher

Table 13.5 Content of elements in sorghum plants grown on soils of experimental zones, mg/kg DW (INNA, ICP MS)

Soil collection site	Variety, part	*V*	*Cr*	*Mn*	*Fe*	*Zn*	*Co*	*As*	*Mo*	*Sb*	*Ba*
Background	Sorghum Sucro, shoot	0.3	1.14	78	497	35	0.06	0.38	0.42	0.06	7
Background	Sorghum Sucro, roots	12.8	16.1	118	3460	24	2.08	0.76	0.57	0.16	3
Lenin Avenue	Sorghum Sucro, shoot	0.3	0.81	32	254	43	0.02	0.04	0.16	0.01	16
Lenin Avenue	Sorghum Sucro, roots	3.5	4.9	289	8770	75	0.38	1.66	0.43	0.35	168
KMP	Sorghum Sucro, shoot	0.1	0.47	16	189	43	0.06	0.03	0.25	0.03	6
KMP	Sorghum Sucro, roots	7.1	4.3	389	13200	76	0.43	2.63	0.35	0.56	231
TCh	Sorghum Sucro, shoot	0.5	0.82	122	284	22	0.05	0.45	1.04	0.03	6
TCh	Sorghum Sucro, roots	45.6	9.7	1780	96100	47	0.52	1.94	0.53	0.88	159
Background	Sorghum Biomass, shoot	0.11	0.60	76	153	29	0.04	0.33	0.17	0.01	5
Background	Sorghum Biomass, roots	6.5	10.9	177	3580	41	1.69	0.60	0.11	0.08	76
Lenin Avenue	Sorghum Biomass, shoot	0.1	0.48	33	131	63	0.02	0.27	0.22	0.03	4
Lenin Avenue	Sorghum Biomass, roots	9.9	7.6	260	9300	138	1.31	0.92	0.21	0.34	62
KMP	Sorghum Biomass, shoot	0.1	0.47	122	1400	82	0.06	0.35	0.25	0.05	6
KMP	Sorghum Biomass, roots	7.1	4.3	1440	8300	142	0.43	1.92	0.35	0.38	38
TCh	Sorghum Biomass, shoot	0.4	0.52	33	183	21	0.03	0.27	0.32	0.03	4

(continued)

Table 13.5 (continued)

Soil collection site	Variety, part	*V*	*Cr*	*Mn*	*Fe*	*Zn*	*Co*	*As*	*Mo*	*Sb*	*Ba*
TCh	Sorghum Biomass, roots	27.2	13.3	260	31100	26	0.66	1.37	0.62	0.16	28
Reference Plant, Markert 1992		*0.5*	*1.5*	*200*	*150*	*50*	*0.2*	*0.1*	*0.5*	*0.1*	*40*
Sufficient or Normal, Kabata-Pendias and Pendias 2001		*0.2–1.5*	*0.1–0.5*	*30–300*	–	*27–100*	*0.02–1*	*1–1.7*	*0.2–5*	*7–50*	–
Excessive or Toxic, Kabata-Pendias and Pendias 2001		*5–10*	*5–30*	*400–1000*	–	*100–400*	*15–50*	*5–20*	*10–50*	*150*	*500*
Element		*V*	*Cr*	*Mn*	*Fe*	*Zn*	*Co*	*As*	*Mo*	*Sb*	*Ba*

Uncertainty of determination (%) for the determined elements grouped by intervals: 5–10% (Ti, V, Cr, Mn, Fe, Co, As, and Sb), 10–15% (Mo and Ba)

than that given in the literature (Kabata-Pendias and Pendias 2001). The transfer factor of the transfer of an element from their soils to the roots was 0.17–0.79 for the Sucro sorghum and 0.07–0.11 for the Biomass variety on the soils of metallurgical industries. For the shoots of sorghum, the values of the transfer factor of the transfer of the element from the soil were 1–2 orders of magnitude lower and amounted to 0.02–0.002.

Bioaccumulation of *Ni* in sorghum roots in the soils of the experimental zones varied in the range of 4.1–11 mg/kg of DW. The enrichment factor of Ni in roots relative to the Reference plant was 2.7–7.3. The Ni content in the shoots of plants in the experimental zones was <0.5–0.57, i.e., 10 times less than that in the root system.

Zn content in sorghum roots varied in the range of 26–142 mg/kg DW and was maximum in Biomass sorghum roots on the soils of Lenin Avenue and KMP. The transfer factor for sorghum roots in this case was 1 and 0.4, respectively. This is a good indicator for recommending the use of sorghum for rhizofiltration of zinc from contaminated soils. The accumulation of zinc in the aboveground organs of sorghum on the test soils was 22–82 mg/kg DW. The transfer factor of Zn from roots to shoots on the soils of Lenin Avenue and KMP was 0.6 for sorghum Sucro and 0.5–0.6 for sorghum Biomass. At the same time, the zinc content in soils by the end of the experiment during sorghum cultivation decreased by 12–19%. Thus, sorghum Biomass can be recommended for phytoremediation of territories from Zn in case of polyelemental soil contamination.

The bioaccumulation of *As* by sorghum plants grown on the soils of the experimental zones in the root system varied within 0.41–2.6 mg/kg DW. The arsenic content in the shoots was 0.03–0.45 mg/kg DW. At the same time, the concentration of this element, which initially exceeded the MPC in soils by 2 times, decreased by 2 times during sorghum cultivation. Due to the fact that almost all uranozems of the model study region are characterized by an excess of the maximum permissible concentration for As, sorgo is of interest as phytoremediates of soils from As (mostly by the root system).

The *Mo* content in shoots and roots was comparable and varied within 0.16–1.04 mg/kg DW for shoots and 0.11–0.62 mg/kg DW for the root system (Table 13.5). These values are in the range of average concentrations of the element in plants 0.2–5 mg/kg (Kabata-Pendias and Pendias 2001).

Antimony was not considered as an element – contaminant in the soils of sanitary protection zones of enterprises and the highway. The accumulation of *Sb* by sorghum shoots was lower or within the mean values for vegetation (Markert 1992; Kabata-Pendias and Pendias 2001) and amounted to 0.01–0.06 mg/kg DW. The content of antimony in the roots of sorghum grown on the soils of the experimental zones was 0.16–0.88 mg/kg DW (Table 13.5).

Ba accumulation by sorghum shoots was 4–16 mg/kg DW. On soils with multi-element anomalies, the root system of Sucro sorghum accumulated from 159 to 231 mg/kg DW of barium. The coefficient of enrichment of the roots of this variety with Ba relative to the Reference plant was 4–5.7. However, the sorghum cultivar Biomass accumulated in the root system from 28 to 62 mg/kg DW barium. These values were within the average values for plants and only on the soils of Lenin Avenue were 1.5 times higher.

Correlation analysis of the accumulation of elements of sorghum revealed the following correlations of bioaccumulation of elements by organs of sorghum (shoot, root) (Table 13.6). A hierarchical cluster analysis was carried out: dendrograms were built using the transformed data (centered log-ratio transformation) (Figs. 13.9 and 13.10). Cluster analysis of the accumulation of elements in the shoots of sorghum identified a separate group of essential elements: K, Cl, Ca, Mg. At the same time, the relationship of monovalent ions K-Cl, and divalent ions Ca-Mg was shown. Also, two clusters of trace elements were highlighted. The cluster of elements, which includes V, includes La, Se, Co, Cs, Sb, Th, Sc. The third identified cluster includes Ni-Cr, Ba, Br, Rb, Sr, Zn-Mn, Ti, Al, Fe, Na (Fig. 13.9). The last 4 elements of the group are associated with the composition of the lithosphere.

Hierarchical cluster analysis of the accumulation of elements by the root system of sorghum revealed the following clusters: 1. also includes a group of essential elements, to which 2 elements of the earth's crust are added: Fe and Al. Iron is necessary for the synthesis of chlorophylls and the normal functioning of cytochromes (enzymes of photosynthesis and respiration), Fe-S proteins and other enzymatic systems of plants. Aluminum, being an element of the lithosphere, is most likely absorbed by the root system in the same way as iron by similar mechanisms.

Two large clusters includes two subclusters and, in addition to trace elements and rare earth elements, also includes Na, which causes soil salinization. The first subcluster of the second cluster includes elements such as Ba, Sr, Zn, Ni, V, Cr, Mo, Sb, As and Co. They are associated with rare earth elements. This cluster reflects the components – soil pollutants. The last subcluster includes Mn, Na, Ti (Fig. 13.10).

Table 13.6 Pearson correlations in element accumulation by Sorghum Organs (shoots, * roots)

	V	CR	MN	FE	NI	CO	ZN	AS	SE	BR	RB	SR	MO	SB	BA	CS
NA	−0,17	−0,50	0,37	0,53	−0,09	0,51	0,29	0,39	0,63	0,60	0,06	0,19	0,23	0,38	0,49	0,18
MG	0,94	0,23	0,80	0,35	0,31	0,31	0,76	0,40	0,51	−0,36	0,34	0,58	0,66	0,48	0,59	0,17
AL	0,95	0,09	0,81	0,36	0,20	0,12	0,84	0,57	0,51	−0,26	0,38	0,44	0,62	0,39	0,53	0,16
CL	0,58	−0,17	0,35	0,30	−0,52	−0,21	0,73	0,45	−0,13	−0,32	−0,06	0,71	0,44	0,71	0,09	−0,49
K	0,54	0,41	0,12	−0,25	0,40	0,41	0,16	−0,11	0,01	−0,26	0,14	0,35	0,05	0,19	0,00	0,10
CA	0,90	0,18	0,76	0,13	0,33	0,00	0,68	0,49	0,36	−0,30	0,13	0,43	0,59	0,18	0,46	0,07
SC	0,09	−0,13	0,46	0,79	0,08	0,67	0,39	0,18	0,85	0,16	0,65	0,05	0,34	0,47	0,66	0,54
TI	0,12	0,07	−0,26	−0,05	−0,48	−0,23	0,12	−0,12	−0,52	−0,40	−0,09	0,35	−0,03	0,40	−0,34	−0,45
V	1,00	0,32	0,74	0,25	0,29	0,09	0,74	0,36	0,36	−0,52	0,35	0,48	0,63	0,35	0,47	0,12
CR	0,32	1,00	0,02	−0,10	0,82	0,40	−0,32	−0,75	0,16	−0,81	0,58	−0,22	0,09	−0,25	0,19	0,60
MN	0,74	0,02	1,00	0,73	0,15	0,21	0,83	0,52	0,72	−0,29	0,28	0,58	0,92	0,55	0,88	0,14
FE	0,25	−0,10	0,73	1,00	−0,09	0,42	0,61	0,25	0,75	−0,20	0,38	0,48	0,79	0,74	0,87	0,18
NI	0,29	0,82	0,15	−0,09	1,00	0,54	−0,29	−0,53	0,46	−0,42	0,65	−0,40	0,03	−0,42	0,32	0,83
CO	0,09	0,40	0,21	0,42	0,54	1,00	−0,01	−0,38	0,70	−0,12	0,69	0,03	0,16	0,30	0,52	0,71
ZN	0,74	−0,32	0,83	0,61	−0,29	−0,01	1,00	0,79	0,42	−0,08	0,07	0,73	0,75	0,73	0,56	−0,22
AS	0,36	−0,75	0,52	0,25	−0,53	−0,38	0,79	1,00	0,13	0,46	−0,32	0,45	0,35	0,37	0,16	−0,44
SE	0,36	0,16	0,72	0,75	0,46	0,70	0,42	0,13	1,00	−0,08	0,70	0,08	0,57	0,32	0,88	0,69
BR	−0,52	−0,81	−0,29	−0,20	−0,42	−0,12	−0,08	0,46	−0,08	1,00	−0,38	−0,23	−0,48	−0,15	−0,35	−0,19
RB	0,35	0,58	0,28	0,38	0,65	0,69	0,07	−0,32	0,70	−0,38	1,00	−0,29	0,15	0,03	0,47	0,89
SR	0,48	−0,22	0,58	0,48	−0,40	0,03	0,73	0,45	0,08	−0,23	−0,29	1,00	0,72	0,87	0,42	−0,53
MO	0,63	0,09	0,92	0,79	0,03	0,16	0,75	0,35	0,57	−0,48	0,15	0,72	1,00	0,68	0,87	−0,03
SB	0,35	−0,25	0,55	0,74	−0,42	0,30	0,73	0,37	0,32	−0,15	0,03	0,87	0,68	1,00	0,53	−0,28
BA	0,47	0,19	0,88	0,87	0,32	0,52	0,56	0,16	0,88	−0,35	0,47	0,42	0,87	0,53	1,00	0,40
CS	0,12	0,60	0,14	0,18	0,83	0,71	−0,22	−0,44	0,69	−0,19	0,89	−0,53	−0,03	−0,28	0,40	1,00

NA*	−0,01	−0,37	−0,32	−0,14	−0,16	−0,08	−0,62	−0,14	−0,37	−0,64	−0,36	−0,58	−0,52	−0,71	−0,15	0,41	−0,66	0,61	−0,91	−0,01	−0,39	−0,31	−0,61	−0,71
MG*	−0,29	−0,02	−0,30	0,19	0,28	−0,10	−0,45	0,41	−0,05	0,30	−0,07	0,01	−0,09	0,00	−0,14	−0,41	−0,35	−0,53	−0,38	0,53	0,27	0,32	0,03	−0,42
AL*	0,11	−0,83	−0,86	−0,48	−0,57	−0,67	−0,33	−0,17	−0,87	−0,40	−0,52	−0,22	−0,40	−0,37	−0,57	−0,17	−0,46	0,42	−0,67	−0,21	−0,35	−0,29	−0,37	−0,42
CL*	−0,34	0,66	0,68	0,94	0,35	0,53	−0,02	0,67	0,78	0,10	0,50	0,31	−0,24	−0,13	0,74	0,34	−0,01	−0,56	0,08	0,71	0,58	0,65	0,25	−0,32
K*	−0,08	−0,48	−0,59	0,16	0,12	−0,59	−0,36	0,52	−0,54	−0,36	−0,69	−0,39	−0,60	−0,15	−0,33	−0,15	−0,71	0,33	−0,58	0,16	−0,51	0,15	−0,67	−0,61
CA*	−0,19	0,02	−0,13	0,28	−0,07	−0,16	0,09	0,43	0,05	0,42	0,21	0,54	0,01	0,22	0,04	−0,44	0,11	−0,73	0,14	0,43	0,55	0,49	0,45	−0,04
SC*	0,37	−0,38	−0,47	−0,10	−0,14	−0,30	−0,30	−0,09	−0,54	−0,72	−0,28	−0,18	−0,64	−0,32	−0,09	0,31	−0,45	0,64	−0,88	0,29	−0,19	0,12	−0,33	−0,72
TI*	0,09	−0,77	−0,87	−0,39	−0,43	−0,67	−0,36	−0,05	−0,83	−0,33	−0,51	−0,18	−0,41	−0,28	−0,55	−0,25	−0,48	0,31	−0,69	−0,06	−0,28	−0,15	−0,33	−0,48
V*	0,03	0,74	0,78	0,71	0,11	0,69	0,23	0,20	0,79	−0,02	0,88	0,64	−0,14	−0,08	0,90	0,54	0,38	−0,46	0,10	0,75	0,91	0,67	0,67	−0,19
CR*	−0,66	0,45	0,56	0,74	0,11	0,51	−0,29	0,57	0,71	0,24	0,37	0,08	−0,11	−0,46	0,51	0,24	−0,17	−0,66	0,04	0,37	0,45	0,22	0,08	−0,28
MN*	−0,14	−0,47	−0,68	−0,11	−0,06	−0,67	−0,07	0,38	−0,51	0,31	−0,42	0,09	−0,04	0,29	−0,52	−0,74	−0,22	−0,33	−0,04	0,06	−0,09	0,17	−0,06	−0,05
FE*	−0,21	0,24	0,15	0,76	0,16	0,17	−0,28	0,64	0,28	−0,17	0,25	0,25	−0,58	−0,31	0,48	0,26	−0,33	−0,35	−0,49	0,87	0,52	0,69	0,09	−0,76
NI*	0,37	0,40	0,22	−0,02	0,19	0,14	0,61	−0,14	0,25	0,48	0,54	0,74	0,46	0,80	0,20	−0,32	0,76	−0,49	0,60	0,31	0,63	0,50	0,84	0,54
CO*	0,14	−0,53	−0,64	−0,09	−0,22	−0,45	−0,43	0,08	−0,63	−0,55	−0,39	−0,21	−0,63	−0,39	−0,25	0,08	−0,58	0,41	−0,89	0,26	−0,19	0,08	−0,38	−0,76
ZN*	0,29	0,65	0,60	0,14	0,17	0,47	0,66	−0,19	0,59	0,46	0,79	0,78	0,51	0,64	0,48	−0,03	0,88	−0,53	0,72	0,29	0,77	0,46	0,93	0,60
AS*	−0,21	−0,22	−0,38	0,40	0,00	−0,27	−0,45	0,57	−0,22	−0,19	−0,18	0,02	−0,60	−0,32	0,00	−0,06	−0,57	−0,19	−0,68	0,61	0,17	0,44	−0,18	−0,79
SE*	−0,25	0,79	0,60	0,33	0,69	0,72	−0,10	0,12	0,79	0,67	0,57	0,19	0,51	0,30	0,37	−0,13	0,28	−0,78	0,29	0,51	0,63	0,32	0,50	0,17
BR*	0,49	0,09	0,23	0,37	−0,02	0,01	0,31	0,07	−0,02	−0,83	0,03	0,07	−0,64	−0,11	0,47	0,75	−0,02	0,75	−0,24	0,24	−0,14	0,36	−0,19	−0,36
RB*	0,17	−0,63	−0,74	0,01	−0,30	−0,80	0,00	0,37	−0,72	−0,32	−0,47	0,12	−0,57	0,04	−0,33	−0,28	−0,34	0,20	−0,40	0,18	−0,18	0,32	−0,22	−0,42
SR*	0,44	0,43	0,34	0,65	0,17	0,25	0,25	0,27	0,28	−0,46	0,53	0,59	−0,56	0,08	0,73	0,55	0,16	0,04	−0,31	0,94	0,64	0,93	0,42	−0,53
MO*	−0,54	0,51	0,37	0,66	0,51	0,34	−0,19	0,67	0,62	0,58	0,27	0,16	0,13	0,10	0,30	−0,24	−0,08	−0,87	0,20	0,55	0,47	0,45	0,21	−0,10
SB*	−0,20	−0,33	−0,56	0,11	0,03	−0,41	−0,41	0,44	−0,37	0,07	−0,29	−0,02	−0,32	−0,08	−0,28	−0,40	−0,48	−0,28	−0,52	0,42	0,08	0,29	−0,14	−0,53
BA*	−0,06	−0,45	−0,67	−0,03	−0,04	−0,48	−0,42	0,29	−0,52	−0,10	−0,37	−0,08	−0,38	−0,12	−0,35	−0,34	−0,51	−0,05	−0,64	0,34	−0,04	0,20	−0,22	−0,57
CS*	0,30	−0,45	−0,59	−0,10	−0,11	−0,43	−0,30	0,03	−0,61	−0,58	−0,35	−0,14	−0,61	−0,22	−0,20	0,10	−0,47	0,48	−0,83	0,31	−0,18	0,18	−0,32	−0,69
	NA	MG	AL	CL	K	CA	SC	TI	V	CR	MN	FE	NI	CO	ZN	AS	SE	BR	RB	SR	MO	SB	BA	CS

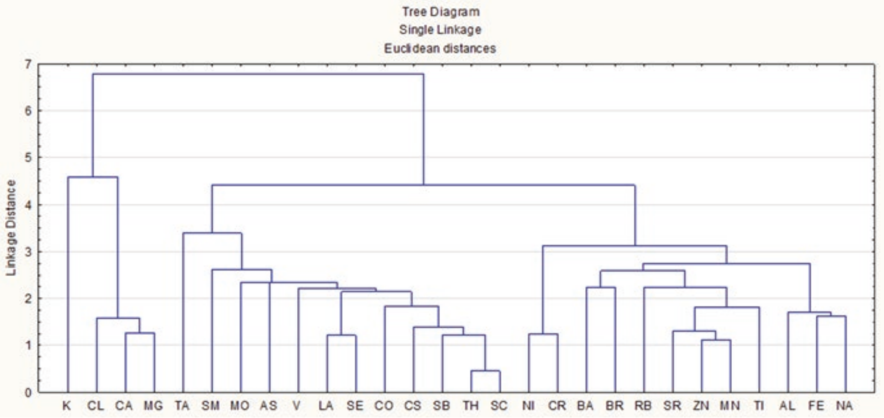


Fig. 13.9 Dedrogram of elements accumulation by shoots of sorghum

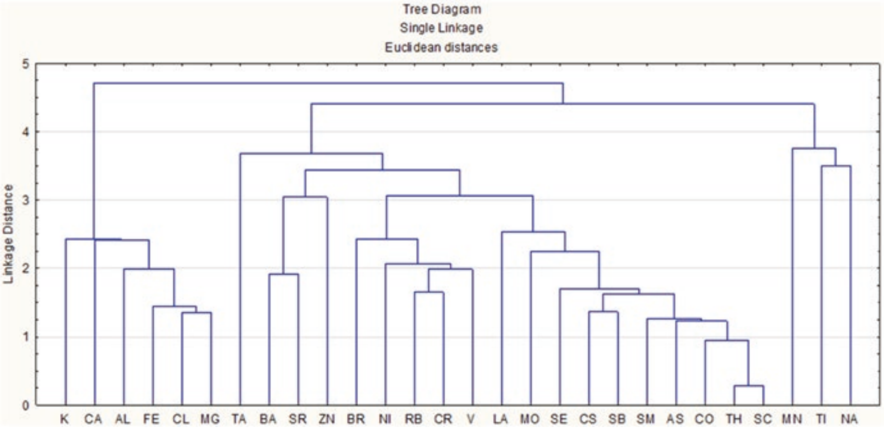


Fig. 13.10 Dedrogram of elements accumulation by the sorghum root system

13.4 Sorghum Rhizosphere Microorganisms and Resistance to Heavy Metals

Bacteria make up the largest group of soil microorganisms and their active participation in soil remediation from various organic and inorganic pollutants is beyond doubt. Among the most common genera of soil bacteria are *Acinetobacter, Agrobacterium, Alcaligenes, Arthrobacter, Bacillus, Brevibacterium, Caulobacter, Cellulomonas, Clostridium, Corynebacterium, Flavobacterium, Hyphomicrobium, Metallogenium, Micrococcus, Mycobacterium, Pseudomonas, Saracia, Streptococcus u Xanthomonas* (Lenart-Boro and Boro 2014). Representatives of many of these genera are characterized by resistance to heavy metal ions (Trevors et al. 1985), participate in their transformation in the environment, and therefore, a change in the quantitative and qualitative composition of soil microbial communities can serve as an indicator of soil pollution (Trevors et al. 1985; Gremion et al. 2004; Epelde et al. 2009).

Among the microorganisms involved in the conversion of metals to soil, microbial communities associated with the plant rhizosphere deserve special attention, since they can directly improve the efficiency of the phytoremediation process, affecting the mobility and availability of trace elements for plants by releasing chelators by changing soil pH and oxidatively -reduction reactions (Jing et al. 2007; Ma et al. 2011; Aafi et al. 2012; Yang et al. 2012; Hussain et al. 2018). At the same time, rhizospheric microbial communities affect the phytoremediation of metal-contaminated soil not only through a change in the bioavailability of metals (Jing et al. 2007), but also through stimulation of plant growth under pollutant stress by fixing N2, production of phytohormones (IAA, cytokinins, and gibberellins), siderophores, enzymes (ACC deaminases), and nutrient transformation (Santoyo et al. 2016; Ojuederie and Babalola 2017; Hussain et al. 2018). Therefore, the isolation, study, and application of active plant-growth-promoting rhizobacteria (PGPR) resistant to heavy metals is an urgent task of modern research on phytoremediation of metal-contaminated soil and an important tool to increase its effectiveness (Ojuederie and Babalola 2017). The successful use of microbial inoculants to improve soil cleaning from metals and metalloids has been shown in a number of works (Sheng et al. 2008; Yang et al. 2012; Hussain et al. 2018).

The microbial communities of the rhizosphere of *Sorghum bicolor* L. Moench., as widely cultivated and of great agricultural importance plants, have been repeatedly described (Acosta-Martínez et al. 2010; Tshabuse 2012; Schlemper et al. 2018). The main objectives of such studies were to clarify the effect of various abiotic (soil type, drought effects) and biotic (inoculation with PGPR strains) factors on the structure of the microbiome associated with the root zone of sorghum, as well as the identification of microbial taxa that contribute to the improvement of growth of this plant. The influence of the genotype (variety) and the stage of plant development on the composition of the rhizosphere microbiome is noted (Schlemper et al. 2018). Studies of the taxonomic structure of the rhizosphere community of sorghum (Oberholster et al. 2018; Tshabuse 2012; Schlemper et al. 2018) show that there are a sufficient number of taxa in the sorghum rhizomicrobiome that can enhance the growth of this plant.

Along with traditional agricultural use, broom sorghum *Sorghum bicolor* (L.) Moench. It is widely used in experiments on phytoremediation of soil contaminated with heavy metals (Marchiol et al. 2007; Zhuang et al. 2009; Soudek et al. 2014). However, studies of the rhizosphere community of sorghum grown in soil contaminated with heavy metals and/or metalloids have not been previously reported. At the same time, the successful application of inoculation of sorghum plants with active PGPR strains to improve soil cleaning from heavy metals has been described (Ali et al. 2017).

The objective of the present work was a comparative analysis of the bacterial microflora of the rhizosphere of two varieties of *Sorghum bicolor* grown on soils contaminated with heavy metals, and the isolation of rhizobacterial strains resistant to heavy metals.

The soil samples from rhizosphere of *S. bicolor* cv. Sucro and *S. bicolor* cv. Biomass were explored in this study. Plants were grown in three types of industrially contaminated soils, as well as in control clean soil. The technogenically contaminated soil was taken from three sites in Tula City: I) Lenin Avenue (LP); II) the sanitary protection zone of Joint-Stock Company "Kosogorsky Metallurgical Plants" (KMP)); and III) the territory of Joint-Stock Company "Tulachermet" (TCh). The characteristics of soil pollution by heavy metals are presented in Table 13.2. All experimental soil samples were characterized by complex pollution by heavy metals.

Microbiological analysis of the plant rhizosphere was carried out using cultural methods, because an additional objective of the work was the isolation of plant-associated rhizobacteria strains, which to be resistant to heavy metals and, preferably, to be capable of plant growth promotion. The total number of cultured heterotrophic microorganisms (THM) was determined by the Koch technique, i.e., by seeding ten-fold dilutions of the soil suspension on a nutrient agar medium MPA and counting CFUs. Microorganisms exhibiting resistance to heavy metal, detected in the soils studied, were taken into account by plating on LB agar medium containing ions of one of the metals at a concentration of 0.5 mmol/L. For the analysis, soluble salts of $CuSO_4$, $ZnSO_4$, $Pb(NO_3)_2$ and Na_3AsO_4 were used. Inoculated plates were incubated at a temperature of 28–30 °C for 5–7 days, after that the microbial colonies were counted, CFU was calculated, and the morphological diversity of the grown microorganisms was estimated. Colonies differing in morphotype were taken as a pure culture. For statistical processing of the results obtained, the Microsoft Excel 2007 program was used.

The results of the analysis of THM in the rhizosphere of two sorghum varieties are given in Fig. 13.11. According to the data obtained the THM number in the rhizosphere of *S. bicolor* cv. Sucro grown in industrially contaminated soil was 5.8–23 times higher than in uncontaminated control soil. This value was maximal for TCh soil contained a relatively low concentration of toxic Pb and the heightened concentrations of important for microbial growth microelements (Fe, Zn, Mn).

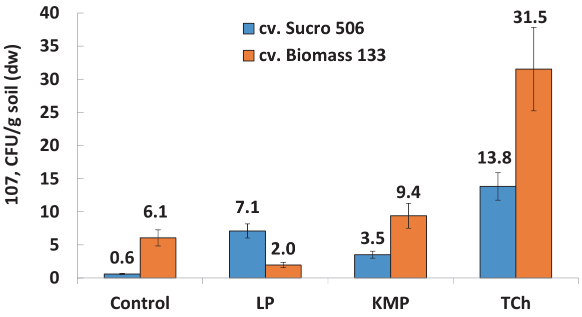


Fig. 13.11 Total number of cultivable heterotrophic bacteria in rhizosphere of two varieties of *S. bicolor* plants grown in uncontaminated control and heavy metal contaminated industrial soil

In the rhizosphere of *S. bicolor* cv. Biomass, the THM number was higher than in the rhizosphere of cv. Sucro (by 10 and 2.3 times for control and for TCh soils, respectively). Only in the LP soil THM number in rhizosphere of cv. Sucro 133 was 3 times lower than in the control. This may be due to the highest toxicity of the LP soil, which was characterized by 1.7-, 6-, and 1.5-fold excess of approximate allowable concentrations values for Zn, Cu, and As, respectively, in comparison with other soil samples (Table 13.2). The toxic effect of heavy metals on soil bacteria is primarily determined by their concentration. Despite the great involvement of metals as trace elements in the vital activity of soil microorganisms, their high concentrations have a toxic effect on the microbiota, which is associated with a violation of redox reactions, damage of enzymes, alterations in the conformational structures of nucleic acids and proteins, which leads to the formation of complexes of metals with protein molecules and inactivates them (Lenart-Boro and Boro 2014). According to numerous studies, the bacterial community, unlike the fungal community, is more sensitive to soil pollution with metals (Lenart-Boro and Boro 2014).

In each experiment variant, the number of microorganisms resistant to the metal whose concentration was exceeded in the soil tested sample was determined (Fig. 13.12).

In all cases, the abundance of metal-resistant microorganisms in the rhizosphere *of S. bicolor* cv. Biomass was higher than in the rhizosphere of *S. bicolor* cv. Sucro. A close correlation was revealed between the THM number and the number of microorganisms resistant to zinc ($R^2 = 0.88$, $P < 0.05$). On the one hand, this may indicate the widespread occurrence of this trait among soil microorganisms, and on the other hand, zinc concentrations (from 136 to 185 mg kg^{-1}) had insufficient selective effect to suppress the bulk of rhizobacteria and to stimulate resistant strains. The share of zinc-resistant microorganisms in the rhizosphere of cv. Biomass was significantly higher than in the rhizosphere cv. Sucro. It increased under the influence of pollutant from 8% and 5% (in the control soil) to 45% and 19% (in TCh soil) for two plants, respectively.

In Pb-contaminated soil (KMP), the share of microorganisms resistant to this metal was the same for both sorghum varieties – about 3.6% of the total heterotroph population. At the same time, the rhizospheric microflora of two sorghum varieties responded differently to contamination of soil with Cu. In comparison with KMP soil not contaminated with Cu, the excess of this metal in the LP soil markedly stimulated the number of Cu-resistant microorganisms in the rhizosphere of cv. Sucro 506, where the share of them reached 29% (versus 2% in KMP soil) of the total microbial population. The number of microorganisms resistant to Cu in the rhizosphere of sorghum cv. Biomass was higher and reached 100% of the total microbial population. Taking into account the previously described inhibitory effect of LP soil on the rhizosphere microflora of cv. Biomass (Fig. 13.11), it can be assumed that the overall rhizosphere microbial population, which was reduced in comparison with other types of soils, was represented by precisely microorganisms resistant to Cu. Despite higher number of THM in the KMP soil, the share of Cu-resistant microorganisms in the rhizosphere cv. Biomass 133 was significantly lower (42%).

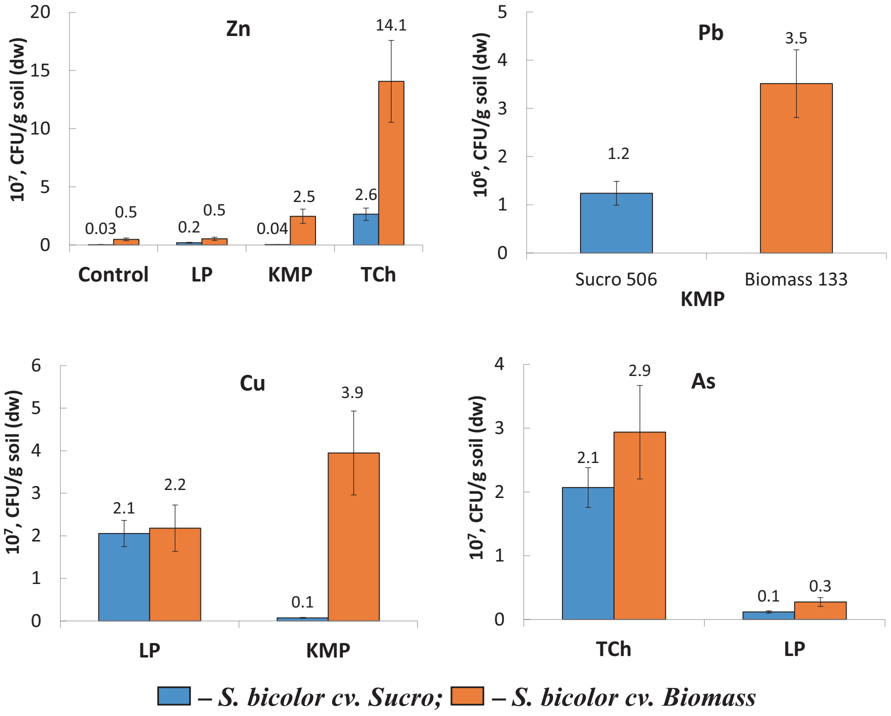


Fig. 13.12 The number of heavy-metal-resistant bacteria in the rhizosphere of sorghum plants grown in uncontaminated control and heavy metal contaminated industrial soil. 🟦 – *S. bicolor cv. Sucro;* 🟧 – *S. bicolor cv. Biomass*

As with Cu, the abundance of As-resistant microorganisms in the rhizosphere of *S. bicolor* cv. Biomass was higher than in the rhizosphere of cv. Sucro. Their number reached 9% and 14% in the As-contaminated TCh and LP soils, respectively. The share of As-resistant microorganisms in the rhizosphere of cv. Sucro 506 was 15% and 2% for TCh and LP soils, respectively.

The cultural characteristics of the isolated microorganisms suggested that the rhizosphere of *S. bicolor* cv. Biomass had greater microbial diversity in comparison with rhizosphere of *S. bicolor* cv. Sucro. Twenty eight microbial isolates exhibiting resistance to heavy metals and metalloid were selected (8 to Zn, 3 to Pb, 3 to Cu, and 14 to As). Nineteen isolates were selected from the rhizosphere of cv. Biomass (3 to Zn, 6 to Pb, 1 to Cu, and 9 to As).

In general, the study showed that, with the exception of LP soil, in which the content of Cu and As was significantly exceeded, all samples of technogenically contaminated soil had a stimulating effect on the formation of the rhizospheric microflora of two studied varieties of sorghum plants *S. bicolor* cv. Biomass and *S. bicolor* cv. Sucro in comparison with uncontaminated control soil. The abundance and the cultural-morphological diversity of rhizomicroflora of *S. bicolor* cv. Biomass exceeded the rhizomicroflora of *S. bicolor* cv. Sucro. In turn, the rhizosphere of Sucro was characterized by increased number of microorganisms in highly contaminated LP soil, whereas the number of microorganisms in the rhizosphere of cv. Biomass was less than in the control for the same soil. Such observations allow us to conclude that Sucro plants could be more effective for cleaning of LP soil. The presented data are supplemented by a metagenomic analysis of the rhizosphere microbiomes of these varieties of sorghum (Muratova et al. 2020). It was found that the taxonomic profile of microbial communities at the phylum level did not differ significantly between Biomass and. Sucro varieties, but the Biomass microbiome was rich in species. As a result of the research, 47 heavy-metal-resistant microbial isolates were collected. A more detailed study of the metal resistance of the isolated strains, as well as the evaluation of plant growth-promoting abilities of these rhizobacteria will allow us to select a promising inoculant to improve the growth of sorghum plants in heavy metal contaminated soil and increase the efficiency of its phytoremediation.

13.5 Prospects for the Use of Sorghum for Phytoremediation of Urban Soils in Temperate Climates

The results of the model experiment showed that at crops overcrowding sorghum is capable of forming elevated biomass of 682–3252 g/m^2 (Table 13.7). The minimum was the productivity of plants grown on the soils of the background zones.

On soils with multi-elemental anomalies, the productivity of sorghum of both varieties was higher in comparison with background: 1.7–4.2 times for the Biomass variety and 1.9–2.8 times for the Sucro variety. The maximum increase in biomass was characteristic for plants grown on the soils of KMP and Lenin Avenue. The biomass of dry matter of shoots, the data which are necessary for further calculations of the removal of elements from the soil, was 351–1027 g/m^2 for the Biomass variety and 176–542 g/m^2 for the Sucro variety. The maximum biomass was obtained

Table 13.7 Productivity of Sorghum cultivated on the soil with multi-elemental anomalies

Variety	Collection site	Roots biomass, g/m^2	Shoots biomass, g/m^2	Biomass of dry weight (roots), g/m^2	Biomass of dry weight (shoots), g/m^2
Biomass	Background	504 ± 47	909 ± 86	87 ± 8	351 ± 32
	TCh	1219 ± 85	1737 ± 145	173 ± 12	488 ± 44
	KMP	1616 ± 123	3252 ± 237	213 ± 18	871 ± 74
	Lenin Avenue	2151 ± 184	3793 ± 295	295 ± 24	1027 ± 97
Sucro	Background	421 ± 38	682 ± 56	49 ± 5	176 ± 16
	TCh	714 ± 68	1356 ± 89	140 ± 92	393 ± 34
	KMP	1261 ± 112	1880 ± 154	175 ± 16	542 ± 46
	Lenin Avenue	1665 ± 154	1882 ± 148	320 ± 28	528 ± 50

Table 13.8 Influence of polyelement soil anomalies on the content of AOC components in sorghum (in % to control)

Variants		Carotenoids	Ascorbic acid	GSH	Total phenolic content
Sorghum Biomass	TCh	65%↑	11%↑	27%↑	14%↑
	KMP	9%↑	58%↑	75%↑	4%
	Lenin Av.	4%	67%↑	51%↑	22%↓
Sorghum Sucro	TCh	19%↑	3%↑	2%↑	89%↑
	KMP	13%↑	18%↑	12%↑	80%↑
	Lenin Av.	7%↑	18%↑	20%↑	77%↑

on the soils of the highway sanitary protection zone. Similarly, the biomass and dry weight of the root system of the studied plants increased (Table 13.8), it varies within 421–2151 g/m^2 of wet matter and 49–320 g/m^2 of dry matter and was maximum on the soils of the highway sanitary protection zone.

According to the generalized data, there is a picture of the adaptive potential of the studied sorghum varieties for the work of the antioxidant system (Table 13.8).

The content of all studied AOS components increased in Sorghum Sucroon soils with polyelement anomalies: the content of carotenoids increased by 7–19%, ascorbic acid and glutathione by 12–20% or remains at the control level, phenolic compounds by 77–89% (Table 13.8).

The content of carotenoids in Biomass sorghum on soils with polyelemental pollution was 4–19% higher; low molecular weight antioxidants – ascorbic acid and glutathione – are 11–67% and 27–75% more than on background soils. The total amount of phenolic compounds was reliably higher only on Tulachermet soils. On the soils of Lenin Avenue, it was 22% lower than on the background ones.

The content of four AOC components in sorghum showed good adaptation of the studied varieties to polymetallic stress. This is achieved not only due to the physiological response of the plant to toxicants, but also due to the delay of most of them at the level of the root system (Tables 13.4 and 13.5). Due to the good adaptation of plants to stress, by the end of the growing season there is a significant increase in the length of the shoots of sorghum on soils contaminated with heavy metals from 40% to 77%, depending on the variety and pollutant elements in relation to the control.

According to the data obtained in the course of a model experiment on soils with polyelement pollution, the root system of both sorghum varieties absorbed a large amount of Fe (3460–96100 mg/kg DW), Mn (289–1780 mg/kg DW), V (3.5–45.5 mg/kg DW), Cr (4.3–16 mg/kg DW) from soils (Tables 13.4 and 13.5). Differences in the accumulation of elements such as Pb, Cu, As and Ba are observed between the varieties (Tables 13.4 and 13.5). The root system of the Sucro cultivar accumulates them in large quantities, while in the Biomass cultivar the content of these elements in the roots remains at the average level. At the same time, the transfer factor of these elements from roots to shoots is low. The root system of sorghum in this case exhibits a barrier function. The mechanism of phytoremediation for these elements is rhizofiltration.

At the same time, zinc accumulation is observed in shoots with a transfer factor to the root system from 0.4 to 1 and from the root system to the shoot 0.5. Despite the values of zinc accumulation by shoots was in the range of 21–83 mg/kg DW, due to the formation of good biomass, the amount of Zn in soils with an excess of MPC decreases by 12–19%. Thus, among the elements presented in the work, zinc is the only one that undergoes phytoextraction. Sorghum can be recommended for soil remediation from Zn on soils with multielement anomalies.

Calculation of the removal of elements (mineralomass) from the soil by the organs of sorghum showed that the shoots of sorghum carry from 42 to 428 g/ha of Pb. Phytoextraction of lead by shoots of sorghum cv. Sucro is more effective and amounts to 141–290 g/ha on contaminated soils. Phytoextraction of lead in sorghum cv. Biomass is effective only on the soils of SPZ highways and amounts to 134 g/ha. The root system accumulates lead more efficiently, and on contaminated soils, the removal of the element by sorghum roots reached to 671–2109 g/ha (Table 13.9).

The removal of *Cd* from the soil by the shoots of sorghum was maximum for the soils of highways is 111–113 g/ha. Sorghum Sucro also actively removes Cd on KMP soils. The obtained values of the removal of cadmium from sorghum on the soils of the sanitary protection zones of metallurgical enterprises and highways were 10–12 times higher than the values given in the literature for sorghum, sunflower, tobacco, and corn (Keller et al. 2003). Forming less biomass, the root system takes out less Cd than shoots (4–48 g/ha) (Table 13.9).

In our study, sorghum effectively phytoextracted *Cu*. The removal of copper by the shoots of sorghum is 1033–8000 g/ha. The values obtained on urban soils of temperate climates zone were higher than those presented in the literature for other crops of 50–474 g/ha (Murillo et al. 1999) (Table 13.1). This is also due to moderate soil pollution, which maximizes phytoextraction efficiency (Kolbas et al. 2011). The most effective variety in phytoextraction of copper is the Sucro (2185–8000 g/ha on contaminated soils). The Biomass variety actively phytoextracts Cu on the soils of the SPZ highways (more than 3 kg/ha). Phytoextraction of copper by

Table 13.9 Removal of Pb, Cd, and Cu from soil by organs of sorghum, g/ha

Sample point	Variety	Pb	Cd	Cu
Shoots				
Background	Sucro	428	62	1033
TCh		197	55	2185
KMP		141	136	3209
Lenin Av.		290	111	8000
Background	Biomass	42	91	3689
TCh		39	20	1327
KMP		78	35	1768
Lenin Av.		134	113	3923
Roots				
Background	Sucro	170	4	673
TCh		671	8	2064
KMP		1701	40	5553
Lenina Avenue		2109	48	9571

sorghum roots was comparable with phytoextraction by shoots and varies 673 g/ha on background soils up to 2064–9571 g/ha on soils with multielement anomalies (Table 13.9).

Sorghum effectively extracts *V*, *Cr*, and *Mn* (Table 13.10). Sorghum cv. Biomass most actively removed these elements from contaminated soils. Thus, the removal of *V* from soils with polyelement anomalies by sorghum shoots was 54–158 g/ha for sorghum Sucro and 87–195 g/ha for sorghum Biomass. Phytoxtraction of the element by the root system is 11–40 times greater than by shoots and amounts to 627–6384 g/ha for sorghum Sucro and 1512–4707 g/ha for sorghum Biomass.

Table 13.10 Removal of elements from soil by organs of sorghum, g/ha

Soil collection site	Variety, part	V	Cr	Mn	Fe	Zn	Co	As	Mo	Sb	Ba
Background	Sucro, shoots	53	201	13728	87472	6160	11	67	74	11	1232
Background	Sucro, roots	627	789	5782	169540	1176	102	37	28	8	147
Lenin avenue	Sucro, shoots	158	428	16896	134112	22704	11	21	84	5	8448
Lenin avenue	Sucro, roots	1120	1568	92480	2806400	39600	122	531	138	112	53760
KMP	Sucro, shoots	54	255	8672	102438	23306	33	16	136	16	3252
KMP	Sucro, roots	1243	753	68075	2310000	13300	233	460	61	98	40425
TCh	Sucro, shoots	197	322	47946	111612	8646	20	177	409	12	2358
TCh	Sucro, roots	6384	3812	249200	13454000	6580	73	272	93	282	22260
Background	Biomass, shoots	39	211	26676	53703	10179	14	116	60	4	1755
Background	Biomass, roots	2282	948	15399	311460	3567	147	52	10	7	6612
Lenin Avenue	Biomass shoots	103	493	33891	134537	64701	21	277	226	31	4108
Lenin Avenue	Biomass roots	2921	2242	76700	2743500	40710	386	271	62	100	18290
KMP	Biomass shoots	87	409	106262	758800	71422	52	305	218	44	5226
KMP	Biomass roots	1512	916	424800	1452500	30246	92	409	75	81	8094
TCh	Biomass shoots	195	254	16104	71919	10248	15	132	156	15	1952
TCh	Biomass roots	4706	2301	44980	4354000	4498	114	237	107	28	4844

Uptake of *Cr* by Sucro shoots was 255–428 g/ha and that by sorghum Biomass was 753–1568 g/ha. Phytoextraction of chromium by the root system was slightly higher and amounted to 254–916 g/ha for Sucro sorghum and 916–2301 g/ha for Biomass sorghum (Table 13.10). The data obtained make it possible to recommend Biomass sorghum for phytoremediation of soils from V and Cr on the soils of the Tulachermet and Polema SPZs, where cast iron, vanadium, and chromium are produced.

Mn removal by sorghum was measured kg/ha and amounted to 8.672–47.956 kg/ha for shoots of sorghum Sucro; 68,075–249,200 for sorghum Biomass. The maximum removal of the element was observed on the soils of the Tulachermet SPZ. The phytoextraction of manganese by the sorghum root system was slightly higher and amounted to 16.104–106.262 kg/ha for the cultivar Sucro and 44.98–424.800 kg/ha for the cultivar Biomass. The removal of the element by roots was more efficiently carried out on the soils of the KMP.

A high affinity for Fe and a maximum removal of the element from sorghum soils by both studied varieties were observed. Phytoextraction of the element by shoots reached 102.438–134.112 kg/ha for the Sucro variety, 71.919–758.800 kg/ha for the Biomass variety. The removal of the element by the root system was measured in tons and amounted to 2.310–13.454 t/ha for the Sucro variety and 1.453–4.354 t/ha for the Biomass variety. The ability of sorghum to remove iron from soils quickly including it in biogeochemical cycles is especially important for the model region, where soils contain a large amount of iron even in background zones.

Sorgo actively remove *Zn* from soils. The removal of the element by sorgo shoots was 8.646–23.306 kg/ha for the variety Sucro and 10.248–71.422 kg/ha for the variety Biomass. Phytoextraction of zinc by the root system was comparable, and in some cases lower than by shoots and amounted to 6.580–39.600 kg/ha and 4.498–40.710 kg/ha for Sucro and Biomass varieties, respectively. The maximum removal was observed on the zinc-contaminated soils of the KMP and Lenin Avenue.

Co is a pollutant of all soils in the region without exception, and the selection of phytoremediates for soil remediation from cobalt is very relevant.

Phytoextraction of Co from contaminated soils was 11–33 g/ha for shoots of sorghum Sucro and 15–52 g/ha for shoots of variety Biomass. The data on the removal of the element from soils are close to the literature (20–30 g/ha) (Marchiol et al. 2007); however, for sorghum Biomass on KMP soils, they were slightly higher and amounted to 52 g/ha. The root system extracted the element more actively: 73–233 g/ha and 271–409 g/ha for the Sucro and Biomass varieties, respectively.

The removal of arsenic, which is also a contaminant of the region's soils, including the soils of the sanitary protection zones of enterprises and the highway, amounted 16–177 g/ha for shoots of Sucro sorghum and 132–277 g/ha for shoots of Biomass variety. These values correspond to the literature data obtained for sorghum on contaminated soils in Italy (158–219 g/ha) (Marchiol et al. 2007). The root system extracted arsenic at slightly higher levels: 73–233 g/ha and 237–409 g/ha for Sucro and Biomass, respectively.

Thus, taking into account the removal of elements on the dry mass, formed by sorghum on soils contaminated with TTE, sorghum should be recommended for phytoextraction of elements such as Pb, Cd and Cu (cv. Sucro for all studied soils, cv. Biomass for soils of the SPZ highway). In addition, sorghum of the studied varieties can be recommended for phytoextraction of V, Cr, Mn, Fe, Zn, Co and As from soils. The most active phytoextractant in relation to the listed elements is the Biomass variety.

13.6 Conclusions

This work aimed at assessing sustainable phytoremediation options for urban Me-contaminated soils using sorghum, as promising biomass crop with C-4 assimilation. It includes both the assessment of initial and residual risks (biomonitoring) and long-term sustainable decontamination options using plants and associated microbes, with the secondary purposes of producing plant-based feedstock and restoring ecosystem services.

Based on our results and other research studies, a phytomanagement plan is suggested in the purpose of full cycle phytoremediation of Me-contaminated sites using sustainable phytoextraction or rhizofiltration strategy tandem with high biomass production, including four principal stages: (1) evaluation of the initial level of pollution and environmental risks; (2) selection of plant/microorganisms/and suitable options; (3) implementation of the selected remediation strategy in the field condition; and (4) biomass valorization and developing the remediation strategy and implementation in the large scale.

The usefulness of two commercial cultivars of sorghum (*Sorghum bicolor*) for the phytoremediation of Me-contaminated soils was investigated. The physiological parameters in relation to multielement soil anomalies generally showed a greater resistance to complex pollution of urban soils. For most of the elements, with the exception of cooper, preferential root removal and low transfer to the shoots were revealed.

The use of cultural and culture-independent methods for the analysis of the rhizosphere microbiomes of remediating plants makes it possible to better understand the formation of plant-microbial associations, to identify key (constitutive or core) and situational (formed under the influence of selective environmental conditions) microbial partners of plant, to isolate of new isolates with target properties to improve plant growth under unfavorable conditions and achieve maximal phytoremediation effect. A more detailed study of the metal resistance of the new isolates, as well as the evaluation of their plant growth-promoting abilities will allow us to select a promising inoculant to improve the growth of sorghum plants in heavy metal contaminated soil and increase the efficiency of its phytoremediation.

In our work, the first stages of phytomanagement were tested. The subsequent stages on field scale are carried out on the Me-contaminated soils in Tula and Brest. Ecological restoration options for Me-contaminated soils based on phytoremediation using annual Me-secondary accumulator plants with a high shoot biomass would (1) result in the progressive decontamination of Me-contaminated soils during crop rotations, (2) provide a financial return through biomass valorization, and (3) promote ecosystem services.

Acknowledgement The study was carried out with the financial support by the Russian Foundation for Basic Research project No 19-29-05257 "Technogenic soil pollution with toxic elements and possible methods for its elimination."

References

Aafi NE, Brhada F, Dary M, Maltouf AF, Pajuelo E (2012) Rhizostabilization of metals in soils using *Lupinus luteus* inoculated with the metal resistant rhizobacterium *Serratia* sp. MSMC 541. Int J Phytoremediation 14:261–274. https://doi.org/10.1080/15226514.2011.604693

Acosta-Martínez V, Dowd SE, Bell CW, Lascano R, Booker JD, Zobeck TM, Upchurch DR (2010) Microbial community composition as affected by dryland cropping systems and tillage in a semiarid sandy soil. Diversity 2:910–931. https://doi.org/10.3390/d2060910

Ali A, Guo D, Mahar A, Ma F, Li R, Shen F, Wang P, Zhang Z (2017) *Streptomyces pactum* assisted phytoremediation in Zn/Pb smelter contaminated soil of Feng County and its impact on enzymatic activities. Sci Rep 7(1):1–13. https://doi.org/10.1038/srep46087

A.V. Gorbunov, S.V. Gorelova, S.M. Lyapunov Monitoring akkumulyacii i raspredeleniya toksichnyh elementov v pochvah g. Tuly 2013-2019 GODY. Izvestiya Tul'skogo gosudarstvennogo universiteta. Nauki o Zemle. 2020; 2: 3-13 [in Russian]

Baker AJM, McGrath SP, Reeves RD, Smith JAC (2000) Metal hyperaccumulator plants: a review of the ecology and physiology of a biological resource for phytoremediation of metal-polluted soils. Phytorem Contaminated Soil Water:85–107

Bityuckij NP (2011) Mikroelementy vysshih rastenij. SPb.: Izd-vo S.-Peterb. un-ta, : 368 p. [in Russian]

Boyd RS (2007) The defense hypothesis of elemental hyperaccumulation: status, challenges and new directions. Plant Soil 293:153–176

Brooks R, Wither ED, Zepernick B (1977) Cobalt and nickel in Rinorea species. Plant Soil 47:707–712

Carrier M, Loppinet-Serani A, Absalon C, Marias F, Aymonier C, Mench M (2011) Conversion of fern (Pteris vittata L.) biomass from a phytoremediation trial in sub- and supercritical water conditions. Biomass Bioenergy 35:872–883

Chaney RL (1989) Toxic element accumulation in soils and crops: protecting soil fertility and agricultural food-chains. pp. 140–158

Claus D, Dietze H, Gerth A, Grosser W, Hebner A (2007) Application of agronomic practice improves phytoextraction on a multipolluted site. J Environ Eng Landsc Manag 15:208–212

Epelde L, Mijangos I, Becerril JM, Garbisu C (2009) Soil microbial community as bioindicator of the recovery of soil functioning derived from metal phytoextraction with sorghum. Soil Biol Biochem 41:1788–1794. https://doi.org/10.1016/j.soilbio.2008.04.001

Faessler E, Robinson BH, Stauffer W, Gupta SK, Papritz A, Schulin R (2010) Phytomanagement of metal-contaminated agricultural land using sunflower, maize and tobacco. Agric Ecosyst Environ 136:49–58

Faucon MP, Shutcha MN, Meerts P (2007) Revisiting copper and cobalt concentrations in supposed hyperaccumulators from SC Africa: influence of washing and metal concentrations in soil. Plant Soil 301:29–36

Foyer CH, Noctor G (2005) Redox homeostasis and antioxidant signaling: a metabolic interface between stress perception and physiological responses. Plant Cell 17(7):1866–1875

Gabrielli dos Santos GC, Rodella A, de Abreu CA, Coscione AR (2010) Vegetable species for phytoextraction of boron, copper, lead, manganese and zinc from contaminated soil. Sci Agric 67:713–719

GN 2.1.7.2041-06. (2006) Predel'no dopustimye koncentracii (PDK) himicheskih veshchestv v pochve: Gigienicheskie normativy. – M.: Federal'nyj centr gigieny i epidemiologii Rospotrebnadzora, (Hygienic standards GN 2.1.7.2041-06. Maximum Permissible Concentrations (MPCs) of Chemicals in the Soil. Moscow); – 15 p. https://files.stroyinf.ru/Data2/1/4293850/4293850511.pdf [in Russian]

GN 2.1.7.2511-09. (2009) Orientirovochno dopustimye koncentracii (ODK) himicheskih veshchestv v pochve: Gigienicheskie normativy. – M.: Federal'nyj centr gigieny i epidemiologii Rospotrebnadzora, (Hygienic standards GN 2.1.7.2511-09. Approximate allowable concentrations (AAC) of chemical substances in soils. Moscow); – 10 p. https://files.stroyinf.ru/Data2/1/4293828/4293828439.pdf (in Russian)

Gorbunov AV, Frontasyeva MV, Lyapunov SM, Okina OI, Pavlov S, Ilchenko IN (2015) Nuclear and related analytical techniques in geomedicine: assessment of the impact of environmental factors on human health. A revivew. Phys Elementary Part At Nuclei 46(3):424–451

Gorelova SV, Gorbunov AV, Frontasyeva MV, Sylina AK (2020) Toxic elements in the soils of urban ecosystems and technogenic sources of pollution. WSEAS Trans Environ Dev 16:608–618

GOST 28168-89. Pochvy. Otbor prob

GOST R 53123-2008 Kachestvo pochvy. Otbor prob

Gremion F, Chatzinotas A, Kaufmann K, Sigler WV, Harms H (2004) Impacts of heavy metal contamination and phytoremediation on a microbial community during a twelve-month microcosm experiment. FEMS Microbiol Ecol 48:273–283. https://doi.org/10.1016/j.femsec.2004.02.004

Gupta UC, Gupta SC (1998) Trace element toxicity relationships to crop production and livestock and human health: Implications for management. Commun Soil Sci Plant Anal 29:1491–1522. https://doi.org/10.1080/00103629809370045

Hagerberg D, Manique N, Brandt KK, Larsen J, Nybroe O, Olsson S (2011) Low concentration of copper inhibits colonization of soil by the arbuscular mycorrhizal fungus glomus intraradices and changes the microbial community structure. Microb Ecol 61:844–852. https://doi.org/10.1007/s00248-010-9795-2

Hussain SS, Mehnaz S, Siddique KHM (2018) Harnessing the plant microbiome for improved abiotic stress tolerance. In: Egamberdieva D, Ahmad P (eds). Plant microbiome: stress response, Springer Nature, Singapore, pp 21–43. https://doi.org/10.1007/978-981-10-5514-0_2

Jing Y, He Z, Yang X (2007) Role of soil rhizobacteria in phytoremediation of heavy metal contaminated soils. J Zhejiang Univ Sci B (Biomed Biotechnol) 8:192–207. https://doi.org/10.1631/jzus.2007.B0192

Kabata-Pendias A, Pendias H (2001) Trace elements in soil and plants, 3rd edn. CRC Press, Boca Raton, London, New-York, Washington, D.C., 432 P

Kayser A, Wenger K, Keller A, Attinger W, Felix HR, Gupta SK, Schulin R (2000) Enhancement of phytoextraction of Zn, Cd, and Cu from calcareous soil: the use of NTA and sulfur amendments. Environ Sci Technol 34:1778–1783

Keller C, Hammer D, Kayser A, Richaer W, Brodbeck M, Senhauser M (2003) Root development and heavy metal phytoextraction efficiency: comparison of different plant species in the field. Plant Soil 249:67–81

Kidd P, Mench M, Kolbas A, Álvarez-López V, Bert V, Dimitriou J et al (2015) Agronomic practices for improving gentle remediation of trace-element-contaminated soils. Int J Phytoremediation 17:1005–1037

Kolbas A, Mench M, Herzig R, Nehnevajova E, Bes CM (2011) Copper phytoextraction in tandem with oilseed production using commercial cultivars and mutant lines of sunflower. Int J Phytorem 13(Suppl 1):55–76

Kolbas A, Marchand L, Herzig R, Nehnevajova E, Mench M (2014) Phenotypic seedling responses of a metal-tolerant mutant line of sunflower growing on a Cu-contaminated soil series: potential uses for biomonitoring of Cu exposure and phytoremediation. Plant Soil 376:377–397

Kolbas A, Kidd P, Guinberteau J, Jaunatre R, Herzig R, Mench M (2015) Endophytic bacteria take the challenge to improve Cu phytoextraction by sunflower. Environ Sci Pollut Res 22:5370–5382

Kos B, Lestan D (2004) Chelator induced phytoextraction and in situ soil washing of Cu. Environ Pollut 132:333–339

Lenart-Boro A, Boro P (2014) The effect of industrial heavy metal pollution on microbial abundance and diversity in soils – a review. In: Hernandez Soriano MC (ed) Environmental risk assessment of soil contamination. InTech, pp 759–783. https://doi.org/10.5772/57406

Lichtentaller HK, Welburn AR (1983) Determinations of total carotenoids and chlorophylls a and b of leaf extracts in different solvents. Biochem Soc Trans 11(6):591–592

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. https://doi.org/10.1016/j.biotechadv.2010.12.001

MacNicol RD, Beckett PHT (1985) Critical Tissue Concentration of Potentially Toxic Elements. Plant and Soil 85:107–129. https://doi.org/10.1007/BF02197805

Madejon P, Murillo JM, Maranon T, Cabrera F, Soriano MA (2003) Trace element and nutrient accumulation in sunflower plants two years after the Aznalcollar mine spill. Sci Total Environ 307:239–257

Marchiol L, Fellet G, Perosa D, Zerbi G (2007) Removal of trace metals by *Sorghum bicolor* and *Helianthus annuus* in a site polluted by industrial wastes: a field experience. Plant Physiol Biochem 45:379–387. https://doi.org/10.1016/j.plaphy.2007.03.018

Markert B (1992) Establishing of 'reference plant' for inorganic characterization of different plant species by chemical fingerprinting. Water Air Soil Pollut 64:533–538

Meers E, Ruttens A, Hopgood M, Lesage E, Tack FMG (2005) Potential of Brassica rapa, Cannabis sativa, Helianthus annuus and Zea mays for phytoextraction of heavy metals from calcareous dredged sediment derived soils. Chemosphere 61:561–572

Mench M, Dellise M, Bes C, Marchand L, Kolbas A. Le Coustumer P, Oustrière N (2018) Phytomanagement of Cu-contaminated soils by high yielding crops at a former wood preservation site: sunflower biomass and ionome, and remediation of soil functions. Frontiers in Environmental Science, section Agroecology and Land Use Systems, pp. 1–17. https://doi.org/10.3389/fevo.2018.00123

Mittler R (2002) Oxidative stress, antioxidants and stress tolerance. Trends Plant Sci 7(9):405–410

Murakami M, Ae N (2009) Potential for phytoextraction of copper, lead, and zinc by rice (Oryza sativa L.), soybean (Glycine max L. Merr.), and maize (Zea mays L.). J Hazard Mater 162:1185–1192

Muratova AY, Gorelova SV, Sungurtseva IY, Zelenova NA (2020) Rhizospheric microbi-omes of Sorghum bicolor grown on soils with anthropogenic polyelement anomalies. In: BIO web of conferences, vol 23. EDP Sciences, p 03008. https://doi.org/10.1051/bioconf/20202303008

Murillo JM, Maranon T, Cabrera F, Lopez R (1999) Accumulation of heavy metals in sunflower and sorghum plants affected by the Guadiamar spill. Sci Total Environ 242:281–292

Nehnevajova E, Herzig R, Erismann K-H, Schwitzguebel J-P (2007) In vitro breeding of Brassica juncea L. to enhance metal accumulation and extraction properties. Plant Cell Rep 26:429–437

Oberholster T, Vikram S, Cowan D, Valverde A (2018) Key microbial taxa in the rhizosphere of sorghum and sunflower grown in crop rotation. Sci Total Environ 624:530–539. https://doi.org/10.1016/j.scitotenv.2017.12.170

Ojuederie O, Babalola O (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

Pilon-Smits E (2005) Phytoremediation. Ann Rev Plant Biol 56:15–39

Reeves RD (2006) Hyperaccumulation of trace elements by plants. In: Phytoremediation of metal-contaminated soils. J L E G N Morel, pp 25–52

Saet YU E, Revich B A, YAnin E P Geohimiya okruzhayushchej sredy. M.: Nedra, 1990: 335 p. [in Russian]

Santoyo G, Moreno-Hagelsieb G, Orozco-Mosqueda MC, Glick BR (2016) Plant growth-promoting bacterial endophytes. Microbiol Res 183:92–99. https://doi.org/10.1016/j.micres.2015.11.008

Sathya A, Kanaganahalli V, Srinivas Rao P, Gopalakrishnan S (2016) Cultivation of sweet sorghum of heavy metal concotaminated soils by phytoremediation approach for production of bioethanol. In: Bioremediation and bioeconomy. Elsevier, Amsterdam, pp 271–292

Schlemper TR, van Veen JA, Kuramae EE (2018) Co-variation of bacterial and fungal communities in different sorghum cultivars and growth stages is soil dependent. Microb Ecol 76(1):205–214. https://doi.org/10.1007/s00248-017-1108-6

Sheng X, 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. https://doi.org/10.1016/j.jhazmat.2007.10.107

Sheoran V, Sheoran AS, Poonia P (2009) Phytomining: a review. Miner Eng 22:1007–1019

Sonowal S, Narasimha M, Prasad V, Sarma H (2018) C3 and C4 plants as potential phytoremediation and bioenergy crops for stabilization of crude oil and heavy metal co-contaminated soils-response of antioxidative enzymes. Trop Plant Res 5(3):306–314

Soudek P, Petrová Š, Vaňková R, Song J, Vaněk T (2014) Accumulation of heavy metals using *Sorghum* sp. Chemosphere 104:15–24. https://doi.org/10.1016/j.chemosphere.2013.09.079

Takahama U, Oniki T (2000) Flavonoids and some other phenolics as substratis of peroxidase: physiological significans of the redox reactions. J Plant Res 113:301–309

Tihonov A N (1999) Zashchitnye mekhanizmy fotosinteza. Sorosovskij obrazovatel'nyj zhurnal. 1999; 11: 16-21. [in Russian]

Trevors JT, Oddie KM, Belliveau BH (1985) Metal resistance in bacteria. FEMS Microbiol Rev 32:39–54. https://doi.org/10.1111/j.1574-6968.1985.tb01181.x

Tshabuse F. Identification of rhizospheric microorganisms associated with sorghum. Submitted in partial fulfilment of the requirements for the degree of Magister Scientiae (M.Sc.) in the Department of Biotechnology, University of the Western Cape. 2012. https://pdfs.semanticscholar.org/9e7a/3f9f989c05901a4bc3ec2d76bd6bbfe6e6b4.pdf

Vamerali T, Bandiera M, Mosca G (2010) Field crops for phytoremediation of metal-contaminated land. A review. Environ Chem Lett 8:1–17

Vangronsveld J, Colpaert JV, Van Tichelen KK (1996) Reclamation of a bare industrial area contaminated by non-ferrous metals: Physicochemical and biological evaluation of the durability of soil treatment and revegetation. Environ Pollut 94:131–140

Vangronsveld J, Herzig R, Weyens N, Boulet J, Adriaensen K, Ruttens A, Thewys T, Vassilev A, Meers E, Nehnevajova E, Van Der Lelie D, Mench M (2009) Phytoremediation of contaminated soils and groundwater: lessons from the field. Environ Sci Pollut Res 16:765–794. https://doi.org/10.1007/s11356-009-0213-6

Yang Q, Tu S, Wang G, Liao X, Yan X (2012) Effectiveness of applying arsenate reducing bacteria to enhance arsenic removal from polluted soils by *Pteris vittata* L. Int J Phytoremediation 14:89–99. https://doi.org/10.1080/15226510903567471

Zagoskina NV Fenol'nye soedineniya i ih uchastie v zashchite rastenij ot stressovyh vozdejstvij/N V Zagoskina. Fenol'nye soedineniya: funkcional'naya rol' v rasteniyah. M.: Izd.PRESS-BOOK. RU. 2018: 150-153. [in Russian]

Zaprometov M N Fenol'nye soedineniya i metody ih issledovaniya // Biohimicheskie metody v fiziologii rastenij / Pod red. Pavlinovoj O.A. M.: Nauka, 1971:185–197. [in Russian]

Zaprometov M N Osnovy biohimii fenol'nyh soedinenij/ Pod red. M.N. Zaprometova/. M.: Vysshaya shkola, 1974:74–100. [in Russian]

Zaprometov M N Fenol’nye soedineniya i ih rol' v zhizni rastenij: 56-e Timiryazevskoe chtenie / MN Zaprometov. M.: Nauka, 1996: 45 p. [in Russian]

Zhuang P, Shu W, Li Z, Liao B, Li J, Shao J (2009) Removal of metals by sorghum plants from contaminated land. J Environ Sci 21(10):1432–1437. https://doi.org/10.1016/s1001-0742(08)62436-5

Chapter 14

Comparative Effect of Cadmium on Germination and Early Growth of Two Halophytes: *Atriplex halimus* L. and *A. nummularia* Lindl. for Phytoremediation Applications

Bouzid Nedjimi

Abstract Cadmium (Cd) is a heavy metal (HM), which is highly toxic and hazardous to all living organisms, even in low concentrations. The choice of the better species for seeding and sowing the Cd-ontaminated soils is of fundamental importance, especially in arid areas. *Atriplex* spp. are characterized by high tolerance to salinity, extreme temperatures, and HMs. In this work, the toxicity impacts of Cd on germinability characteristics and subsequent seedlings growth of two halophytic species (*Atriplex halimus* and *A. nummularia*) have been investigated. Seeds were treated with $CdCl_2$ at various concentrations (0, 100, 200, and 300 μM) for 15 days under controlled conditions (25 ± 1 °C with 16/8-h photoperiods). Results indicate that Cd significantly affected the final germination, germination rate, and both hypocotyl and radicle lengths of the studied halophytes. Both *Atriplex* seeds were usually tolerant to Cd at low concentrations, but high Cd concentrations significantly reduced all cited parameters. Based on the results of the tolerance index and degree of phytotoxicity, *A. halimus* seemed to be more resistant to Cd toxicity than *A. nummularia*.

Keywords Cadmium tolerance index · Germination bioassays · Phytoremediation · Phytotoxicity · Saltbushes · *Timson's* index

---

B. Nedjimi (✉)
Laboratory of Exploration and Valorization of Steppe Ecosystem, Faculty of Science of Nature and Life, Ziane Achour University of Djelfa, Djelfa, Algeria

L. Newman et al. (eds.), *Phytoremediation*, https://doi.org/10.1007/978-3-031-17988-4_14

14.1 Introduction

Cadmium (Cd) pollution is among the most serious environmental threats to human health. Mine tailings, combustion emissions, phosphate fertilizers, pesticides, wastewater, atmospheric deposition, and sewage sludge are the principal sources of Cd pollution (Haider et al. 2021). Physiochemical procedures for Cd-decontamination of soils such as chemical leaching, excavation, precipitation, and heat treatment are quite very costly and may lead to soil modifications (Raza et al. 2020).

Germination inhibition, stunted growth, chlorosis, root browning, nutriments and water disturbance, and hormonal status failure were the major symptoms of Cd-toxicity in plant species (Moreira et al. 2020).

Phytoremediation using trees and shrubs is a promising, inexpensive, and environmentally friendly technique to eliminate pollutants and toxins from water and polluted soils (Nedjimi 2021). The success of this approach is related to the identification of promising shrub species to absorb, tolerate, and store a large amount of pollutants (HMs and toxins). In this context, the use of halophytic species with deep root systems and considerable green biomass constitutes an interesting tool for rehabilitating contaminated soils, especially in arid areas (Mujeeb et al. 2020; Joshi et al. 2020).

Seed halophyte germination and the subsequent seedlings' development are the initial delicate phases to environmental changes (Gul et al. 2013). The first critical phases of phytoremediation are the germination and seedling establishment in the HMs-polluted soils (Nedjimi 2020).

Atriplex spp. are group of the Amaranthaceae family (halophytes) growing indigenously in arid areas of the world, some of them are extremely resistant to harsh conditions such as salt and drought stresses, soil pollution, and extreme temperatures (Le Houérou 1992). They are persistent saltbushes that keep their leaves throughout the year and are usually used as forage by livestock in arid and semi-arid rangelands (El Shaer 2010; Nedjimi 2018). Though some works have examined the seed tolerance capacity of *Atriplex* species to salinity (Bhatt and Santo 2016; Shaygan et al. 2017; Bueno et al. 2017), little information is known about the effect of HMs on the germination of these halophytic species. Thus, the present investigation aims to evaluate the impact of Cd stress on the seed germinability and initial establishment of two *Atriplex* species widely cultivated in Algerian arid areas. This work is supposed to be useful in assessing the Cd tolerance and phytoremediation potential of *A. halimus* and *A. nummularia* to clean up polluted soils.

14.2 Materials and Methods

14.2.1 Species Description and Seed Source

Atriplex halimus L. (common name: Mediterranean saltbush) (Fig. 14.1a) is a perennial shrub reaching up to 1–3 m high, native to North African countries (Algeria, Tunisia, Morocco, and Libya). It is extremely resistant to water and salt

Fig. 14.1 (**a**) *Atriplex halimus* L. (Mediterranean saltbush) and (**b**) *A. nummularia* Lindl. (Old man saltbush)

stresses and can survive for several months without rainfall (Le Houérou 1992). *Atriplex nummularia* Lindl. (common name: Old man saltbush) introduced from Australia is erect evergreen saltbush that reaches 2.5–3 m high and grows in inland saline soils (Fig. 14.1b). It is very resistant to drought and grazing and produces a high leaf and wood biomass (Falasca et al. 2014).

Both *Atriplex* seeds were procured from the HCDS nursery of *Taâdmit*, located about 50 km from Djelfa province, Algeria (2° 59′ E long., 34° 17′ N lat., and 1049 m alt.). The annual precipitation in this region is about 250 mm. Minimum and maximum monthly temperatures occur respectively in January (3 °C) and July (34 °C). The seeds were kept in paper bags at 4 °C until the start of the germination test.

14.2.2 Germination Experiment and Seedling Measurements

Before germination, *Atriplex* seeds were disinfected for 10 min with 70% ethylic alcohol, treated with 8% H_2O_2 for 5 min, and finally rinsed with deionized water. Seeds of each species were deposed in petri dishes (90 mm diameter) lined with two disks of sterilized Whatman filter paper. The petri dishes were kept moistened with 5 mL of corresponding Cd-treatments (0, 100, 200, 300 μM $CdCl_2$). These concentrations were selected according to the Cd levels reported in Algerian arid soils

(Nedjimi and Daoud 2009). The petri dishes were arranged in a completely randomized design (CRD), with four replications, and each replicate contains 25 sterilized seeds (100 seeds/treatment).

Petri dishes were placed in an incubator in an alternating photoperiod of 16 h light/8 h obscurity at 25 °C temperature with photon flux intensity of 200 μmol m^{-2} s^{-1}. The germinated seeds were counted for 15 consecutive days till no further germination was detected. The protrusion of visible radicle by 2 mm through the seed coat was considered a germination criterion.

At the end of each experiment, the rate of germination (RG), using *Timson's* index, was determined by the following formula:

RG = Σ pg/t, where (pg) is the % of germination after 48 h interval, and (t) is the total time of the experiment (Nedjimi et al. 2020). Hypocotyl and radicle sizes were measured using a graduate scale.

The tolerance index (TI %) was measured by the equation given by Wilkins (1978):

TI % = [radicle size in Cd treatment/radicle size control] × 100.

The phytotoxicity index (PI %) was assessed using the method given by Hsu and Chou (1992):

PI % = [radicle size control − radicle size in Cd treatment/radicle size control] × 100.

14.2.3 Statistical Analysis

The statistical difference between the Cd-treatments was calculated using analysis of two-way ANOVA. Results are reported as mean ± standard error of four replicates for each treatment. Significance level was performed by post-hoc *Duncan*'s test ($P < 0.05$) using the software package STATISTICA 8.0.

14.3 Results and Discussion

14.3.1 Cadmium Effects on Germination Percentage

Results exhibited that the germination percentage was correlated to the Cd concentrations and the studied species (Fig. 14.2). The analysis of variance (ANOVA) indicates a significant effect of the *Atriplex* species ($F = 71.68$, $P < 0.001$), Cd-treatments ($F = 48.29$, $P < 0.001$) and their combination ($F = 802$, $P < 0.001$) on the seed germination percentage (Table 14.1). Seeds of both species are capable to germinating at all Cd concentrations (Fig. 14.2).The highest values of germination were detected in the control and low Cd treatments, but a gradual increase in Cd concentrations significantly reduced seed germination (Figs. 14.2 and 14.3). The prevention effect of this HM was more pronounced for *A. nummularia*, particularly when seeds were exposed to the highest concentrations (200 and 300 μM $CdCl_2$) (Fig. 14.2).

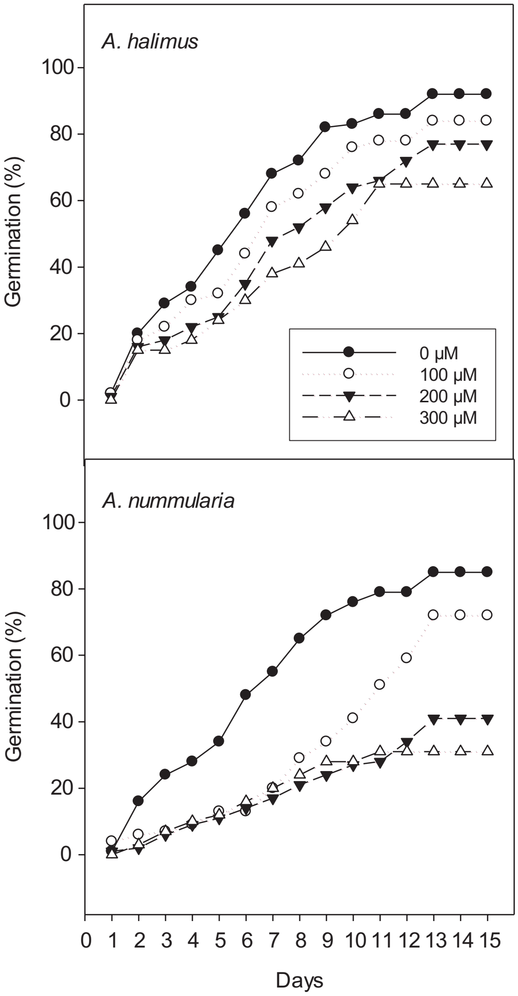


Fig. 14.2 Cumulative germination percentage as a function of time of *Atriplex halimus* and *A. nummularia* seeds treated with $CdCl_2$ concentrations (0, 100, 200, and 300 µM)

In this work, the impact of Cd application on the germination characteristics of two halophytes was examined. The findings showed that this HM affected the final germination in both halophytes. The depressive effect of Cd on germinability was more pronounced on *A. nummularia* seeds compared to *A. halimus*. These results were found in agreement with previously reported results such as *Arabidopsis thaliana* (Li et al. 2005), *Salicornia brachiata* (Sharma et al. 2011), and *Suaeda salsa* (Liu et al. 2012). Heavy metals may impair seed germination and seedling establishment by water imbibition failure, metal harmfulness, mineral nutrition imbalance, or the interaction of these factors (Kranner and Colville 2011). Cadmium possesses an effect on seed–water exchanges, causing a direct decrease in water uptake. If Cd crosses the seed coat, it affects the metabolic activities (mobilization of nutrients) that occur in the germination process (Nedjimi and Daoud 2009; Tran and Popova

Table 14.1 A two-way ANOVA of the effects of species (Sp), concentrations (C), and their combination (Sp × C) on germination, seedling growth, tolerance index, and phytotoxicity index of *Atriplex halimus* and *A. nummularia*

Independent variables	Species (Sp)	Concentrations (C)	Interaction (Sp × C)
Germination percentage	71.68^{***}	48.29^{***}	8.02^{***}
Rate of germination	133.39^{***}	62.97^{***}	6.28^{**}
Hypocotyl length	4.87^{*}	4.07^{*}	0.11^{ns}
Radicle length	48.23^{***}	43.03^{***}	8.01^{**}
Tolerance index	126.49^{***}	313.97^{***}	20.12^{***}
Phytotoxicity index	54.51^{***}	135.07^{***}	8.66^{**}

Note: Data represent *F*–values significant at $^{*}P < 0.05$, $^{**}P < 0.01$, $^{***}P < 0.001$, ns, not significant

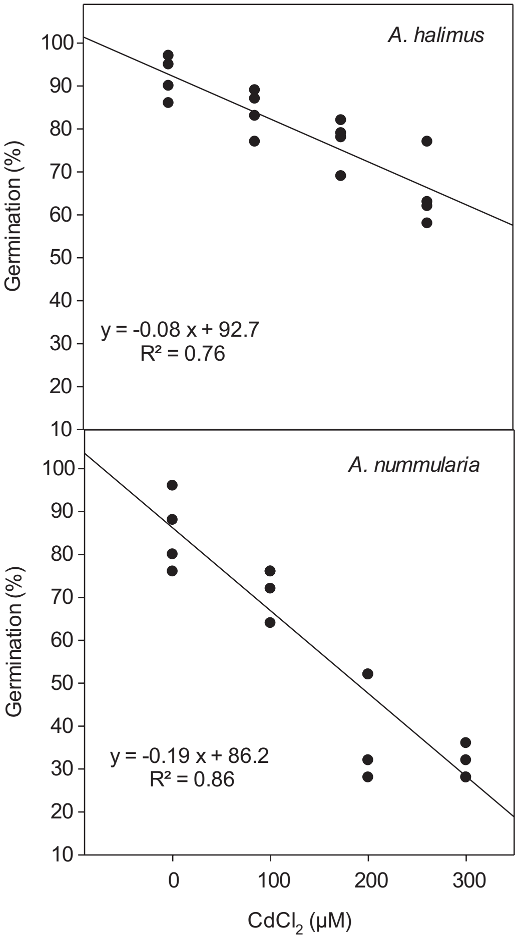


Fig. 14.3 Regression plots of mean germination percentage of *Atriplex halimus* and *A. nummularia* seeds treated with $CdCl_2$ concentrations (0, 100, 200, and 300 μM)

2013). This difference in the germination failure between species can be attributed to their different selective absorption across the seed teguments (anatomy and structure of coat) and embryo metal-tolerance (Siddiqui et al. 2014). The external coat of the seed acts like a barrier that avoids the penetration of a considerable amount of Cd inside the embryo from the polluted soil and protects the embryo from Cd toxicity (Amin et al. 2018).

14.3.2 Cadmium Effects on the **Timson's** *Index*

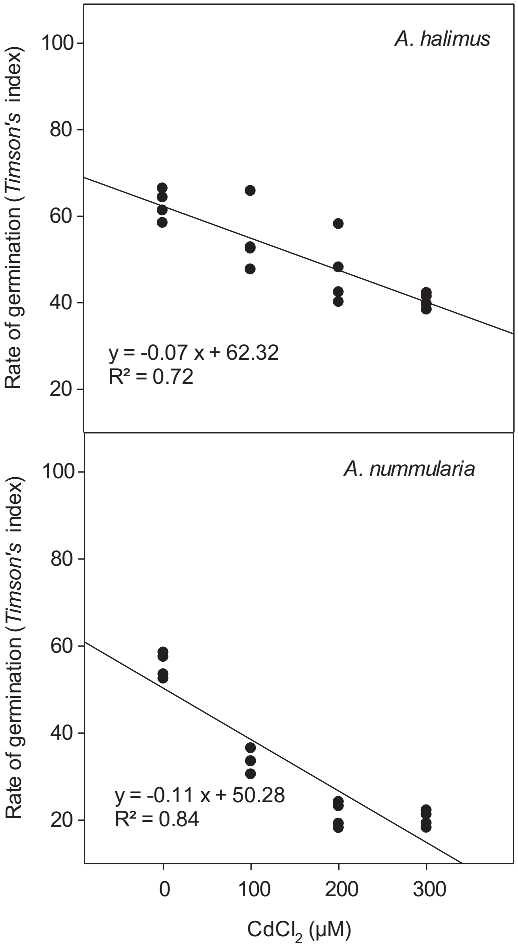
Analysis of variance (ANOVA) shows that *Timson's* index (germination rate) was significantly affected by the *Atriplex* species ($F = 133.39$, $P < 0.001$), Cd-treatments ($F = 62.97$, $P < 0.001$) and the combination of these two factors ($F = 6.28$, $P < 0.01$) (Table 14.1). The rate of germination of both halophytic species was affected significantly by Cd application as compared to control (Fig. 14.4). Rate of germination decreased with exposure to increasing Cd treatments, and this reduction was more apparent for the highest concentrations. At high Cd concentration (300 μM $CdCl_2$), the rate of germination was reduced by 35.46% and 63.58%, respectively, for *A. halimus* and *A. nummularia*. The depressive effect of Cd on seed germination rate was also reported in other halophytes such as *Spartina alterniflora* (Mrozek 1980); *Suaeda salsa* (Liu et al. 2012).

The influence of Cd on the seed germinability depends on their aptitude to penetrate embryonic tissues across the seed teguments (coats). The anatomy and thickness of the coat differ between plant species, and consequently, the same concentration of Cd had a different impact among species. The germination depends on the cotyledon reserve mobilization (starch and polysaccharides) for the embryo development; however, the presence of Cd can cause oxidative stress (ROS) and disturbs the hydrolyzing enzyme involved in the germination event (Kuriakose and Prasad 2008; Kranner and Colville 2011).

14.3.3 Cadmium Effects on Early Seedling Growth

Plant morphology is a better character for the description of plant growth changes in the presence of HMs (Amin et al. 2018). The impact of different treatments of Cd on hypocotyl length of *Atriplex* species is presented in Fig. 14.5. The analysis of variance (ANOVA) indicated that the *Atriplex* species ($F = 4.87$, $P < 0.05$) and Cd-treatments ($F = 4.07$, $P < 0.05$) had a significant effect on hypocotyl elongation, but their combination was not significant ($F = 0.11$, $P > 0.05$) (Table 14.1). The increase of Cd doses produced a significant reduction in the hypocotyl elongation of both species. The highest concentrations of Cd clearly affected the hypocotyl elongation of *A. nummularia*, while *A. halimus* was less affected (Fig. 14.5).

Fig. 14.4 Regression plots of the *Timson's* Index (rate of germination) of *Atriplex halimus* and *A. nummularia* seeds treated with $CdCl_2$ concentrations (0, 100, 200, and 300 μM)



Radicle elongation was also affected by Cd application (Fig. 14.5). The analysis of variance (ANOVA) demonstrated that the *Atriplex* species ($F = 48.23$, $P < 0.001$), Cd-treatments ($F = 43.03$, $P < 0.001$) and their combination ($F = 8.01$, $P < 0.01$) significantly affected radicle elongation (Table 14.1). An elevation in Cd concentrations significantly reduced the radicle elongation of both species. At 300 μM $CdCl_2$ the radicle length was reduced by 46.97% and 57.71%, respectively, for *A. halimus* and *A. nummularia.* This aspect has also been mentioned in other halophytic species belonging to the Amaranthaceae family such as *Salicornia brachiata* (Sharma et al. 2011) and *Halogeton glomeratus* (Yao et al. 2021). However, Santos et al. (2015) showed an opposite pattern in the halophyte *Juncus acutus*, who found that application of 0.05, 0.1, 0.5, and 1 μM $CdSO_4$ significantly increased seedling length compared to control. This impairment in radical growth caused by Cd application can be due to its effect on cell division and/or cell wall elasticity (Kranner and Colville

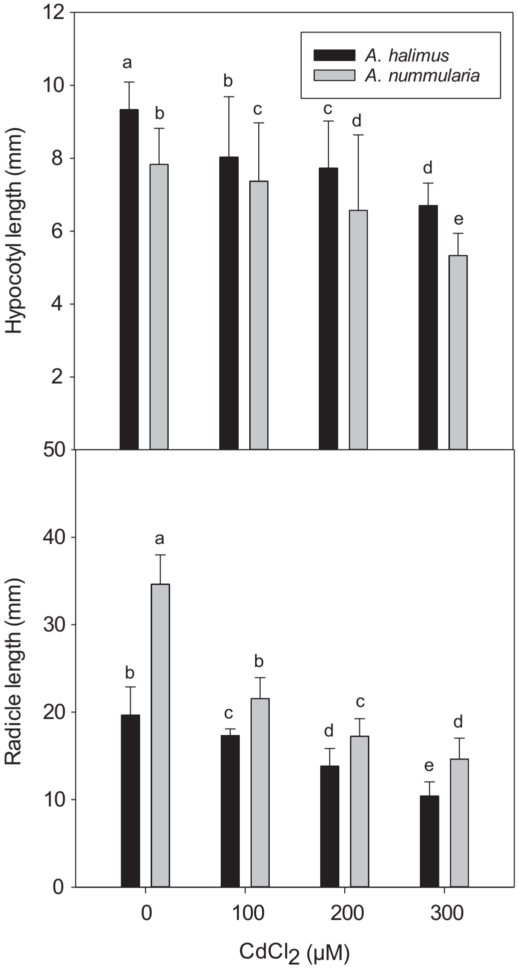


Fig. 14.5 Hypocotyl and radicle elongations of *Atriplex halimus* and *A. nummularia* seedlings treated with $CdCl_2$ concentrations (0, 100, 200, and 400 μM). Bars represent means ± S.E. ($n = 3$). Different letters indicate a significant difference between treatments ($P < 0.001$, *Duncan*'s multiple–range test)

2011). The root system is the first plant organ exposed to pollutants and is more sensitive to metal exposure than the aerial part (Zhang et al. 2020). Root growth reduction, underdeveloped root hair, and browning of roots were the main symptoms of Cd toxicity (Mahmood et al. 2007; Moreira et al. 2020). Cadmium stress blocks cell division, thus decreasing plant elongation, preventing mineral nutrition and water improvement, and leads to reducing aerial part development (Yao et al. 2021). Several reasons can be anticipated to explain the stunted growth of hypocotyl induced by Cd application: inhibition of mitosis, polysaccharide metabolism breakdown, changes in photosynthesis, and reduction in the water potential (Nagajyoti et al. 2010).

14.3.4 Cadmium Tolerance Index (TI %)

Tolerance index (TI %) was significantly affected by *Atriplex* species ($F = 126.49$, $P < 0.001$), Cd-treatments ($F = 313.97$, $P < 0.001$), and their combination ($F = 20.12$, $P < 0.001$) (Table 14.1). In both halophytes, this parameter was significantly reduced in the presence of Cd treatments (Fig. 14.6). At 300 μM $CdCl_2$, *A. nummularia* and *A. halimus* had a tolerance index of 42% and 53%, respectively. *Atriplex halimus* seems to be more tolerant to Cd than *A. nummularia.* Zhang et al. (2020) mentioned that the tolerance index was a good parameter to classify a plant species as tolerant at germination stage and initial seedling growth. In our investigation, significant impairment in germination and early seedling growth induced by Cd-stress indicated that *A. nummularia* is less tolerant to Cd compared to *A. halimus*.

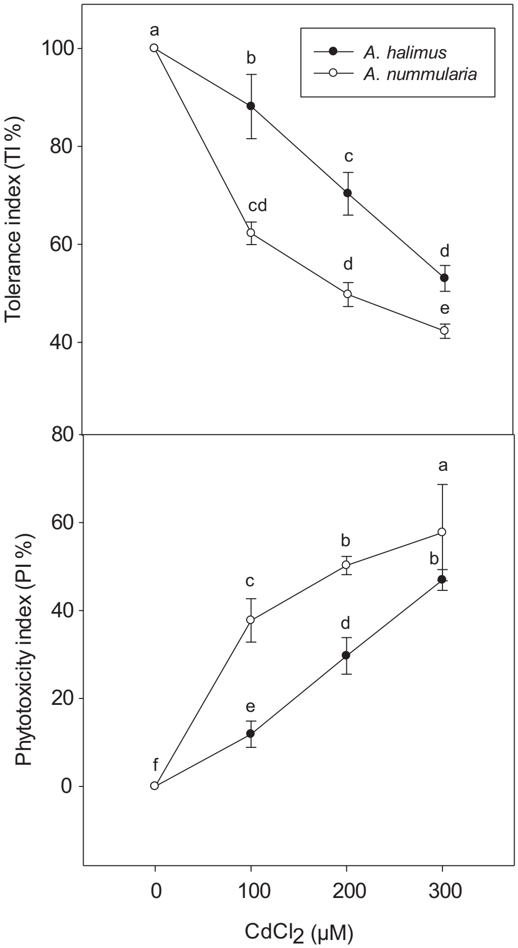


Fig. 14.6 Phytotoxicity and tolerance index of *Atriplex halimus* and *A. nummularia* seedlings treated with $CdCl_2$ concentrations (0, 100, 200, and 300 μM). Values represent means ± S.E. ($n = 3$). Different letters indicate a significant difference between treatments ($P < 0.001$, *Duncan*'s multiple-range test)

14.3.5 Phytotoxicity Index (PI %)

The analysis of variance (ANOVA) indicates a significant effect of the *Atriplex* species ($F = 54.51$, $P < 0.001$), Cd-treatments ($F = 135.07$, $P < 0.001$), and the combination of these two factors ($F = 8.66$, $P < 0.01$) on the PI % (Table 14.1). The phytotoxicity of Cd on seedling growth of *Atriplex* species is presented in Fig. 14.6. This parameter in both species increased significantly with the increasing concentration of $CdCl_2$.The lowest phytotoxicity was recorded for *A. halimus.* These findings suggest that *A. halimus* have a higher tolerance to Cd toxicity than *A. nummularia.* These facts were in conformity with the results found by Sharma et al. (2011) in *Salicornia brachiate* subjected to Cd stress. The phytotoxic impact of Cd on the germinability and early growth of plants is well recognized; however, the degree of Cd-phytotoxicity differs substantially depending on the plant species, varieties, and Cd concentration in the growth medium (Haider et al. 2021).When Cd enters across the cytoplasmic membrane, it affects the cellular metabolic processes in the cytosol by interacting with lipids and proteins, which affects the membrane conductivity, the enzymatic reactions, and induces oxidative stress (ROS) by free radical production (Raza et al. 2020).

14.4 Conclusion

This work indicated that Cd had an adverse impact on *Atriplex* seed germination and initial stage growth of two halophytes. The increase of this HM leads to decrease germination and initial growth parameters in both species. However, *A. halimus* seems to be more tolerant to Cd than *A. nummularia.* These saltbushes can be used for phyto-rehabilitation of soils affected by Cd. Further study is required to confirm these findings in field conditions.

Acknowledgments This research received a specific grant from the Algerian Ministry of Higher Education and Scientific Research, through PRFU Project # D04N01UN170120200001, entitled “Trace element determination in some vegetable species by XRF analysis: Phytoremediation and implications for human health.”

Conflict of Interest The author declares no conflict of interest.

References

Amin H, Arain BA, Abbasi MS, Jahangir TM, Amin F (2018) Potential for phytoextraction of Cu by *Sesamum indicum* L. and *Cyamopsis tetragonoloba* L.: a green solution to decontaminate soil. Earth Syst Environ 2:133–143

Bhatt A, Santo A (2016) Germination and recovery of heteromorphic seeds of *Atriplex canescens* (Amaranthaceae) under increasing salinity. Plant Ecol 217:1069–1079

Bueno M, Lendínez ML, Aparicio C, Cordovilla MP (2017) Germination and growth of *Atriplex prostrata* and *Plantago coronopus*: two strategies to survive in saline habitats. Flora 227:56–63

El Shaer HM (2010) Halophytes and salt–tolerant plants as potential forage for ruminants in the near east region. Small Rumin Res 91:3–12

Falasca SL, Pizarro MJ, Mezher RN (2014) The agro–ecological suitability of *Atriplex nummularia* and *A. halimus* for biomass production in Argentine saline drylands. Int J Biometeorol 58:1433–1441

Gul B, Ansari R, Flowers TJ, Khan MA (2013) Germination strategies of halophyte seeds under salinity. Environ Exp Bot 92:4–18

Haider FU, Liqun C, Coulter JA, Cheema SA, Wu J, Zhang R, Wenjun M, Farooq M (2021) Cadmium toxicity in plants: impacts and remediation strategies. Ecotoxicol Environ Saf 211:111887

Hsu FH, Chou CH (1992) Inhibitory effects of heavy metals on seeds germination and seedling growth of *Miscanthus species*. Bot Bull Academia Sinica 33:335–342

Joshi A, Kanthaliya B, Rajput V, Minkina T, Arora J (2020) Assessment of phytoremediation capacity of three halophytes: *Suaeda monoica*, *Tamarix indica* and *Cressa critica*. Biol Futura 71:301–312

Kranner I, Colville L (2011) Metals and seeds: biochemical and molecular implications and their significance for seed germination. Environ Exp Bot 72:93–105

Kuriakose SV, Prasad MNV (2008) Cadmium stress affects seed germination and seedling growth in *Sorghum bicolor* (L.) *Moench* by changing the activities of hydrolyzing enzymes. Plant Growth Regul 54:143–156

Le Houérou HN (1992) The role of saltbushes (*Atriplex* spp.) in arid land rehabilitation in the Mediterranean basin: a review. Agrofor Syst 18:107–148

Li W, Khan MA, Yamaguchi S, Kamiya Y (2005) Effects of heavy metals on seed germination and early seedling growth of *Arabidopsis thaliana*. Plant Growth Regul 46:45–50

Liu S, Yang C, Xie W, Xia W, Fan P (2012) The effects of cadmium on germination and seedling growth of *Suaeda salsa*. Procedia Environ Sci 16:293–298

Mahmood T, Islam KR, Muhammad S (2007) Toxic effects of heavy metals on early growth and tolerance of cereal crops. Pak J Bot 39:451–462

Moreira IN, Martins LL, Mourato MP (2020) Effect of Cd, Cr, Cu, Mn, Ni, Pb and Zn on seed germination and seedling growth of two lettuce cultivars (*Lactuca sativa* L.). Plant Physiol Rep 25:347–358

Mrozek E (1980) Effect of mercury and cadmium on germination of *Spartina alterniflora* Loisel seeds at various salinities. Environ Exp Bot 20:367–377

Mujeeb A, Aziz I, Ahmed MZ, Alvi SK, Shafiq S (2020) Comparative assessment of heavy metal accumulation and bio–indication in coastal dune halophytes. Ecotoxicol Environ Saf 195:110486

Nagajyoti P, Lee K, Sreekanth T (2010) Heavy metals, occurrence and toxicity for plants: a review. Environ Chem Lett 8:199–216

Nedjimi B (2018) Elemental characterization of *Suaeda mollis* L. (Amaranthaceae) from Algerian rangelands using gamma–ray spectrometry technique. Spectrosc Lett 51(3):130–133

Nedjimi B (2020) Germination characteristics of *Peganum harmala* L. subjected to heavy metals: implications for the use in polluted dryland restoration. Int J Environ Sci Technol 17:2113–2122

Nedjimi B (2021) Phytoremediation: a sustainable environmental technology for heavy metal decontamination. SN Appl Sci 3:286

Nedjimi B, Daoud Y (2009) Cadmium accumulation in *Atriplex halimus* subsp. *schweinfurthii* and its influence on growth, proline, root hydraulic conductivity and nutrient uptake. Flora 204:316–324

Nedjimi B, Souissi ZE, Guit B, Daoud Y (2020) Differential effects of soluble salts on seed germination of *Marrubium vulgare* L. J Appl Res Med Aromat Plants 17:100250

Raza A, Habib M, Kakavand SN, Zahid Z, Zahra N, Sharif R, Hasanuzzaman M (2020) Phytoremediation of cadmium: physiological, biochemical, and molecular mechanisms. Biology 9:177

Santos D, Duarte B, Caçador I (2015) Biochemical and photochemical feedbacks of acute Cd toxicity in *Juncus acutus* seedlings: the role of non–functional Cd–chlorophylls. Estuar Coast Shelf Sci 167:228–239

Sharma A, Gontia-Mishra I, Srivastava AK (2011) Toxicity of heavy metals on germination and seedling growth of *Salicornia brachiata*. J Phytology 3:33–36

Shaygan M, Baumgartl T, Arnold S (2017) Germination of *Atriplex halimus* seeds under salinity and water stress. Ecol Eng 102:636–640

Siddiqui MM, Abbasi BH, Ahmad N, Ali M, Mahmood T (2014) Toxic effects of heavy metals (Cd, Cr and Pb) on seed germination and growth and DPPH-scavenging activity in *Brassica rapa* var. *turnip*. Toxicol Ind Health 30:238–249

Tran TA, Popova LP (2013) Functions and toxicity of cadmium in plants: recent advances and future prospects. Turk J Bot 37:1–13

Wilkins DA (1978) The measurement of tolerance to edaphic factors by means of root growth. New Phytol 80:623–633

Yao L, Wang J, Li B, Meng Y, Ma X, Si E, Yang K, Shang X, Wang H (2021) Influences of heavy metals and salt on seed germination and seedling characteristics of halophyte *Halogeton glomeratus*. Bull Environ Contam Toxicol 106:545–556

Zhang H, Jiang L, Tanveer M, Ma J, Zhao Z, Wang L (2020) Indexes of radicle are sensitive and effective for assessing copper and zinc tolerance in germinating seeds of *Suaeda salsa*. Agriculture 10:445

Chapter 15
Phytoremediation of Soils Polluted by Heavy Metals and Metalloids: Recent Case Studies in Latin America

Sabrina N. Hernández Guiance, I. Daniel Coria, Ana Faggi, and Gabriel Basílico

Abstract The complexity of the soil matrix makes conventional physicochemical remediation treatments costly and not always suitable for large areas. Therefore, phytoremediation, the application of plants and microorganisms associated with their rhizosphere, has emerged as an interesting alternative and the most economical. The physicochemical and biological processes that phytoremediation encompasses are removal, transfer, stabilization, and neutralization, among others. It is an effective, inexpensive method to restore the functional and structural properties of the soil and promote the activity of organisms. It is also applicable to large surfaces and to prevent erosion. This work consists of a review of different recent case studies on the phytoremediation of metal-polluted soil in several Latin American countries. The selection of native plant species, the isolation and inoculation of microorganisms that contribute to improving the removal of metals, and the joint application of amendments are common characteristics among many cases analyzed.

Keywords Phytoremediation · Soils pollution · Heavy metals · Plant species

---

S. N. Hernández Guiance
Universidad del Centro Educativo Latinoamericano, Rosario, Argentina

Instituto de Física de Rosario, Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Rosario, Argentina

I. D. Coria
Universidad del Centro Educativo Latinoamericano, Rosario, Argentina

A. Faggi
Universidad de Flores, Facultad de Ingeniería, Laboratorio de Bioindicadores y Remediación, Ciudad Autónoma de Buenos Aires, Argentina

G. Basílico (✉)
Museo Argentino de Ciencia Naturales, CONICET,
Ciudad Autónoma de Buenos Aires, Argentina
e-mail: gbasilico@conicet.gov.ar

L. Newman et al. (eds.), *Phytoremediation*, https://doi.org/10.1007/978-3-031-17988-4_15

15.1 Introduction

Phytoremediation is defined as the use of plants and the microorganisms associated with their rhizosphere, with the physiological and biochemical capacity to treat contaminants in a given environment. In the rhizosphere, microbial activity increases considerably. The greater presence and microbial activity are attributed to the great diversity of molecules present in the exudates that plants release towards this environment, where the chemical compounds of said exudates can inhibit the growth of a certain species of an organism or attract another type (Muñoz Castellanos et al. 2010). Plant roots also release oxygen, which provides the proper oxidation-reduction conditions for the proliferation and survival of diverse microorganisms. Therefore, to achieve successful phytoremediation, it is very important that an adequate plant-microorganism combination can be established.

The set of phytoremediation techniques uses different types of plant species to treat effluents, air, soils, or sediments that contain heavy metals, radioactive elements, organic compounds, and petroleum-derived compounds, among other pollutants. Some important processes that phytoremediation encompasses are the following:

- Absorption
- Accumulation
- Metabolization
- Volatilization
- Stabilization

The term phytoremediation comes from the Greek *Phyto*, which means "plant," and *remedium*, which means "to restore balance." It is presented as an alternative to the physicochemical methods that have traditionally been used to solve environmental pollution problems. Such a practice has the following advantages (León Romero 2017):

- Low cost
- The plant waste can be disposed of after incineration
- High treatment efficiency
- High applicability for the rehabilitation of contaminated environments

Plants have great versatility to degrade and/or biotransform pollutants. In the case of organics, the goal is to mineralize them to substances such as CO_2, NO_3, and NH_4. On the other hand, inorganic pollutants do not degrade. The phytoremediation of elemental pollutants, such as metals and metalloids, implies the absorption of the toxic cation, its translocation to the aerial plant tissues for its subsequent harvest, the transformation to a less toxic chemical type, the accumulation of the element in the roots to avoid leaching and the decrease in the solubility of the element and consequently in its mobility and bioavailability, through the release of root exudates.

15.1.1 Heavy Metals

Heavy metals could be defined as "*a block of all the metals in Groups 3 to 16 that are in periods 4 and greater*" (Hawkes 1997) or metals with a density higher than 5 g/cm^3. Some of these elements could be classified into two groups:

1. Trace elements: they play a biological role in cell functions, however toxic at high concentrations (As, Co, Cr, Se, and Zn).
2. Toxic elements: Ba, Cd, Hg, Pb, Bi, and Sb. They are also called potentially toxic elements (PTS).

There are three factors that determine the availability of heavy metals in the soil: the pH defines the mobility of the cation, the texture conditions the infiltration in the soil, and the organic matter reacts with the metals forming coordination complexes and chelates. It should be taken into account that some of these elements can bioaccumulate and contribute to biomagnification (Bello et al. 2001).

15.1.2 Impact on Soils

Such is the impact that this type of metals causes in the environment in which they are found that in cases of their presence in agricultural soils, these compounds can be absorbed by crops and then ingested by humans, causing different types of pathologies. Evidence shows development problems in children from an early age, carcinogenic effects, or kidney problems, among others (Ali et al. 2013). For example, the accumulation of lead is especially dangerous for children because their brains are in a developing stage, and they are more vulnerable to brain damage and the appearance of behavioral disorders because this metal affects the central nervous system (Téllez-Rojo et al. 2017).

15.2 Types of Phytoremediation

There are six different methods that are grouped into two sets:

1. Those used as a means of containment: rhizofiltration, phytostabilization, and phyto-immobilization.
2. Those used as a means of elimination: phytodegradation, phytoextraction, and phytovolatilization.

The method type is selected depending on the pollutant, its concentration, and the environment in which it is found. The most used are phytostabilization for the containment of contaminants and phytoextraction for their elimination.

15.2.1 Phytostabilization

This method makes it possible to immobilize pollutants in the soil through their absorption and accumulation in the plant roots or by precipitation in the rhizosphere. Plant species that accumulate low amounts of pollutants are used. As plants grow, change and stabilize the soil, the mobility of the pollutants is reduced.

Phytostabilization is applied mainly to large areas of soil where there is surface contamination, as it is easy to apply, has low cost, has a positive aesthetic impact, and animals can ingest these plants without the risk of poisoning. Some of the species that are used are *Anthyllis vulneraria* for Zn, Cd, and Pb, *Lupinus albus* for Cd and As, and *Brassica juncea* for Cd, Zn, Cu, Mn, Fe, and Pb.

15.2.2 Phytoextraction

This method, also known as phytoaccumulation, consists of the absorption of contaminating metals through the roots, and their accumulation in stems and leaves.

As the plant grows, it is harvested and incinerated, transferring the ashes to a security landfill. The advantage of this method is that it can be repeated unlimitedly until a concentration of pollutant in the medium reaches the limits present in the regulations.

This method, also known as phytoaccumulation, consists of the absorption of contaminating metals through the roots and their accumulation in stems and leaves. The plants are selected according to the characteristics of the site and the metals that are present. Some of the plants that have been used are *Thlaspi caerulescens* for Cd, *Vertiveria zizanioides* for Zn, Cd, and Pb, and *Pistia stratiotes* for As, Cd, Cr, Cu, Hg, Ni, Pb, and Zn. However, these plants should be used only in the regions in which they are native, avoiding possible problems related to biological invasions.

15.2.3 Rhizofiltration

It is used for the eliminationof pollutants from the water environment through the plant's roots. Therefore, it is a phytoremediation technique to decontaminate waters where metals are absorbed and accumulated, forming complexes that interact with the roots, either on their surface or internally. Surface absorption is a combination of physical and chemical processes such as chelation, ion exchange, and precipitation. Contaminants are then removed through harvesting and processing.

15.3 Study Cases by Country

Some recent investigations on phytoremediation carried out in Latin American countries are described below.

15.4 Argentina

The water pollution of some rivers in Argentina, such as the Matanza-Riachuelo or the Reconquista, has been alarming for decades. As a product of the industrial activity, in some sections, the sediments of the bed and banks of these watercourses are severely contaminated with metals such as Cr, Cu, or Zn (de Cabo et al. 2019). The main sectors affected are the middle and lower river basins, which cross a large part of the Metropolitan Area of Buenos Aires (AMBA). In the case of the Matanza-Riachuelo river, in recent years, riverbank rehabilitation initiatives have been carried out on a pilot scale by incorporating native vegetation on the riverbanks (de Cabo et al. 2019). Some of the implanted species, for example, the herbaceous *Sagittaria montevidensis* and *Tradescantia fluminensis* or the woody *Erythrina crista-galli or Senna corymbosa*, can stabilize or tolerate heavy metals present in sediments (Basílico et al. 2016, 2018; Gómez et al. 2020). In the case of *E. crista-galli*, there is a certain potential for Pb translocation (TF = 1.41) (Basílico et al. 2018). On the other hand, Arreghini et al. (2017) found that the reed *Schoenoplectus californicus* growing in contaminated sediments of the Reconquista River accumulated Zn and Pb in roots, with TF < 1.

In another recent work, Saran et al. (2020) evaluated the phytoremediation capacity of the aromatic plant *Helianthus petiolaris* growing in soils contaminated with Pb and Cd. The authors emphasize that aromatic species are often used in the production of essential oils; therefore, the phytoremediation of soils contaminated with metals through these species would not present great risks to food chains. The authors observed the translocation of both metals to be more relevant in the case of Cd.

One of the cases in which the phytoextraction process has been applied is in the city of Cinco Saltos, Río Negro province, where sectors contaminated with traces of mercury were determined in urban sites and in the main irrigation canal, both in the sediments as in plants and fish (Latzke et al. 2011). The main source of contamination was the former industrial plant that operated between 1951 and 1996, producing trichloroethylene, sodium hydroxide, and chlorine by electrolysis of sodium chloride, using a cathode technology of mercury. Remediation works of soil and water began in 1998 and continue today. The capacity of two species of grasses with and without the application of biosolids compost was evaluated by Latzke et al. (2011) to remediate these soils contaminated with Hg by the waste disposal of the chemical industry. To this end, the researchers evaluated the degree of contamination of soils with Hg and performed a greenhouse assay to assess the use of ryegrass

(*Lolium perenne*) and wheatgrass (*Agropyron elongatum*) to remediate soil with differential doses of compost according to the degree of contamination. The soil presented a concentration of 16 ppm of Hg. In order to increase the degree of contamination, Cl_2Hg/kg of dry soil was added to half of the soil, achieving a concentration of 63 ppm. To facilitate the phytoremediation effect, it was added as compost in doses of 20 g/kg of soil and 40 g/kg of soil (dry basis) for the lowest and highest concentration of mercury, respectively. After carrying out these tests, it was observed that the production of plant biomass of ryegrass and wheatgrass was significantly higher in the treatments added with the application of compost; however, the plant growth did not correspond to the degree of phytoremediation reached by the soils (Latzke et al. 2011). Therefore, the decrease in mercury concentration in high and low contamination doses was independent of the applied compost doses. In addition, the plant growth of both species in 120 days contributed to the decrease in the concentration of Hg in all the treatments, although the values allowed by the National Law 24,051 on hazardous waste were not reached. All the treatments increased the concentrations of organic matter in the soil, ensuring that the concentrations of mercury detected in the soil did not compromise the development of any of the species tested.

In another study, the concentrations of heavy metals in foliar material of the woody *Prosopis laevigata* and *Schinus molle* were determined to compare the environmental impact of different land use (agricultural, periurban, urban, and mining) (Alcalá Jáuregui et al. 2018). The concentrations of Al, As, Co, Cu, Cd, Pb, Ti, V, and Zn were determined seasonally in 30 sampling points. The results indicated that the presence of heavy metals depends on the species, land use, and the season, as well as the possible association between these factors. *P. laevigata* turned out to be more efficient in the bioaccumulation of Pb, Co, and Al. In the case of *S. molle* it was only more efficient with respect to Ti. The trees in mining areas showed the highest concentrations of Cu, Zn, Cd, Pb, Co, and As. In the spring season, the highest concentrations of Cu, Co, Ti, and V were determined. As, Co, Cd, Pb, Ti, and Zn presented concentrations above the normal limit in leaves. The authors highlight that, in addition to the influence of anthropogenic activities, environmental factors and physiological differences to develop physicochemical processes in the absorption and transport of these elements to the leaves are determining factors (Alcalá Jáuregui et al. 2018).

15.5 Brazil

Mining activities are important sources of soil contamination with heavy metals such as Cd, Cu, Cr, Pb, and Zn. Camaquã Mines are located in Southern Brazil, where an area has been selected to evaluate the potential use of *Solanum viarum* in the phytoremediation of sites contaminated with heavy metals (Afonso et al. 2019). This plant is native to the region and was registered as spontaneous in the study area.

The identification of native plants with the capacity to remove metals and metalloids from the soil is an interesting approach because these species are adapted to the climate and soils of each site. The study revealed that the species has the potential for the removal of Cu, Zn, Mn, and Ni (≈1000 g/ha) and, to a lesser extent Pb (100 g/ha). In another study in the same region (Afonso et al. 2020), other spontaneous growing species with potential for phytoremediation were identified. The species studied were *Baccharis dracunculifolia*, *Baccharis trimera*, *Cynodon dactylon*, *Ruestraia cristata*, *Equisetum giganteum*, *Eryngium horridum*, *Juncus* sp., *Oenothera* sp., *Plantago tomentosa*, and *Verbena bonariensis*, in addition to *S. viarum*. It should be noted that many of these species are also found in other countries in the region (for example, Argentina, Paraguay, and Uruguay). Among the results, the authors highlight *B. trimera*, *B. dracuncufolia*, *R. cristata*, *V. bonariensis*, *C. dactylon*, and *Juncus* sp. They have the potential for the phytoextraction of Pb, with TF values >1. On the other hand, *E. horridum*, *E. giganteum*, and *B. trimera* have the potential for the phytostabilization of Cu, with BCF values >1.

In Lavras do Sul, another site in southern Brazil also affected by mining activity, Boechat et al. (2016) studied the concentrations of metals in soils and plants of spontaneous growth. Among the most notable results, it can be mentioned that the TF values were higher than unity in almost all the species found: *Dicranopteris nervosa*, *E. horridum*, *Senecio brasiliensis*, *Senecio leptolobus*, *Cyperus eragrostis*, and *B. trimera*. In the case of Cd, the species with TF values higher than one were *S. brasiliensis* (TF = 2.93), *C. eragrostis*, and *B. trimera*. Although no hyperaccumulator species were found, the levels of metals found in plant tissues were high compared to representative values corresponding to uncontaminated sites.

Rhizofiltration can be a relevant phytoremediation mechanism in marsh species such as *S. montevidensis* (Demarco et al. 2019). In this work, the authors evaluated the content of nutrients and metals in tissues of the mentioned species growing in the Santa Bárbara stream (Pelotas, southern Brazil). A rhizofiltration potential of As, Cd, Cu, Cr, Mn, Ni, Pb, and Zn was verified, with values of BCF > 1 and TF < 1. Although these factors were calculated in relation to the concentrations in water, it highlighted the contribution of this species to the natural decontamination of the area and its possible use of other bodies of water affected by pollution.

The inoculation of mycorrhizal fungi in conjunction with the application of vermicompost can be an alternative for the phytostabilization of Cu in sandy soils (Santana et al. 2015). In the aforementioned study, the phytoremediation of a sandy soil artificially contaminated with Cu by the *Canavalia ensiformis* species was optimized using the arbuscular mycorrhizal fungus *Rhizophagus clarus* and the use of vermicompost made from grape bagasse.

15.6 Chile

In addition to the use of mycorrhizae and compost, the addition of $CaCO_3$ can be beneficial in phytoremediation processes of acidic and sandy-textured soils and sediments contaminated with metals. Lam et al. (2017) describe a trial carried out with three native species (*Prosopis tamarugo*, *Schinus mole*, and *Atriplex nummularia*) for the phytoremediation of acidic mining tailings in northern Chile (Cu mining). The addition of organic amendments and $CaCO_3$ (with the objective of neutralizing sulfuric acid) increased the removal of metals in the three species. However, no statistically significant differences were observed between the addition of compost + $CaCO_3$ and the addition of compost + $CaCO_3$ + mycorrhizae. Because of BCF values <1, the studied species can be considered to exclude Cu, Mn, Fe, Pb, and Zn. *A. nummularia* and *S. molle* are considered accumulators (TF values >1) of Mn, Pb, and Zn, in addition to Cu in the case of *S. molle*. *A. nummularia* is considered promising for the phytostabilization of Cd (Lam et al. 2017).

The survival and growth of plant species are important characteristics in evaluating the potential for phytoremediation. Likewise, the variability of metal concentrations in soils, sediments, and mining tailings deposits, as well as the time since the application of organic amendments that favors phytoremediation, can affect survival and plant growth. Milla-Moreno and Guy (2021) found that, after 6 years of the application of an organic amendment, there was no noticeable effect on the survival and growth of different species of native plants growing on mining tailings in the Coquimbo region. However, there were differences in growth and survival when making comparisons between species. The authors recommend the use of the endemic tree *Quillaja saponaria* in the phytostabilization of the mining tailings deposits used in the trial.

Industrial sources of soil contamination with metals are also relevant in some regions of the country, such as Puchuncaví-Ventanas, in central Chile (Salmani-Ghabeshi et al. 2021). In this work, it was found that the species *Oenothera picensis*, *Sphaeralcea velutina*, and *Argemone subfusiformis* have the potential for the accumulation of the elements Cu, Pb, As, Ni, and Cr. The concentrations of the elements analyzed in plant tissues were inversely correlated with the distance to sources of contamination, especially for Cu, As, Cr, Zn, V, and Ni, associated with industrial activities.

The inoculation of isolated microorganisms in soils contaminated with metals and metalloids can favor plant establishment by reducing the toxicity of these elements. Soto et al. (2019) found that the inoculation of *Pseudomonas gessardii* and *Brevundimonas intermedia*, and two As-resistant fungi (*Fimetariella rabenhortii* and *Hormonema viticola*), isolated from contaminated soils of the Puchuncaví region, increased the dry biomass, as well as the expression of associated genes to the production of enzymes involved in the detoxification of metals (metallothionein, superoxide dismutase, ascorbate peroxidase, and phytochelatin synthetase) in wheat plants.

15.7 Colombia

The reuse of surface water and treated liquid effluents can be an interesting alternative for irrigation and plant production; however, it must be ensured that the water used does not contain heavy metals that can accumulate in plants, especially if they are edible. Lizarazo et al. (2020) found that the use of surface waters (Bogotá river basin) in the Sibaté region (Cundinamarca) can result in the translocation and accumulation of metals and metalloids in edible species such as *Cynara scolymus* (artichoke), *Daucus carota* (carrot), and *Petroselinum crispum* (parsley), particularly for the elements As, Pb, and Cr. The transfer of metals to the aerial parts was higher in *P. crispum*.

The contamination levels of mercury, iron, and copper in agricultural soils (inceptisols) and their relationship with some chemical characteristics of the soil in "El Alacrán" gold mines (northern Colombia) were evaluated by Martínez et al. (2017). Twenty-five observation wells were georeferenced and sampled within a 5 km radius around the mine, where the parameters analyzed were: pH, organic matter, CEC, macronutrients (S, P, Ca, Mg, K, and Na), available micronutrients (Cu, Fe, Zn, Mn, and B), exchangeable aluminum, and total concentrations of heavy metals Hg, Cu, and Fe (THg, TCu, and TFe). The pH values fluctuated between 3.99 and 5.09, with an average of 4.76, classifying soils as extremely acids. This condition increases the solubility of the micronutrients boron, copper, and zinc, which can become phytotoxic, also reducing the capacity of the plant to absorb other nutrients. Heavy metals showed mean, minimum, and maximum concentrations according to the Fe > Cu > Hg pattern, TCu exhibiting a coefficient of variation close to 100% and abnormally high, possibly associated to an anthropogenic pollution source.

The fixation of atmospheric nitrogen in soils by bacteria in the root nodules of Fabaceae family plants can result in a decrease in soil pH that favors the translocation and bioaccumulation of metals by other plants used in phytoremediation. However, for this reason, the spontaneous growth of the Fabaceae species is not recommended if the cultivated plants are edible (Marrugo-Madrid et al. 2021). In research carried out in the same area, a good adaptation of *Jatropha curcas* was found in soils contaminated with Hg due to gold mining, with metal removals of up to 65% after 16 months (Marrugo-Madrid et al. 2021).

Another study, which also used soils from the El Alacrán mines, revealed that a species of grass (*Paspalum fasciculatum*) has the ability to phytostabilize metals, increasing the pH and the soil organic matter content (Salas-Moreno and Marrugo-Negrete 2020). In the study, the soil was fortified with salts of Cd and Pb until reaching concentrations of 15, 30, and 50 mg/kg. The species presented tolerance to the evaluated metals, in addition to potential for the phytostabilization of Cd and the phytoextraction of Pb. However, the researchers detected signs of phytotoxicity after 90 days of exposure to Cd. The accumulation of metals in different plant organs was higher in roots, intermediate in leaves, and lower in stems.

15.8 Ecuador

The accumulation of Cd in cocoa beans (*Theobroma cacao*) can put at risk the sustainability of its production in different regions of Latin America, in particular in Ecuador, given the new regulations in relation to the maximum levels of Cd in chocolate that apply in the European Union (Argüello et al. 2019). This species has the ability to translocate and accumulate Cd in grains, establishing in the aforementioned study that 45% of the samples extracted from crops throughout the country exceeded the level of 0.6 mg Cd/kg. The content of this metal in cocoa beans increased with a higher concentration of the metal in soil and lower pH, oxalate-extractable manganese, and organic carbon, highlighting the importance of increasing the solubility of Cd as a factor that contributes to the increase of the metal absorption (Argüello et al. 2019). As mitigation measures, the authors' work proposed the incorporation of amendments to reduce the availability of Cd and, therefore, its accumulation in grains. The uptake of other trace elements by *T. cacao* plants has also been related to the physical–chemical properties of the soil or physiological aspects (Barraza et al. 2021).

Mining activity, including artisanal mining, is also an important source of soil contamination in forested regions of the Ecuadorian Andes. In a trial with three native plant species, Chamba et al. (2016) found that *Erato polymnoides* have the potential for the phytoremediation of soils contaminated with Pb, Zn, Cd, and Cu, with BCF and TF values higher than 1.

15.9 Honduras

Soils in agroecosystems could be affected by environmental pollution. Morales et al. (2019) evaluate the contamination conditions present in soils with agricultural use that receive industrial waste in the municipality of San José de las Lajas. The analysis revealed that the soil is classified as moderately contaminated in Cr, Co, Zn, and Pb and need of urgent remediation due to the content of Ni and Cu. The soil samples were taken in a production area close to an industrial dumping area. The danger that can be caused by producing vegetables in these lands has been warned because most of them have high contents of heavy metals, which can be dangerous for human and animal health (Morales et al. 2019).

After conducting the tests, the authors determined that the contaminated soil values were higher than the reference values proposed in the Dutch Soil Standards. In addition, the soil samples under study were classified as moderately contaminated in Cr, Co, Zn, and Pb and in need of urgent remediation because of the concentrations of Ni and Cu being much higher than those reported for the earth's crust and those proposed as Upper Allowable Limits.

15.10 Mexico

The processes of remediation and ecological restoration or rehabilitation in arid or semi-arid areas can be favored by the incorporation of a layer of soil or uncontaminated substrate, which promotes the growth of implanted or spontaneously growing vegetation. Salas-Luévano et al. (2017) describe the flora present in a 40-ha property containing mining tailings in the Fresnillo area (Zacatecas state). Rehabilitation activities at the site began in the 1980s with the establishment of a 40-cm thick substrate layer over the slag piles and through vegetation with tree, shrub, and herbaceous species, both native and exotic. At present, the vegetation has been enriched by native and endemic plants that can grow spontaneously, some with potential for the phytoremediation of soils and mining tailings with high concentrations of metals and metalloids. The incorporation of uncontaminated soil on the slag piles had positive effects on the rehabilitation of the property, increasing soil fertility and promoting vegetation establishment and growth.

Plant cover in soils contaminated with potentially toxic elements (PTEs) not only promotes remediation but also prevents the dispersion of these elements associated with erosion while reducing their leaching (Sánchez-López et al. 2015). *Aster gymnocephalus*, *Dalea bicolor*, *Juniperus* sp., and *Viguiera dentata*, among other species from semi-arid regions, have been identified by Sánchez-López et al. (2015) in mining tailings in the Zimapan region (Hidalgo state). The authors highlight the importance of these species since they ensure soil coverage throughout the year and are also present in other mining areas in different regions of Mexico. In the aforementioned article, the usefulness of calculating BCF, taking into account the extractable fraction in DTPA (BCFD), is also highlighted since it represents the bioavailable fraction of PTEs. Taking into account the BCFDs, TFs, and phytotoxicity levels (PLs), the species *A. gymnocephalus* would have the potential for the phytoextraction of Zn, Cd, Pb, and Cu; *Gnaphalium* sp. for Cu and *Crotalaria pumila* for Zn, while *Pteridium* sp. it would be promising for the phytostabilization of Zn and Cd.

Tree species such as *Prosopis laevigata* can be used in the phytoremediation of abandoned mining tailings contaminated with Cu, Fe, Pb, and Zn due to their appearance and dominance in these sites, as well as their ability to translocate and accumulate these metals in roots and leaves. (Muro-González et al. 2020). The authors highlight that the accumulation of Pb had deleterious effects at the genetic level and decreased the number of leaves, while Zn affected the total weight of *P. laevigata* with respect to individuals growing on noncontaminated substrates. However, the species developed and survived in the contaminated substrate from mining tailings in Tlalquitenango (Morelos state).

In mining tailings from El Fraile-Taxco (Guerrero state), Quiterio et al. (2020) isolated 151 morphotypes of bacteria, present both in rhizospheric soil, as well as inside the roots, in leachates, and in water, identifying some microorganisms with the potential to promote plant growth, and that therefore could have useful in bio and phytoremediation projects, among other applications. Characteristics highlighted by the authors as promoters of plant growth include the ability to fix atmospheric nitrogen (diazotrophs), dissolve phosphate, or produce substances such as indole acetic acid, gibberellins, and siderophores.

15.11 Peru

The accumulation of Cd in *Theobroma cacao* beans is a problem of growing interest also in Peru, one of the world's largest exporters of this product. In a study carried out in 70 cacao plantations between 10 and 15 years old in the northern, central, and southern regions of the country, Arévalo-Gardini et al. (2017) found Cd concentrations from 0.17 ± 0.41 µg/g (Cuzco) to 1.78 ± 0.35 µg/g (Tumbes), exceeding in some cases the critical value of 0.8 µg/g. On the other hand, the differential accumulation of this metal was related to the genetic variability of the crops. The concentration of other metals in leaves and grains in several genotypes analyzed was below the critical levels established for agronomic crops (Kabata-Pendias 2000); however, these values were exceeded in several cases. Another remarkable result of the study is the existence of significant correlations between the levels of Cd and Zn, both in plants and in soils, with a possible effect of Zn on the accumulation of Cd in cocoa beans.

Soil contamination with heavy metals is a significant potential damage caused by Mining Environmental Liabilities (MEL) sites, which can seriously compromise the alternative use of abandoned mining sites. The environmental quality of soils from MEL in the district of Hualgayoc in the Peruvian Andes was evaluated by Cruzado-Tafur et al. (2021). Soil samples collected for the upper soil layer (30 cm, arable soil layer) and the subsoil (30–60 cm) were classified as Gleyic Cambisols and show an extremely acidic pH (3.50–4.19 in site 1 and 2.74–4.02 at site 2). The mineralogical composition of the soils is dominated by illite, kaolinite, quartz, and jarosite. The authors determined the concentrations of six PTEs (Pb, Zn, As, Cu, Ag, and Cd). High concentrations of Pb (4683 mg/kg), Zn (724.2 mg/kg), Cu (511.6 mg/kg), Ag (33.4 mg/kg), and As (3611 mg/kg) exceeded the maximum permissible limits for agricultural soils in accordance with Peruvian and Canadian regulations. The applied geochemical indices classified some of the soils as extremely contaminated; therefore, the studied mining environmental liabilities represent a very high ecological risk. Twenty-two species of native flora belonging to 12 species of the family were inventoried in these contaminated sites, so they have the potential to be used for phytoremediation purposes.

Another recent study evaluated the accumulation of metals in native plants of the central-northern Andean region of Peru, and its potential use in the remediation of MEL (Kee et al. 2018). The authors collected soil samples from mining regions and individuals of the species *Achyrocline alata*, *Calamagrostis recta*, *Cortaderia jubata*, *Festuca glyceriantha*, *Juncus bufonius*, *Medicago lupulina*, *Pennisetum clandestinum*, *Stipa ichu*, and *Werneria nubigena*. These plants were propagated in a greenhouse and then grown on contaminated soils. The soil samples showed levels of heavy metals above the national levels for agricultural soil. For example, the level of Pb in soil from Santa Rosa de Jangas exceeded the detection level (>5000 mg/kg), while the concentrations of Cu, Ni, and Zn were also high (1187 mg/kg, 8.70 mg/kg, and 7100 mg/kg, respectively). The species with the highest bioaccumulation factors (BAF) (and >1) were *W. nubigena* (Cd; Cu; Ni), and *J. bufonius* (Ni; Zn), while the highest BCF were observed in *C. recta* (Cd; Cu; Ni), *J. bufonius* (Cd; Cu; Ni), and *A. alata* (Ni; Zn). The highest TF values were observed in *W. nubigena* (Cd; Cu; Ni; Pb; Zn), *A. alata* (Cd; Pb), *J. bufonius* (Ni; Zn), and *P. clandestinum* (Zn) (Kee et al. 2018).

As in other cases described in this chapter, the isolation and identification of rhizospheric and endophytic microorganisms is an approach used in a recent study with contaminated soils from Callejón de Huaylas (Ancash) (Tamariz-Angeles et al. 2021). The authors highlight that the work constitutes the first report on siderophore-producing microorganisms in the study area, which could have potential use in phytoremediation and other biotechnologies.

15.12 Final Remarks

In recent years, interesting research on phytoremediation has been carried out in several Latin American countries. From the analysis of the case studies included in this chapter, some interesting points can be highlighted:

- Mining and various industrial activities appear to be the most frequent sources of soil pollution with heavy metals, or at least the most studied ones. These sources of pollution can affect nearby areas used for agriculture and therefore pose environmental and health risks.
- With good judgment, research increasingly tends to identify native and even endemic species in each region rather than using exotic species. Native species have adapted to local conditions, particularly climate and soil, and therefore possibly have a better chance of survival. Furthermore, by using these species, possible biological invasions are avoided.
- The addition of amendments, both organic and inorganic, can favor the process of phytoremediation of soils contaminated with metals; however, each case, in particular, must be analyzed locally. For each metal, the processes involved in phytoremediation (phytostabilization, phytoextraction, etc.) vary, not only according to the physical–chemical characteristics of the soil but it is also dependent on the plant species used, even observing variability associated with genetic diversity within the same species.
- The isolation and identification of rhizospheric and mycorrhizal microorganisms that favor phytoremediation processes are increasingly being studied in the countries of the region and may be useful also in other biotechnological applications.
- The contamination of soils with cadmium and other PTEs, and the accumulation of these elements in tissues of some edible plants, have generated the need for more demanding regulatory frameworks in relation to the maximum levels allowed in food. However, in the short and medium term, this situation may put food security at risk and affect the economy of the producing countries; therefore, effective soil and crop management strategies must be identified urgently to reduce levels of PTEs in food.

References

Afonso TF, Demarco CF, Pieniz S, Camargo FA, Quadro MS, Andreazza R (2019) Potential of *Solanum viarum* Dunal in use for phytoremediation of heavy metals to mining areas, southern Brazil. Environ Sci Pollut Res 26(23):24132–24142

Afonso TF, Demarco CF, Pieniz S, Quadro MS, Camargo FA, Andreazza R (2020) Bioprospection of indigenous flora grown in copper mining tailing area for phytoremediation of metals. J Environ Manag 256:109953

Alcalá Jáuregui J, Rodríguez Ortíz JC, Hernández Montoya A, Filippini MF, Martínez Carretero E, Diaz Flores PE (2018) Capacidad de dos especies vegetativas en la acumulación de metales pesados. Rev FCA UNCuyo 50(1):123–139

Ali H, Khan E, Sajad MA (2013) Phytoremediation of heavy metals—concepts and applications. Chemosphere 91(7):869–881

Arévalo-Gardini E, Arévalo-Hernández CO, Baligar VC, He ZL (2017) Heavy metal accumulation in leaves and beans of cacao (Theobroma cacao L.) in major cacao growing regions in Peru. Sci Total Environ 605:792–800

Argüello D, Chavez E, Lauryssen F, Vanderschueren R, Smolders E, Montalvo D (2019) Soil properties and agronomic factors affecting cadmium concentrations in cacao beans: a nationwide survey in Ecuador. Sci Total Environ 649:120–127

Arreghini S, de Cabo L, Serafini R, de Iorio AF (2017) Effect of the combined addition of Zn and Pb onpartitioning in sediments and their accumulation by the emergent macrophyte Schoenoplectus californicus. Environ Sci Pollut Res 24(9):8098–8107. https://doi.org/10.1007/s11356-017-8478-7

Barraza F, Schreck E, Uzu G, Lévêque T, Zouiten C, Boidot M, Maurice L (2021) Beyond cadmium accumulation: distribution of other trace elements in soils and cacao beans in Ecuador. Environ Res 192:110241

Basílico G, de Cabo L, Faggi A, Miguel S (2016) Low-tech alternatives for the rehabilitation of aquatic and riparian environments. In: Ansari et al (eds) Phytoremediation. Springer, Cham, pp 349–364

Basílico G, Faggi A, de Cabo L (2018) Tolerance to metals in two species of fabaceae grown in riverbank sediments polluted with chromium, copper, and lead. In: Phytoremediation. Springer, Cham, pp 169–178

Bello RR, Cajuste LJ, Román DF, Calderón NEG (2001) Metales pesados, sales y sodio en los suelos de chinampa en México. Agrociencia 35(4):385–395

Boechat CL, Pistóia VC, Gianelo C, de Oliveira Camargo FA (2016) Accumulation and translocation of heavy metal by spontaneous plants growing on multi-metal-contaminated site in the Southeast of Rio Grande do Sul state, Brazil. Environ Sci Pollut Res Int 23(3):2371–2380

Chamba I, Gazquez MJ, Selvaraj T, Calva J, Toledo JJ, Armijos C (2016) Selection of a suitable plant for phytoremediation in mining artisanal zones. Int J Phytoremediation 18(9):853–860

Cruzado-Tafur E, Torró L, Bierla K, Szpunar J, Tauler E (2021) Heavy metal contents in soils and native flora inventory at mining environmental liabilities in the Peruvian Andes. J S Am Earth Sci 106:103107

de Cabo LI, Faggi AM, Miguel S, Basílico GO (2019) Rehabilitación de las riberas de un sitio de la cuenca baja del río Matanza-Riachuelo. Biología Acuática 33:005. https://doi.org/10.24215/16684869e005

Demarco CF, Afonso TF, Pieniz S, Quadro MS, Camargo FADO, Andreazza R (2019) Phytoremediation of heavy metals and nutrients by the Sagittaria montevidensis into an anthropogenic contaminated site at Southern of Brazil. Int J Phytoremediation 21(11):1145–1152

Gómez BM, Reale M, El Kassisse Y, Mujica C, Gómez C, de Cabo L, Salemi VR (2020) Metals uptake by *Sagittaria montevidensis* in contaminated riparian area of Matanza-Riachuelo river (Argentina). SN Appl Sci 2(12):1–10

Hawkes SJ (1997) What is a “heavy metal”? J Chem Educ 74(11):1374

Kabata-Pendias A (2000) Trace elements in soils and plants. CRC Press

Kee JC, Gonzales MJ, Ponce O, Ramírez L, León V, Torres A et al (2018) Accumulation of heavy metals in native Andean plants: potential tools for soil phytoremediation in Ancash (Peru). Environ Sci Pollut Res 25(34):33957–33966

Lam EJ, Cánovas M, Gálvez ME, Montofré ÍL, Keith BF, Faz Á (2017) Evaluation of the phytoremediation potential of native plants growing on a copper mine tailing in northern Chile. J Geochem Explor 182:210–217

Latzke MF, Laos F, Schmid P (2011) Fitorremediación de suelos contaminados por una industria química en Cinco Saltos, Río Negro. Ciencia 6(24):21–37

León Romero JA (2017) Una Mirada a la Fitorremediación en Latinoamérica. Universidad Nacional Abierta y a Distancia UNAD. Repositorio Institucional UNAD. https://repository.unad.edu.co/handle/10596/13866

Lizarazo MF, Herrera CD, Celis CA, Pombo LM, Teherán AA, Pineros LG et al (2020) Contamination of staple crops by heavy metals in Sibaté, Colombia. Heliyon 6(7):e04212

Marrugo-Madrid S, Turull M, Montes GE, Pico MV, Marrugo-Negrete JL, Díez S (2021) Phytoremediation of mercury in soils impacted by gold mining: a case-study of Colombia. In: Bioremediation for environmental sustainability. Elsevier, pp 145–160

Martínez Z, Gonzalez MS, Paternina J, Cantero M (2017) Crop soils pollution by heavy metals, the Alacran mining area, Córdoba-Colombia. Rev Temas Agrarios 22(2):20–32

Milla-Moreno E, Guy RD (2021) Growth response, uptake and mobilization of metals in native plant species on tailings at a Chilean copper mine. Int J Phytoremediation 23(5):539–547

Morales ARG, Cruz-La Paz O, Valdés-Carmenate R (2019) Effects of the pollution by heavy metals in a soil with agricultural use. Rev Bras Cienc Agrar 28(1):1–8

Muñoz Castellanos LN, Nevárez Moorillón GV, Ballinas Casarrubias ML, Peralta Pérez MR (2010) Fitorremediación como una alternativa para el tratamiento de suelos contaminados. Rev Int Cienc Tecnol Bioméd 1:1–13

Muro-González DA, Mussali-Galante P, Valencia-Cuevas L, Flores-Trujillo K, Tovar-Sánchez E (2020) Morphological, physiological, and genotoxic effects of heavy metal bioaccumulation in *Prosopis laevigata* reveal its potential for phytoremediation. Environ Sci Pollut Res 27(32):40187–40204

Quiterio AH, Hernández ET, Noyola JLA, Romero Y, Ramos J, Alberto FP, Jiménez JT (2020) Antagonic and plant growth-promoting effects of bacteria isolated from mine tailings at El Fraile, Mexico. Rev Argent Microbiol 52(3):111–120

Salas-Luévano MA, Mauricio-Castillo JA, González-Rivera ML, Vega-Carrillo HR, Salas-Muñoz S (2017) Accumulation and phytostabilization of As, Pb and Cd in plants growing inside mine tailings reforested in Zacatecas, Mexico. Environ Earth Sci 76(23):1–12

Salas-Moreno M, Marrugo-Negrete J (2020) Phytoremediation potential of Cd and Pb-contaminated soils by *Paspalum fasciculatum* Willd. ex Flüggé. Int J Phytoremediation 22(1):87–97

Salmani-Ghabeshi S, Fadic-Ruiz X, Miró-Rodríguez C, Pinilla-Gil E, Cereceda-Balic F (2021) Trace element levels in native plant species around the industrial site of Puchuncaví-Ventanas (Central Chile): evaluation of the phytoremediation potential. Appl Sci 11(2):713

Sánchez-López AS, González-Chávez MDCA, Carrillo-González R, Vangronsveld J, Díaz-Garduño M (2015) Wild flora of mine tailings: perspectives for use in phytoremediation of potentially toxic elements in a semi-arid region in Mexico. Int J Phytoremediation 17(5):476–484

Santana NA, Ferreira PAA, Soriani HH, Brunetto G, Nicoloso FT, Antoniolli ZI, Jacques RJS (2015) Interaction between arbuscular mycorrhizal fungi and vermicompost on copper phytoremediation in a sandy soil. Appl Soil Ecol 96:172–182

Saran A, Fernandez L, Cora F, Savio M, Thijs S, Vangronsveld J, Merini LJ (2020) Phytostabilization of Pb and Cd polluted soils using *Helianthus petiolaris* as pioneer aromatic plant species. Int J Phytoremediation 22(5):459–467

Soto J, Ortiz J, Herrera H, Fuentes A, Almonacid L, Charles TC, Arriagada C (2019) Enhanced arsenic tolerance in Triticum aestivum inoculated with arsenic-resistant and plant growth promoter microorganisms from a heavy metal-polluted soil. Microorganisms 7(9):348

Tamariz-Angeles C, Huamán GD, Palacios-Robles E, Olivera-Gonzales P, Castañeda-Barreto A (2021) Characterization of siderophore-producing microorganisms associated to plants from high-Andean heavy metal polluted soil from Callejón de Huaylas (Ancash, Perú). Microbiol Res 250:126811

Téllez-Rojo MM, Bautista-Arredondo LF, Richardson V, Estrada-Sánchez D, Ávila-Jiménez L, Ríos C et al (2017) Intoxicación por plomo y nivel de marginación en recién nacidos de Morelos, México. Salud Publica Mex 59:218–226

Part VI
Nanotechnology in Management of Environmental Contaminants

Chapter 16
Nano-phytoremediation and Its Applications

Trinath Biswal

Abstract The quality of the water, soil, and air is highly affected by the pollutants of anthropogenic sources such as persistent organic pollutants, chlorinated compounds, polychlorinated biphenyl, and heavy metals, causing serious harm to all the biological community. Hence, wonderful efforts have been made by the researchers to remediate the pollutants present in the environment in order to minimize the pollution load. Nanoremediation and phytoremediation are normally less expensive and have a less negative impact on the environment than any of the physical and chemical remediation methods. There are a wide variety of nanoparticles (NPs) and plant species, which have been recognized as potential sources for the remediation of water and soil. Both these are eco-friendly and sustainable methods of remediation. Both phytoremediation and nanotechnology are potential techniques for removing contaminants from water and soil, especially heavy metals. The simultaneous application of both these techniques is known as nano-phytoremediation, which has a better cumulative effect and enhanced efficiency for the remediation of pollutants from soil and water than the application of only a single technology. In this chapter particularly, we discussed the effective remediation of water and soil in a sustainable, cost-effective, and environmentally friendly pathway using the technology combination of both of these.

Keywords Remediation · Sustainable · Environment · Nanotechnology · Phytoremediation · Heavy metals

16.1 Introduction

The reduction or removal of toxic pollutants such as e-wastes, inorganic and organic contaminants, and metals from polluted sites by adopting nanoparticles synthesized by algae, bacteria, and fungi through the process of nanotechnology

---

T. Biswal (✉)
Department of Chemistry, VSS University of Technology, Burla, India

L. Newman et al. (eds.), *Phytoremediation*, https://doi.org/10.1007/978-3-031-17988-4_16

is termed nano-bioremediation. If such kinds of pollutants are eliminated or reduced through the nanoparticles synthesized by comprising higher plant species, then it is popularly termed nano-phytoremediation. If the particles of atomic dimension are in the range of 1–100 nm, then both physical and chemical properties of these materials are remarkably enhanced than the bulk materials (Nwadinigwe and Ugwu 2018a; Wei et al. 2020). The nanoparticles include natural nanoparticles like lunar dust, the dust of mineral composites, volcanic dust, the incidental nanoparticles mainly produced from various anthropogenic activities including welding fumes, diesel exhaust, particles from coal burning, and man-made nanoparticles such as titanium dioxide, nanogold, nanoaluminium, and nanozinc. There are various kinds of mechanisms adopted for nano-phytoremediation, such as nano-phytoaccumulation, nano-phytodegradation, phytovolatilization, nano-phytostabilization, nano-phytohydraulics, and nano-rhizofilteration depending upon the process used. The use of nanotechnology improves the effectiveness of phytoremediation. The use of nanotechnology stimulates in-situ remediation. The process of nano-phytoremediation promotes the degradation of complex resistant organic materials into comparatively simpler nontoxic substances through combining activities of plants and microbes (Muhammed Shameem et al. 2021; Romeh and Ibrahim Saber 2020). The different specific nanoparticles such as nanosized cerium oxides, zerovalent iron (nZVI), nano-zinc oxides, nanosized manganese oxides, and titanium oxides possess a higher affinity for adsorption of the pollutants on the surface of metalloid and metal. The nanoparticles contain an extremely greater number of active sites at the surface with significantly more surface area, which is the cause of efficient remediation of comparatively more degradable resistance pollutants, including polychlorinated biphenyls (PCBs), 2,4,6-trinitrotoluene, endosulfan, toxic heavy metals, e-wastes, and so on. The phytoremediation assisted by microbes such as rhizoremediation is highly effective for the degradation and removal of organic pollutants present in the soil and water. Phytoremediation is the method of degradation or removal of pollutants from water and soil either indirectly or directly by using various kinds of plant species. It is a nonintrusive, effective, and inexpensive method of remediating water and soil. Nanoparticles show brilliant properties as compared to bulk materials because of their extremely small size, and their electrons are always confined, producing quantum effects. The nanoparticles are effectively applied to clean up the air, soil, and water contaminants. The clean-up of the contaminants is primarily termed remediation; otherwise, if biological agents are used for removing or depredating the contaminates, then it is called bioremediation. If living plant species are used, then the technique is called phytoremediation. The technique of nano-phytoremediation is a collective effect of phytotechnology and nanotechnology for the bioremediation of contaminates from the environment (Khan 2020; Kumar et al. 2021; Song et al. 2019).

16.2 Nano-phytoremediation

The process of reduction or removal of contaminates from nature through biological or chemical processes is known as remediation. The science of producing and utilizing small dimension particles of nanosize is termed nanotechnology, and the small particles produced are termed ultrafine particles or nanoparticles (NPs). Phytoremediation is the process of bioremediation, where higher plant species are used to remove, destroy, transfer, and stabilize the contaminates such as explosives, radionuclides, solvents, pesticides, crude oil, metals, semi-volatile and volatile organic materials from soil, groundwater, sediments, and surface water. Nano-phytoremediation is the technique that is the combination of the technology between phytoremediation and nanotechnology for the remediation or removal of pollutants from nature. Nanotechnology is related to the structural property of both sub-molecular and molecular levels and is applied in a broad field of applications. Nanomaterials (NPs) are now a day more popularly applied in diversified fields such as cosmetics, medicines, paint, and textiles. The use of nanotechnology enhances the efficiency of phytoremediation and the nanoparticles used for the remediation of water and soils, which are seriously contaminated by heavy metal, inorganic, and organic contaminants. Recently, it was reported that highly toxic organic pollutants, including atrazine, chlorpyrifos, and molinate, undergo degradation using nano-sized zerovalent irons. The bioremediation based on enzymes along with nanoparticles may be applied in coagulation with phytoremediation. A large number of nanomaterials are designed and synthesized, which are highly useful in the process of remediation owing to their huge surface area; therefore, these materials are comparatively higher reactive than the corresponding bulk materials. It can be easily penetrated inside the contaminated sites because of extremely small-sized particles. The nanomaterials of Fe-based compounds are highly effective in the process of remediation to clean up our environment. The nano-phytoremediation is also used for the remediation of many highly resistant organic pollutants such as PCBs, PPCPs, PAHs, and organic solvents in the soil. The remediation of TNT also is effective in the process of nano-phytoremediation (Khan 2021; Zhang et al. 2019; Karn et al. 2009).

16.2.1 Nanoparticles

The nanoparticles (NPs) are normally molecular or atomic aggregates having a dimension in the range of 1–100 nm, whose properties are remarkably much improved than the corresponding bulk materials. The NPs are generally classified into two categories

- Organic NPs
- Inorganic NPs

The organic NPs are normally carbon NPs based on fullerenes, whereas the inorganic NPs are noble metal NPs including Ag and Au, magnetic NPs, and semiconductor NPs including TiO_2 and ZnO. Again, nanoparticles are also classified into three categories as:

Natural Nanoparticles These nanoparticles include lunar dust, volcanic dust, and particles of mineral composites

Incidental Nanoparticles These kinds of nanoparticles are normally created from anthropogenic activity, including diesel exhaust, fumes ejected due to welding, and particles from coal combustion.

Engineered Nanoparticles These kinds of nanoparticles includes quantum metal-based substances including nano-Au, nano-Al, nano-Zn, and TiO_2.

The application of nanomaterials has been recognized as an efficient, eco-friendly, cost-effective, and sustainable alternative to the existing materials used both for the remediation of pollutants from nature and the conservation of natural resources (Zheng et al. 2018; Bissessur 2020).

16.2.2 Phytoremediation

Phytoremediation is one of the processes of bioremediation in which various kinds of plant species are used to remove, reduce, transfer, destroy, and stabilize the toxic contaminates present in groundwater and soil. The process of phytoremediation is normally a cost-effective, efficient, and eco-friendly green technology that can successfully remediate a number of pollutants present in soil and water. There are a number of mechanisms suggested to carry out the process of phytoremediation, which are as follows.

- *Phytodegradation*: This is the kind of phytoremediation, where the toxic contaminants are metabolized, destroyed, or biotransformed within the used plant tissues (Vasavi et al. 2010).
- *Rhizosphere biodegradation*: In this remediation process, plant species release natural substances through their roots. Therefore, nutrients are provided to the microorganisms present in the soil nearby the roots (rhizosphere); simultaneously, the microorganism grows comfortable and increases the level of biological degradation of the pollutants.
- *Phytostabilization*: In this process, some chemical substances are produced by the plants, which can immobilize or precipitate sequester the pollutants present in the soil. In this process, the bioavailability of heavy metals present in the soil is also reduced. This is also termed phytosequestration (Ramanjaneyulu and Giri 2006).

- *Phytoaccumulation*: This process is otherwise termed phytoextraction. In this process, the roots of the plants absorb the toxic contaminants with water and other kinds of nutrients. The contamination is not demolished but ends up in the shoots of the plants and leaves. This technique is basically more suitable for the removal of heavy metallic contaminates. The water-soluble form of metals is taken by the plants according to their capability and stored at the aerial shoots of the plants, which are separated either by the significant metal recovery smelting process or disposed of as dangerous waste materials. In this process, the spontaneously bioavailable metals taken by the plants include Cd, Zn, Ni, Cu, As, and Se. The metals moderately bioavailable are Co, Fe, Mg, Cr, and Pb, whereas uranium is poorly bioavailable. Lead can be fitted to be better bioavailable by adding chelating agents to soils. The bioavailability of Cs-137 and U can be increased by the addition of NH_4NO_3 and citric acid, respectively (Kamal 2004).
- *Rhizofiltration*: This process is almost similar to phytoaccumulation, but the only difference is that the plant used for remediation of contaminants grow in greenhouses with their roots systems in water. This method is more commonly used for ex-situ remediation of contaminated groundwater. The groundwater is basically pumped out to the earth's surface for irrigation of these plant species. When roots are saturated by toxic contaminates, they are uprooted and finally disposed of.
- *Phytovolatilization*: In this process, the plant species consume water contaminated by organic pollutants and release these pollutants into the earth's atmosphere through the leaves of the plants during transpiration (Nedjimi 2021).
- *Hydraulic control or Phytohydraulics*: In this process, the trees grows with their dense roots down inside the groundwater, which absorbs huge amounts of water. The trees function as a natural pump; when the roots of these trees go down and enter the water table, then the dense root mass of the tree consumes large quantities of water. In this process, huge amounts of pollutants, including pesticides, fertilizers, toxic herbicides, radioactive materials, and explosives, are reduced, degraded, or eliminated from the groundwater. A polar tree can pull out almost 30 gallons of water/day, and cottonwood can absorb almost 350 gallons of water/day. The examples of the plant species used for remediation of soil, sediments, and groundwater are as follows.

Examples: Pennisetum glaucum such as millet, poplar tree such as *Populus deltoides* (Nwadinigwe and Obi-Amadi), *Brassica juncea* (Indian mustard), Bermuda grass (*Cynodon dactylon*), *Helianthus annuus* (sunflower), *Sorghum vulgare*, water hyacinth (*Eichhornia crassipes*) (Nagendran et al. 2006).

The different applications of nano-phytoremediation are represented in Fig. 16.1.

Factors Influencing the Nano-phytoremediation

The different factors affecting nano-phytoremediation in the present scenario are shown in Fig. 16.2.

The factors affecting the uptake of chemicals and their distribution within living plants area are as follows.

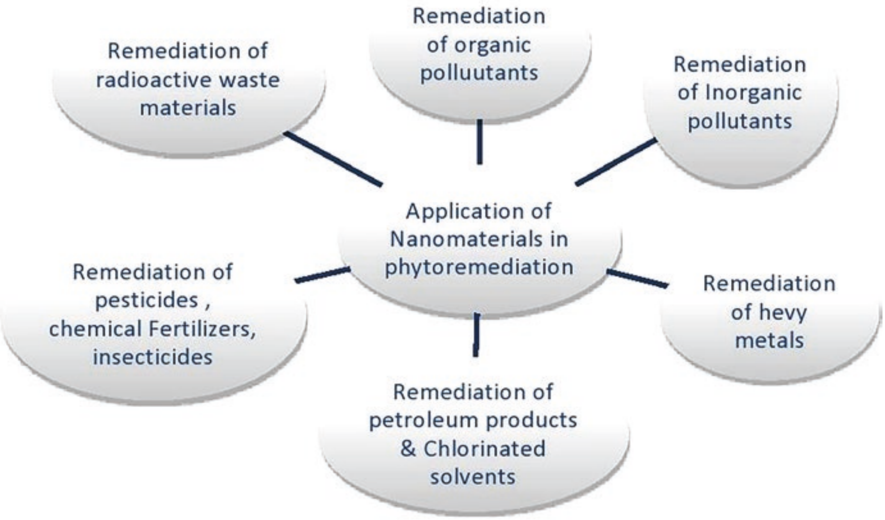


Fig. 16.1 Different applications of nanomaterial in phytoremediation

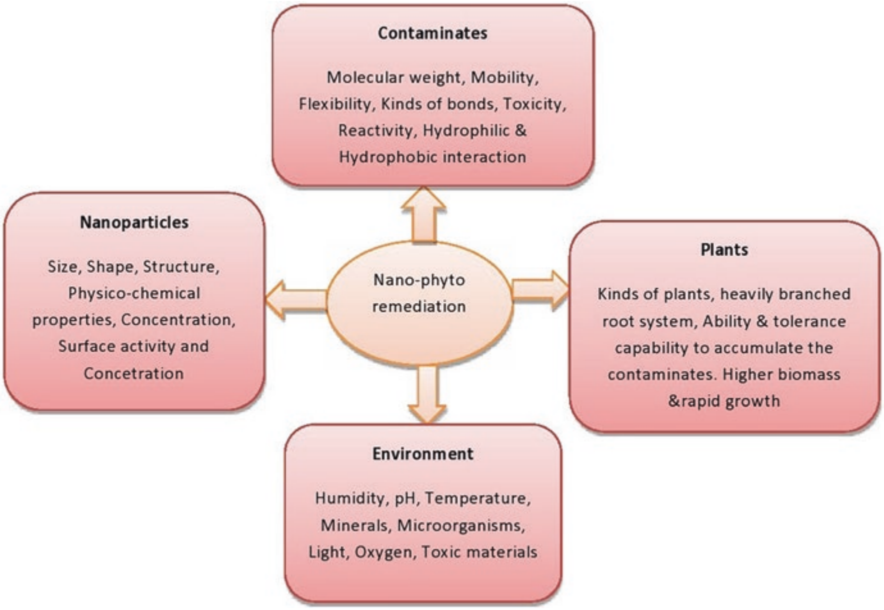


Fig. 16.2 Different factors affecting Nano-phytoremediation

- The various chemical and physical properties of the substances, such as water solubility, molecular weight, and vapor pressure.
- The various environmental characteristics such as temperature, organic matter, pH, and soil moisture content.
- The various plant characteristics such as kinds of enzymes and kinds of the root system
- The activity of nanomaterial and its properties, such as shape, size, concentration, physical and chemical properties, and structure (Razmi et al. 2021).

16.3 Nano-phytoremediation of Pollutants in Soil

The technology of nano-phytoremediation can be effectively used for the remediation of polluted soil, which is the combining effect of both phytoremediation and nanoparticles. The coupling of phytoremediation and its application of nanoparticles involves a significant step in the process of the decontamination of the soil. It was found that a number of nanomaterials and nanoparticles possess the significant property of remediation or detoxification of the heavy metals, inorganic, and organic pollutants present in the soil.

Example: Nano zerovalent iron (nZVI), bimetallic nanoparticles (Pd/Fe), and magnetite nanoparticles (nFe_3O_4) possess the capability of degrading toxic organic pollutants like chlorpyrifos, trichloroethylene (TCE), pyrene, polychlorinated biphenyls (PCBs), ibuprofen, 2,4-dinitrotoluene, atrazine, pentachlorophenol, and lindane from the polluted soil.

The nano TiO_2 ($nTiO_2$) possesses the capability of removing organic pollutants such as diuron, phenanthrene, p,p′-DDT, and pyrene from the soil through photocatalysis, thermal destruction, and redox reaction. Recently, it was reported that atrazine, a pesticide (2-chloro-4-ethylamino-6-isopropylamino-s-triazine), can be effectively degraded by using PEI-copper nanoparticles, which are deposited onto sand and montmorillonite (MMT). The application of NPs shows both negative and positive responses on soil microorganisms. The positive response is observed by applying 1–10 mg/kg of NPs of FeO, whereas negative response of the microorganisms towards plants is observed by applying 0.1–10 mg/kg of the NPs of Ag. There is a wide range of applications of nano-phytoremediation based on the removal of pollutants from soil. The pollutants from toxic heavy metals to volatile organic compounds (VOCs) can be effectively remediated by using this process, along with a higher level of contamination consumption by the plant species. The removal of organic contaminates is predominantly effective through phytoremediation assisted by nanomaterial. Now, it has been found that the use of nanoparticles can enhance the stress tolerance level of plant species in ex situ and in situ situations, thus stimulating phytoremediation efficiency or potential (Rehman et al. 2017; Mahar et al. 2016).

16.3.1 Function of Nanomaterials in the Technique of Phytoremediation

The remediation of pollutants from soil and water through the technique of phytoremediation assisted by nanomaterials consists of three basic parts such as plants, nanomaterials, and pollutants. Hence, suitable application of nanomaterials directly enhances the effectiveness of phytoremediation on plants and pollutants. The addition of nanomaterials participates in the interaction process of plants and pollutants and indirectly influences the efficiency of the final remediation process. There are three aspects of phytoremediation by application of nanomaterials

- Direct removal of the contaminates through nanomaterials
- Stimulation of plant growth
- Enhancing the phytoavailability of the contaminates (Khan et al. 2017)

16.3.2 Applications of Nanomaterials Through the Process of Phytoremediation in Polluted Soil

Now a day, the science behind nanomaterials, nanotechnology is rapidly developing, and extensive research was carried out to remediate the environmental pollutants to clean up the nature. Among the various kinds of nanomaterials, especially metal-based and carbon-based nanomaterials are more popular and widely used in the remediation process for the removal of environmental pollutants. Many engineered nanomaterials are highly applied in most fields in the remediation of pollutants by using the method of phytoremediation from groundwater and soil in countries like the USA and Europe. Recently, it was reported that using suitable nanomaterials in the phytoremediation technique for remediation of contaminated soil is remarkably effective than the conventional phytoremediation method (Zhu et al. 2019).

16.3.3 Nanomaterial Promotes Phytoremediation for Removal of Heavy Metals from the Soil

The soil contamination by heavy metals is due to massive industrial and mining activity, which is a major threat to human health, soil microorganisms, and food safety. Phytoremediation is a cost-effective and sustainable process; therefore, it is used widely for the in-situ method of decontaminating heavy metals from soil. It has been found that the efficiency of phytoremediation for the removal of heavy metals such as Cd, Pb, Ni, Zn, and Cr from the soil is highly increased by the addition of nanomaterials. Normally Cd and Pb are the two most common heavy metals found in higher concentrations in contaminated soil. Lead is a widely utilized metal in various industries, such as storage batteries, solder material, gasoline additives, and ammunition, but also a highly significant contaminant present in the soil, which causes drastic health hazard problems. The method of phytoextraction is found to be the most accepted technique of phytoremediation applied for the removal of Pb from the soil of contaminated sites owing to its comparatively rapid growth, lower cost, and high level of tolerance against Pb. The application of nanomaterials in the process of phytoextraction promotes the efficiency of Pb removal (Ding et al. 2021).

Example: The application of nano-hydroxyapatite (nHA) in phytoextraction for remediation of Pb through ryegrass is highly effective. The impacts of heavy metals on human health due to contamination of soil, water, and air are represented in Fig. 16.3

Cadmium is another toxic heavy metal mixed in the soil because of different industrial activity and from the by-products of mining, electroplating, smelting, color pigments, phosphate fertilizers, and storage batteries. Using the technique of hyperaccumulators to remove Cd from the polluted soil is the major strategy of phytoremediation, whereas the obtainable species of Cd hyperaccumulators are

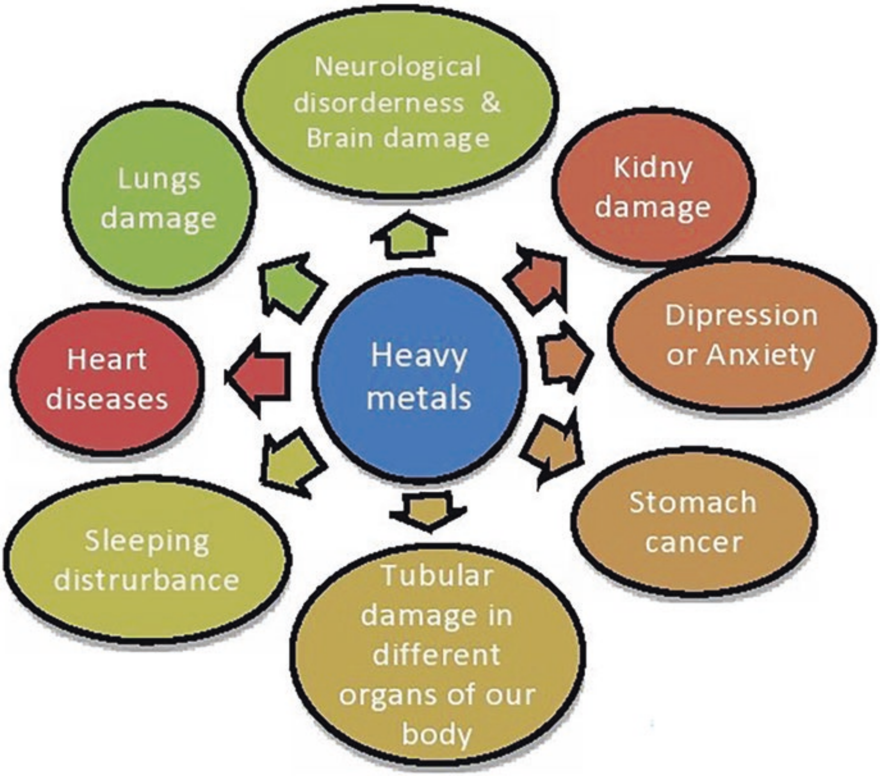


Fig. 16.3 Impact of heavy metals on human health

restricted in capacity and quantity. The nanoparticles of TiO_2 show a positive response to the accumulation of Cd in the soybean plants (Liang et al. 2017).

16.3.4 Nanomaterial Stimulates Phytoremediation for Extraction of As

Arsenic is a typical metalloid used in various sectors and is widely available in nature cause of the degradation of soil, water, and air. Arsenic is highly carcinogenic and toxic, and its concentration in the soil is rapidly increasing because of its extensive application in the production of pesticides, phosphate fertilizers, herbicides, and also used as preservatives for wood and wood products. Phytostabilization and phytoextraction are two major strategies of phytoremediation applied for declining arsenic from contaminated soil. The various plant species possess the capability of absorbing arsenic (As) through three distinct systems such as

- Active consumption through the symplast
- Passive consumption through the apoplast
- Direct transport of transcellular from the surroundings to the vascular system of the plant

Hence, the phytoextraction technique has been favorably used as a suitable process for the remediation of arsenic from contaminated soil. Again, it was found that the addition of nanoparticles of salicylic acid enhances the rate of remediation of arsenic through phytoextraction because salicylic acid plays a vital role in the growth of plants and also arsenic tolerance. The maximum accumulation of arsenic content in the root and shoot touches is 1188 and 705 mg/kg, respectively (Barbafieri et al. 2017; Qian et al. 2020).

16.3.5 Nanomaterial Used in Phytoremediation for Remediation of Organic Contaminants

There are a number of different kinds of organic contaminants that are normally ejected from various anthropogenic sources, and ultimately a major part of it is mixed with soil. The common organic pollutants that cause soil contamination include organochlorine pesticides, chlorinated hydrocarbons, phenols, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and their derivatives. These pollutants not only decrease the fertility of the soil but also cause harm to many soil microorganisms, flora, and fauna owing to its property of bioaccumulation, toxicity, and persistence in the environment. Phytoremediation has been found to be a highly appropriate and effective technique for decontaminating organic contaminants such as pesticides, petroleum products, PAHs, and explosives. Again, it was found that by using nanomaterials in phytoremediation, the efficiency of removal of the organic contaminates (trichloroethylene, trinitrotoluene, and endosulfan) in the soil drastically increases. With the addition of fullerene nanoparticles in the phytoremediation process using eastern cottonwood, the uptake capacity of trichloroethylene is remarkably increased. Again, with the use of the nanoparticles of fullerene, no acute toxicity towards plant species is observed (Gerhardt et al. 2009).

16.3.6 Direct Removal of Contaminants by Using Nanomaterials

Several nanomaterials possess the capability of removing the contaminants directly from the soil in the method of phytoremediation, which retards the load of contaminants via plant species. The mechanism of direct removal of contaminates from the soil is via redox or adsorption reactions with the help of nanomaterials.

Example: Contaminates present in the soil can be immobilized via adsorption through carbon nanotubes (CNTs).

It has been found that CNTs possess the outstanding capability of adsorbing numerous kinds of toxic pollutants (hydrophobic organic contaminates). CNTs stabilize the toxic organic contaminates via electrostatic interaction, p-p bonding, and hydrophobic interaction, whereas the interactions between the heavy metals and CNTs normally involve complexation, surface precipitation, physical adsorption, and electrostatic attraction. Because of the coexistence of a number of interactions, the combination of contaminates and CNTs is becoming stable. There are some other nanomaterials, such as iron-based bimetallic nanoparticles, iron oxide nanoparticles, phosphate-based nanoparticles, and natural mineral nanoparticles, are also used for the remediation of pollutants from soil. Man-made nanomaterials are still the focal point of research for effective remediation of soil contaminants (Almeida et al. 2019; Anjum et al. 2016). Some important nanomaterials used in the phytoremediation are shown in Table 16.1.

The concentration of the contaminates potentially influences the efficiency of phytoremediation. The plant species are usually more effective in metabolizing and accumulating the contaminants of comparatively less concentration. The concentration of the contaminants, particularly more than the tolerance limit, can be used in plants having noticeable phytotoxicity and cause a decrease in biomass and accumulation of pollutants. However, a plant can able to tolerate or accumulate some specific pollutants within a definite range of concentration. Some of the coexisting contaminants or exceptionally high concentration of the targeted contaminants results in the failures of the phytoremediation. The use of nanomaterials can directly remove a major fraction of contaminants in the technique of phytoremediation, which is also the cause of reduction of phytotoxicity. This is due to the stress produced by a high concentration of contaminants. The use of carbon nanotubes

Table 16.1 Nanomaterials used in phytoremediation process (Srivastav et al. 2018)

Nanoparticles	Plant species	Effective conc.	Effects
AgNPs	*Zea mays* L.	–	Rise in the production rate of GA and ABA phytohormones
Co_3O_4	NPs *Raphanus sativus* L.	5 g L^{-1}	Elongation plant roots
AgNPs	*Boswellia ovalifoliolata*	10–30 g mL^{-1}	Increase in seedling growth and germination
TiO_2	*Arabidopsis thaliana* NPs	400 mg L^{-1}	Lengthening of plant root
SANPs	*Isatis cappadocica*	–	Increase in growth of the plants
Aluminum oxide NPs	*Arabidopsis thaliana*	400–4000 mg L^{-1}	Increase in length of the roots
NPs of SiO_2	Changbai larch	500 μL L^{-1}	Increase in the height of the shoot, root length, root collar diameter
NPs of TiO_2	Arabidopsis *thaliana*	400 mg L^{-1}	Increase in length of the plant roots
NPs of CuO	Common wheat	500 mg L^{-1}	Increase in biomass
GNPs	*Arabidopsis thaliana*	10 and 80 μg mL^{-1}	Germination with the growth of root and shoot
Fe_2O_3 NPs	*Arachis hypogaea*	1–1000 mg kg^{-1}	Increase in length of the root, biomass, the height of the plant
ZnO NPs	*Arachis hypogaea*	1000 ppm	Germination, growth of the root, stem, and yield
NPs of MnOx	*Lactuca sativa*	10 mg L^{-1}	Improvement in the growth of the lettuce seedlings through enhancing elongation of root
Graphene oxide	*Gicia faba* L.	400 and 800 mg L^{-1}	Effective germination
NPs of Mn	*Vigna radiata*	50–1000 mg L^{-1}	Increase in consumption of nitrogen, shoot, and root elongation
SWCNTs	*Allium cepa*, *Cucumis sativus*	9, 56, 315, and 1750 mg L^{-1}	Elongation of plant root
MWCNTs	*Lycopersicon esculentum*	10–40 mg L^{-1}	Increase in the germination and growth of seed

(CNTs) for the accumulation of toxic Cd metal did not basis for phytotoxicity at relatively a lower concentration (50 mg/kg); otherwise, it protects the inhabitation of plant growth under the concentration of 200 mg/kg of Cd. The use of CNTs can mitigate the effect of phytotoxicity of Cd by increasing the ionic concentration of K^+ and Ca^{2+} for osmotic modification. It was recognized that the use of nano-carbon black and nano-hydroxyapatite stimulates the Pb phytoextraction through ryegrass. The use of nanomaterials improves the phytotoxicity of soil contaminated by Pb by stabilizing and adsorbing the contaminants. Although the accumulation of Pb in the roots of the plants reduces in the first month, the efficiency of final phytoremediation increases after 1 year because of the reduction in phytotoxicity. Furthermore, the efficiency of phytoremediation in a single growing season is restricted, and it requires some decades for the entire removal of contaminants of relatively higher concentration through the plant alone. Since the use of nanomaterial directly eliminates a major fraction of the contaminates, therefore partly reduces the load of removing the pollutants through plants and also reduces the remediation time. The use of nZVI particles increases the efficiency of phytoremediation of soil contaminated by trinitrotoluene because nZVI particles can directly eliminate a noticeable quantity of trinitrotoluene in a less time interval, whereas plant species in the process of phytoremediation require 120 days for full removal of trinitrotoluene (Carvalho et al. 2014; Klimkova et al. 2011).

16.3.7 Phytoremediation of Contaminated Soil

In the process of phytoremediation, some specific plant species are used for the degradation or removal of contaminates from water, sediment, air, and soil. The technologies of phytoremediation applied for the removal of pollutants from soil include phytoextraction, phytostabilization, phytodegradation, rhizodegradation, and phytovolatilization. The process of phytovolatilization is basically the transpiration and absorption of contaminants by plants. The technique of phytovolatilization is the process of transpiration and absorption of contaminants by plant species. After absorption by the plant species, some of the contaminants are converted into volatile materials and converted into a number of simple products by volatilization. These volatile product materials then moved to the leaves of the tree and then transpired. Hence, Hg and As are the most frequently eliminated metallic contaminates by using phytovolatilization technique because these contaminates are usually present in a volatile state and converted biologically into simple gaseous products by the plant species. Some specific volatile organic materials, such as trichloroethylene, can be eliminated by volatilization from the stems and leaves or from the soil promoted by the activities of the plant roots. The phytoextraction process is nothing, but the accumulation of the contaminants is in the overground portion of the plant species. It is said to be the translocation process of the contaminates and never undergoes transformation but is basically stored in the shoots of the plants after being consumed in by the roots of the plants. During the stage of collecting the overground part, these accumulated contaminants are eliminated from the sites, which can again be recycled or treated. The technique of phytoextraction is treated as the most recognized and effective strategy for phytoremediation to decrease soil contamination. This approach is normally linked with hyperaccumulators and provides more specific contaminates at the level, which is 100 times more than most plants. In India, sunflower and mustard are popularly utilized plant species used for phytoextraction. These two kinds of plant species attract researchers owing to their huge biomass, outstanding accumulation capability, and quick growth for different kinds of contaminates. The process of phytodegradation is the degradation of the organic contaminates by the processes of metabolism in the plant tissues, but if some suitable nanomaterial is coupled in this process, then efficiency is highly amazing. Roots of the plant species consume organic contaminates, where the contaminates are decomposed into simple species and can be incorporated inside the tissues of the plants. The plant species serves as the catalyst for breaking organic contaminates by producing different kinds of enzymes having specific functions, including nitroreductase, dehalogenase, and peroxidases. The pathway of specific decomposition of different plant species is also different. The process of phytostabilization is the immobilization of the contaminants through plant roots. Actually, this process does not occur in the plant body but is identified in the rhizosphere. With the process of adsorption onto the roots of the plant species and precipitation within the rhizosphere, the mobility or velocity of the contaminates can be decreased; hence the probability of entering the pollutants in the food chain, food web, and groundwater is substantially reduced. The process of phytostabilization is highly effective for the removal of toxic metals from soil and water. The contaminates are not essentially eliminated from the soil through phytostabilization, which is treated as a vital demerit of this process. The process of rhizodegradation is nothing but the degradation of the organic contaminants within the rhizosphere with the help of rhizospheric microorganisms, which is a plant-induced method. The microorganisms used in this technique play a leading role in the degradation of the contaminants by the pathway of the metabolic process. The roots of the plant species slacken off the soil, offering the surface attachment for the growth of the microbial community and projecting enzymes, saccharides, amino acids, and other substances, which promotes microbial metabolic activity. Since the interlinking between the rhizospheric microorganisms and roots of the plant species plays a key role in the effectiveness of rhizodegradation, some grasses containing widespread root systems like tall fescue and ryegrass are normally used in this technique. Although the process of phytoremediation has so many benefits in the treatment of polluted soil, the final efficiency of remediation is normally restricted because of the kinds of plant species, soil characteristics, contaminant bioavailability, and weather conditions. Hence, considering the demerits and limiting factors associated with phytoremediation, suitable strategies must have to be required to suit the technique for practical uses (Shrirangasami et al. 2020; Liu et al. 2020; Mukherjee et al. 2015).

16.3.8 Ideal Plant Characteristics for Nano-phytoremediation

Nanomaterials can directly remove the pollutants in the process of phytoremediation. It also stimulates the growth of plants and accelerates the phytoavailability of contaminants. The phytoextraction process is treated as the highest recognized and effective strategy used for phytoremediation to remove contaminants from polluted soil. The ideal plant species that effectively removes pollutants from the soil system possesses the following characteristics.

1. The rapid growth of the plant species for producing more biomass products and productivity.
2. The root system must be properly developed (highly branched) with an increase in the surface area of the roots.
3. The higher capability of tolerating and accumulating the contaminants (the tolerance limit of toxicity must be high).
4. Greater ability for a hyperaccumulation of organic and inorganic pollutants along with heavy metals, particularly in the aboveground area or sink potential
5. Easy and cost-effective harvest
6. It should not be consumed by any animals or human beings.
7. Vulnerable to genetic manipulation

However, some plant species partly fulfill the adequate conditions for phytoremediation. For example, a smaller number of plant species can store heavy metallic contaminates, specifically a higher percentage in their root system, but no negative impact is observed in the growth rate of the plants, commonly termed hyperaccumulation. Otherwise, the plant species having high biomass productivity, like agricultural crops and trees, normally consumes comparatively less concentration of heavy metals in comparison to hyperaccumulation. The deep root system of the trees and some agricultural plants facilitates the extraction of metals from the deeper layers of the soil (Yan et al. 2020; Vangronsveld et al. 2009; Cristaldi et al. 2017).

16.4 Important Plant Species Used for Phytoremediation

16.4.1 Brassica juncea

Particularly mustard plant species such as Indian mustard, leaf mustard, Chinese mustard, and mustard greens are collectively termed *Brassica juncea*. This kind of plant species is one of the important classes of vegetables and has the capability of accumulating Pb in its plant tissues if it grows in polluted soil with the addition of a chelating agent like EDTA. The seeds of these plant species are used to produce cooking mustard, especially Dijon mustard, and the flowers of these plant species are also directly used in cooking. Chinese mustard is a plant species having higher biomass and rapidly grows in polluted soil, which accumulates the heavy metal Cd in its shoots (Mendoza-Hernández et al. 2019).

16.4.2 Pteris vittata

The plant species *Pteris vittata* is normally found in southern Europe, Australia, tropical Africa, and Asia. This plant is a subfamily member of the Pteridaceae and also species of palm leaf. This kind of species reduces ‘As’ concentration in the contaminated soil and also in rice grain (Yan et al. 2019).

16.4.3 Helianthus annuus *or Sunflowers*

The sunflowers are usually meant for common sunflowers, and even they have various kinds of species found in nature. The species sunflower is a native plant to the USA. Sunflower is derived from the term shape of flower's head, which means look like the sun because these flowers move across the sky every day. The flowers of this plant species are used suitably in the synthesis of dyes, medicines, and also manufacturing of cooking oil. The most common sunflower belongs to the family Asteraceae, which is the family of daisies having the botanical name *Helianthus annuus*. This plant grows to amazing heights and is also very beautiful in appearance. It remediates Pb from the contaminated soil and gardener circles. These species of plants are cultivated in the Chernobyl region to remediate some radioactive pollutants from the soil, which are added to the soil due to the nuclear plant meltdown. In addition, it can also accumulate 2.5-fold more Zn in its biomass than previously existing in the soil (Forte and Mutiti 2017).

16.4.4 Salix viminalis *or Willow*

It is a native shrub that grows very quickly and is normally identified in wet or dumped regions. It is most widespread in Britain and Ireland. This kind of plant species was found to be a significant phytoextractor of Cd, Cu, and Zn because Salix viminalis possesses some unique characteristics such as huge quantities of production of biomass and comparatively higher capability of transporting toxic heavy metals from root to shoot. In addition to the remediation of heavy metals from contaminated soil, it can also be used for the production of biomass energy and bioenergy. These plants have flexible branchlets, therefore used in horticulture and basketry. It is originally found in Europe and Asia and is a non-native shrub.

16.4.5 Thlaspi caerulescens *or Alpine Pennycress*

It is the plant that mainly produces flowers and belongs to the family Brassicaceae. It is the native plant species found mainly in central and southern Europe and Scandinavia. These kinds of plant species, *Thlaspi caerulescens*, are particularly effective for consuming and remediating toxic heavy metals such as Zn and Cd. It normally grows effectively in gardens, banks, dry hillside meadows, field margins, pastures, lawns, or bare places. It has the capability of higher resistance to Zn and is effective for the remediation of Zn through accumulating Zn in its shoots.

Example: It can able to absorb 1500 ppm of Cd, whereas usual plants become poisoned if they reach the Cd level of 20–50 ppm.

16.4.6 **Ambrosia artemisiifolia *or Common Ragweed***

It is a weed of annual broad-leaved and also a member of the daisy family. *Ambrosia artemisiifolia* is, although native to the North America, a generally invasive and extensive weed found in Australia, Eurasia, and South America. *Ambrosia artemisiifolia* is specifically used for the remediation of Pb from contaminated soil. One major disadvantage is that it is the only species that is the cause of about 26% of the allergic reactions of the whole US population (Forte and Mutiti 2017).

16.4.7 **Populus *Trees***

Populus is a kind of species of deciduous plant popularly known for flowering and belongs to the family Salicaceae. Its native is mostly in Northern Hemisphere. This kind of species possesses a diversified genetic diversity and requires 15–50 meters of height for its growth. Its trunks are of up to a diameter of 2.5 meters. It is the most frequently used species in the process of phytoremediation. These species play a significant role in the remediation of toxic heavy metals in polluted soil. The major benefits of this species are the quick growth, higher biomass production, high rate of transpiration, which depends upon the groundwater level and easy vegetation propagation. This species is particularly effective in the remediation of alluvial soils (Pulford 2003).

16.4.8 **Mirabilis jalapa**

It is a perpetual herb that mainly grows in tropical and subtropical regions. It is also popularly called Four o'clock and is native to tropical South America. It closed in the early morning, whereas open overnight and mid-afternoon, for which the name *Mirabilis jalapa* was given. This kind of plant possesses a significant history of cultivation and its effective use throughout the world. These plants are mostly found in waste soil and around habitation regions. This is a widely distributed species, which can be used in phytoremediation of concentrations of ≤10,000 mg/kg soil contaminated by petroleum products (Van Aken 2008).

16.4.9 **Apocynum cannabinum**

This plant includes amy root, hemp dogbane, Indian hemp, dogbane, rheumatism root, and prairie dogbane. It is a perpetual herbaceous plant species that grow effectively in the southern half of Canada and all over the United States. This kind of plant can be effectively used in phytoremediation to sequester Pb in its biomass.

16.4.10 Festuca arundinacea

This is a special kind of grass species and is native to northern Algeria, Morocco, northern Libya, northern Africa, Tunisia, Azores, Pakistan, western Asia, and some parts of Europe. This kind of plant looks beautiful, therefore treated as ornamental grass present in gardens. This grass is also effectively used in the phytoremediation of contaminated soil. It is very effective for phytostabilization and highly useful for the remediation of soil containing a small concentration of Cd (Ryz et al. 2017).

16.4.11 Hordeum vulgare *L. or Barley*

It is an important crop found throughout the world and belongs to the Poaceae family, which is the main cereal grain effectively grown in high-temperature region climatic conditions. *Hordeum vulgare* L. is found to be the first grain cultivated particularly in Eurasia before 13,000 years ago. It is widely found in high-temperature regions, where it is cultivated as a summer crop, whereas in tropical regions, it is cultivated as a winter crop. The plant is suitable for separating NaCl to regain lands from the flooded seawater. This species is a cereal grain and belongs to the family of grasses. Currently, barley is found to be the most extensively consumed grain throughout the world and is the first grain cultivated in history. This species is more appropriate for the phytoremediation of soil polluted by waste petroleum products (Wahla and Kirkham 2008).

16.5 Selection of Suitable Nanoparticles for Phytoremediation

With the extensive development of nanotechnology, many different kinds of nanoparticles are developed, which are now a day broadly applied in our day-to-day life. The nanoparticles normally range in the order of 1–100 nm. Nanoparticles are considered as the bridge between atomic and molecular size and bulk material. The properties of nanoparticles are fully different from corresponding bulk material because of their large volume/charge ratio. Nanoparticles are appropriate for phytoremediation for remediation of pollutants because of the following properties.

1. The nanoparticles must be nonhazardous to the plant species.
2. Cause of increase in germination, elongation of root-shoot, increase in biomass, and height of the plant species.
3. Drastically increase in phytoenzymes in the production and growth of plants.
4. The capability of increasing the hormones related to plant growth.

5. The adequate capability of binding the pollutants and increased bioavailability for the plant species.
6. Increase in the rate of phytoremediation.

Therefore, the combined use of phytoremediation and nanotechnology or nanomaterial (phyto-nano-treatment) is highly effective for treating polluted soils. The technologies based on nano-phytoremediation (a combined effect of technology based upon plants and nanoparticle) uses either genetically engineered or naturally obtainable plant species assisted with nanoparticles or nanomaterials for cleaning the polluted environments. The suitable use of selected nanoparticles is the cause of a significant increase in the growth of the plants and nano-augmentation, which increases the efficiency of phytoremediation, leading to the potential removal of pollutants from the soils. A lot of nanoparticles were recognized as a promoter for the growth of many plant species because of their capability to increase the hormones associated with plant growth. It has the capability of improving the uptake of pollutants through plants. There are some specific metal oxide and metals which shows an amazingly positive impact on the growth rate of plant species. Although the performance of nanocarbon particles is highly effective for bioremediation of polluted soil, its high toxicity is dangerous to both soil microorganisms and plant species (Ebrahimbabaie et al. 2020).

Phytoremediation is the technique where green plants and the microbes related to them are used to reduce or completely remove harmful toxic pollutants from the environment. In this process, green plants, waste of vegetables, fruits of green plants, etc., are used for degradation or in situ removal of the pollutants from soils, groundwater, sludge sediments, and surface water. The cost-effective solar energy technique can also be applied in this process. It is a comparatively less expensive method for the remediation of pollutants by using suitable plant species for metabolizing the molecules present in tissues and breaking down the toxic elements from the surroundings. It is the natural capability of some plant species to accumulate, concentrate, or decomposes the pollutants present in the soil, air, and water. Usually, toxic heavy metals and hazardous pollutants are the most important focus for phytoremediation (Luo et al. 2018). The different phytoremediation techniques used to clean up the environment are given in Table 16.2.

16.5.1 Role of Nanoparticles to Clean-up Environment

The nanoparticles (NPs) having a dimension of about 10 nm are synthesized naturally by plant species under the ecologically stressed abiotic situation, and these NPs play a significant role in the remediation of especially heavy metals from air, water, and soil. The NPs mainly divided into the following groups:

- Natural nanoparticles produced from volcanic dust.
- Nanoparticles produced from various anthropogenic activities like the combustion of coal.

Table 16.2 Different phytoremediation technologies (Padmavathiamma and Li 2007)

Remediation techniques	Mechanism of remediation	Medium used
Rhizofiltration	Consumption of toxic metals in the plant roots	Water pumped out through mangers and surface water
Vegetative caps	The evapotranspiration of rainwater by plants to stop leaching the pollutants from sites of disposal	Soil
Phytodegradation	Uptake by plant species and the degradation of organic matter	Groundwater and surface water
Rhizosecretion	A subset associated with molecular farming, developed to secrete and form useful natural products and also recombinant proteins from the plant roots	–
Plant-assisted bioremediation	Increase in the microbial degradation within the rhizosphere	Groundwater within the rhizosphere and soils
Removal of organic matters from the air	Uptake of volatile organic matter by leaves	Air
Phytoextraction	The consumption and absorption of metals directly by plant tissue with succeeding removal of the plant species	Soils
Phytomining	Use of suitable plant species to extract inorganic matter from the ores and minerals obtained from mining	Soils
Phytostabilization	The precipitation of metals by root exudates is the cause of less bioavailable	Soils, mine tailings, and groundwater
Phytovolatilization	Plant evapotranspirates Se, Hg, and volatile organics	Groundwater and soil

- Synthetically engineered nanoparticles based on metals such as nano-Au, nano-Zn, and nano-Ag.
- NPs used for nano-phytoremediation of the polluted soil require nontoxic plant species and their rhizosphere microbiota, which can bind the pollutants and convert these into bioavailable for increasing the process of phytoextraction (Singh 2016).

There are a number of NPs, which can be synthesized by using plant species, and soil microbiota possesses the capability of facilitating the formation of plant growth hormones leading to the production of more biomass and increasing the extraction of pollutants from the soil above the ground tissues of the plant species. The nanomaterials are not only used for the remediation of HMs but also effective against the remediation of hazardous inorganic and organic contaminates.

Example: The soil contaminated by ‘As’ can be remediated in nano-phytoremediation technique by using salicylic acid nanoparticle (SNAPs). The endosulfan can also be removed in the process of nano-phytological remediation by using zerovalent iron NPs.

Till now, the studies based on nano-phytoremediation are only limited to laboratory scale microcosm and experiments based on pot culture, but there is a necessity for some long-term field studies for its practical application. The influence of engineered nanoparticles (ENPs) on the phytoextraction of organic pollutants and HMs by suitable plant species must be extensively studied. The knowledge of ENPs in the nano-phytoextraction of polluted water and soil is highly essential for the design and development of suitable NPs, which are cost-effective and eco-friendly to our environment. It can be used as a suitable alternative to the present NPs for the bioremediation of HMs and organics present in the soil, air, and water. The ENPs can be biologically synthesized comparatively more quickly by plant species growing in polluted areas containing microbial communities such as bacteria, algae, fungi, and actinomycetes, which are related to the roots of these plants. The biologically synthesized NPs having sizes 100–200 nm produced by plants or phytochemicals and microbes can again be purified by using filtration along with antioxidants or the properties of reduction. The ENPs are accountable for the reduction of the toxic HMs into their corresponding NPs, such as Ag, Pt, Cd, Au, and sulfide. The recent development of plant nanobiotechnology is the cause of improving plant nanobionic systems. These studies developed the nano-engineering of the plant organelles, such as chloroplast, for developing nano-bionic plant species with a potential increase in performance at the photosynthetic sensing level. Because of the rapid population growth and impact of frequent changes in climatic conditions, demands to develop ecologically sustainable crops requiring less water for their growth and the use of agrochemicals based on NPs such as nano-fertilizers, nano-pant-stimulators, nano-pesticides, and nano-carriers are drastically increased. The plant species growing on the polluted soils possess some exclusive property of biologically producing NPs to save themselves from the hazardous impact of soil pollutants. The enzymes and NPs, both from the roots of the plants, play a significant role in eliminating the pollutants from the contained soil with reducing or oxidative characteristics. Since these are soluble in water, therefore considered a suitable substitute to remove pollutants and clean up the environment. The NPs synthesized biologically have a large surface area; therefore, they possess the capability of catalyzing or absorbing huge amounts of pollutants. The HMs buried under sediments, and the soil is finally deposited at the uppermost layer of the soil, which is available for the roots of the plants, which is the major point of entry of the HMs into our environment, food chain, and food web. Phytoremediation is more fruitful if the process is coupled with suitable NPs and capable of removing the major fraction of the pollutants accumulated in the upper layer of the soil, which are biologically adsorptive and bioavailable (Patil et al. 2016; Yan et al. 2013).

16.5.2 Challenges of Nano-phytoremediation

The removal of pollutants from soil and water using phytoremediation coupled with nanomaterial is very rare. Although it is highly interesting, still now, it is restricted only to the laboratory scale. The major challenges of the removal of pollutants by using nano-phytoremediation are as follows:

- Only experiments based on microcosm have been carried out till now; however, there is a necessity to use them. Hence, more truthful researches in the future are highly essential for better practical application in this field.
- Continuing research work is needed to identify the actual impact of the nanomaterials and NPs in the process of phytoremediation and improve the fertility level of the soil.
- Nanomaterials possess the better capability to accumulate these and may decrease the mobility of the used nanomaterials; therefore, the polymer coating and other coatings are necessary to increase the mobility or bioavailability.
- The effect of the level of safety and non-toxicity of the applied nanomaterials in the pouted soil must have to be evaluated.
- The nano-phytoremediation in the sustainable pathway mainly depends upon the meteorological situation of the environment; therefore, the highly stable nanomaterial in the present environmental condition must have to be developed and identified. The process of nano-phytoremediation is now treated as an appropriate sustainable method for the sites where the pollution level is moderate owing to unsustainable growth of plants in extensive polluted soil.
- The higher uptake of toxic pollutants by plant species is used in phytoremediation from the soil, which promotes agro-mining and might be used for extraction of pollutants even from the biomass of harvestable plants.

The application of nanomaterials to stimulate the process of phytoremediation is an interesting and potential idea that appeared in the improvement of bioremediation technology and nanotechnology. The vital challenge in the technique of nano-phytoremediation is the toxic effect of nanomaterials on soil and the ecosystem. There are a number of nanomaterials that are dangerous to the biotic community (animals, plants, human beings, and microbes). Hence, more study is necessary to determine the level of risk of the nanomaterials and their toxicity effect on the application in phytoremediation (Mahar et al. 2016; Zhou et al. 2022).

16.6 Applications of Nano-phytoremediation

Nano-phytoremediation can be applied successfully in different fields. NPs are widely applied for removing chemical and biological pollutants, including HMs and toxic waste organic substances. Because of their high surface energy and huge surface area, NPs possesses the capability of absorbing huge amounts of pollutants by catalyzing the reaction. Hence, the reaction proceeded more rapidly; therefore, energy consumption becomes less during the degradation and supports in preventing the pollutant release. The nano-phytoremediation is the cause of a number of significant environmental advantages, which are classified into three different categories.

- Remediation along with treatment
- Detection and sensing
- Prevention of pollution

The reduction or complete removal of pollutants from the environment, such as toxic organic pollutants, HMs, and inorganic contaminates, by applying NPs synthesized from algae, bacteria, and fungi assisted by nanotechnology is termed nano-bioremediation. If such kinds of pollutants are removed or drastically reduced by using the NPs synthesized from higher plants involvement, then it is termed nano-phytoremediation. Again, nano-phytoremediation comprises different subcategories such as nano-rhizofiltration, nano-phytodegradation, nano-phytostabilization, nano-phytovolatilization, and so on. The NPs also be used in bioremediation based on enzymes in combination with phytoremediation. In bioremediation based on the enzyme the NPs can also be used in mixing with phytoremediation. Nanotechnology raises the efficiency of phytoremediation; therefore, NPs can be applied successfully for bioremediation of water, sediments, soil contaminated by HMs, e-wastes, biomedical wastes, organic, and inorganic wastes. Nanotechnology accelerates the efficiency and performance of phytoremediation and, therefore, can be suitably applied for the bioremediation of water resources, soils, HMs, and organic and inorganic pollutants.

Examples: Numerous complex organic materials, including organochlorines, polychlorinated biphenyls (PCBs), and long-chain hydrocarbons specifically resistant to plant and microbial degradation. But, a combining approach of phytoremediation and nanotechnology can able to overcome this kind of limitation. The complex toxic organic matter is degraded into simple substances using nanoencapsulated enzymes, which enhances quick degradation by combining the activity of both plant species and microbes. Iron serves a vital role in the remediation of environment pollutants owing to its reducing characteristics as an electron donor. The more resistant toxic organic wastes, including atrazine, chlorpyrifos, and molinate, can also be degraded using zerovalent iron (nZVI) of nanoscale. Engineered nanoscale iron oxide, cerium oxides, manganese oxides, zinc oxides, and titanium oxides possess a higher capability of absorbing metalloids and metals. This affinity, in association with their large number of reactive sites with extensive surface area, fit them suitable for the remediation of polluted soil and water. Nano-phytoaccumulation can able to remediate TNT and e-waste-polluted soil (Nwadinigwe and Ugwu 2018b; Jesitha and Harikumar 2018).

In addition to these, some specific applications of nano-phytoremediation are given below.

16.7 Stimulating Plant Growth

The rate of growth and plant biomass are two vital parts of selecting the plant species for the technique of phytoremediation. There are many plants used in phytoremediation are not exhibit satisfactory results because of their less plant biomass and slow rate of growth, leading to the imperfect tolerance to the contaminants and less fertility of the soil for the growth of plant species. Hence, some methodology used in the process of phytoremediation is to stimulate the growth of plant species, which includes immunizing the plant growth supporting rhizobacteria (PGPR), use of regulators for plant growth, and application of transgenic plant species. There are some nanomaterials, including carbon nanotubes, nZVI nanoparticles, graphene quantum dots, nanoparticles of ZnO, and nanoparticles of Ag, that could increase the growth of plants. The mechanisms of stimulating the growth of plants are different for different nanomaterials (Shang et al. 2019).

Example: The quantum dots of graphene acts as both pesticide and nanofertilizer to increase the rate of growth of Allium sativum and Coriandrum sativam. The carbon nanotubes (CNTs) activate the reproductive system of the plant species resulting in the growth of tomato plants. In the technique of phytoremediation, the addition of nanomaterials enhances the efficiency of remediation by facilitating the growth of plant species (Shojaei et al. 2019).

The removal of contaminants directly by plant species retards phytotoxicity, which is advantageous to plant growth. Despite these, nanomaterials act on plant species to enhance the level of tolerance to the contaminates. By decreasing the phytotoxicity of Pb and Cd against white popinac in phytoremediation, the nanoparticles of ZnO are applied as physiological regulators for plants towards species. Therefore, the nanoparticle of ZnO enhances the tolerance level of plants by regulating the gene expression of the enzymes. The phytotoxicity of Cr(VI) improved towards pea with the addition of nanoparticles of silicon because the tolerance level to Cr(VI) stress was stimulated by the application of nanoparticles (Tripathi et al. 2015). Besides the improvement in the contaminant phytotoxicity, the nanomaterials may also catalyze the growth of plant species in the system of phytoremediation by promoting the absorption of nutrients and water, regulating and controlling soil microbes, increasing the rate of photosynthesis, and improving the stress due to drought and high salinity. Nano-hydroxyapatite is also used to support the removal of Pb by using ryegrass, and also the growth of plants is facilitated with a subsequent increase in the efficiency of phytoremediation. This is because the phosphorus content in the soil is enhanced by the addition of nano-hydroxyapatite. The NPs of salicylic acid can also be used to enhance the rate of utilization and absorption of nutrients, which improves the plant biomass of the plant species *Isatis cappadocica* in the system of 'As' phytoextraction. But, in the case of Cd phytoextraction via soybean, the nanoparticles of TiO_2 were quite helpful in stimulating the growth of plant species by increasing the rate of photosynthesis. The mechanism behind this is that the nanoparticles of TiO_2 enter the chloroplasts and increase the capability of electron transfer and light adaptation (Gul et al. 2021).

16.8 Accelerating the Phytoavailability of Pollutants

The phytoavailability of contaminants is the vital factor that influences the efficiency of phytoremediation, particularly for phytoextraction. The phytoavailability of the contaminants strongly depends upon the chemical specification and distribution in soil.

Example: The phytoavailability of Cd shows various binding forms. Therefore, it was found that Cd adsorbed on the surface of gibbsite is the greatest available to stem than other oxide minerals, including alumina, manganese oxide, goethite, and magnetite present in the soil. The metals having the highest phytoavailability were found in the soil solution form or exchangeable state, then in the combined state with the organic matters, oxides and minerals are always lowest in a crystalline state. Furthermore, the physicochemical property of the soil and plants also influences the phytoavailability of the waste impurities. Less phytoavailability always restricts the process of phytoremediation (Palani et al. 2021).

Example: Pb is a toxic heavy metal, present in the insoluble state in soil because of its property of adsorption, precipitation, and complexation, which is the cause of difficulty in the method of phytoextraction (Mahar et al. 2015).

Hence, numerous methods are developed to enhance the phytoavailability of the pollutant, which includes fertilization (agronomic management), treatment with chelating agents, application of genetic engineering, and immunization of rhizospheric microorganisms. The increase in the phytoavailability of the pollutants is highly effective for enhancing the efficiency of phytoremediation. Nanomaterials can act as a carrier of contaminants while entering the cell, hence enhancing the property of bioavailability. Otherwise, the adsorption of the contaminants onto nanomaterials outside the organism retards the free impurities leading to the retardation of bioavailability. According to the pathway of nano-phytoremediation, two vital conditions required for improving the properties of phytoavailability of the contaminants in combination with nanomaterials are as follows.

- The nanomaterials used also can couple with the contaminant through adsorption.
- The nanomaterial used must be phytoavailable. The NPs of fullerene are extensively studied to enhance the phytoavailability of contaminants (Wang et al. 2004).

Example: The nanoparticles of fullerene-C_{60} used in the phytoremediation process along with eastern cottonwood promote the removal of trichloroethylene from the contaminated soil (Abhilash et al. 2012).

16.9 Nano-phytoremediation in the Purification of Water

The design and synthesis of phytogenic magnetic nanoparticles (PMNPs) and their use in the treatment of wastewater and water are owing to their dynamic morphology, super paramagnetic behavior, greater saturation magnetization, and preferred size. The process of nano-phytoremediation is a sustainable and environmentally friendly treatment process, which is clean, quick process, cost-effective, nontoxic, and eco-friendly in nature than any other physicochemical technique. Although the commercialization features of this technique are effective in the area of wastewater treatment, there are some demerits of this technique also still exist in terms of reusability, mechanism of fabrication, and regeneration. This is a green technology that is technically feasible and also economically viable but needs some modification for practical applicability. In this technology, for the improvement of phytogenic magnetic nanoparticles, optimization of various production protocol solution parameters such as types of solvent used, the strength of precursor, pH, and additional volume temperature are highly needed. The improvement in the saturation magnetization and morphology will increase the stability of the phytogenic magnetic nanoparticles after the removal of the contaminates and also the production of biomass separation. The impact on health and sustainability using nanomaterials is still under investigation. The hexavalent chromium (Cr (VI)) was also remediated via adsorption using nanoparticles of zerovalent iron with a much higher level of adsorption efficiency. Again, the nanoclusters produced by green synthesis from Cupressus sempervirens; Mediterranean cypress having about 3.0 m radius nanoparticles are effective for the removal of synthetic dyes (Bhati and Rai 2018; Gomes et al. 2014).

16.10 Conclusion and Future Perspectives

The technology based on nano-phytoremediation is a new and sustainable area for remediating pollutants and cleaning up the environment. The efficiency of nano-phytoremediation depends upon many parameters such as soil categories, pH, variation in temperature, moisture concentration, and availability of nutrients. The use of nanotechnology (addition of NPs and nanomaterials) in combination with phytoremediation exhibits sustainable, eco-friendly, and green alternatives for cleaning up the environment without any adverse impact on nature. Although this is a novel technology for the removal of pollutants from soil and water, the major demerit is the toxicity of the added nanomaterials or NPs. The nanomaterials in the diverse state can be suitably used for the elimination of HMs from the environment. The nanomaterials of some plant species, bacteria, and fungi are highly effective for the removal of HMs and toxic organics from contaminated areas. Therefore, it is essential to study the mechanism regarding the transportation of nanomaterials within the environment level of toxicity. The selection of appropriate nanomaterials and plant species and their optimization efficiency is highly important for nano-phytoremediation to clean up the environment. Although phytoremediation is a green and sustainable technology for remediation of pollutants on a long-term basis, the frequent change in topography and phytotoxicity of some pollutants present in higher concentrations retards the efficiency of the process; hence to increase the performance of phytoremediation, some suitable nanomaterials are coupled in it.

The addition of nanomaterials can remove contaminates, stimulates the growth of plants, increases phytoavailability of the pollutants, and can promote the efficiency of phytoremediation of the polluted soil. Still, more research is needed for the practical applicability of the process.

References

Abhilash PC, Powell JR, Singh HB, Singh BK (2012) Plant–microbe interactions: novel applications for exploitation in multipurpose remediation technologies. Trends Biotechnol 30(8):416–420

Almeida JC, Cardoso CED, Tavares DS, Freitas R, Trindade T, Vale C, Pereira E (2019) Chromium removal from contaminated waters using nanomaterials – a review. TrAC Trends Anal Chem 118:277–291

Anjum M, Miandad R, Waqas M, Gehany F, Barakat MA (2016) Remediation of wastewater using various nano-materials. Arab J Chem 12(8):4897–4919

Barbafieri M, Pedron F, Petruzzelli G, Rosellini I, Franchi E, Bagatin R, Vocciante M (2017) Assisted phytoremediation of a multi-contaminated soil: investigation on arsenic and lead combined mobilization and removal. J Environ Manag 203:316–329

Bhati M, Rai R (2018) Nano-phytoremediation application for water contamination. In: Phytoremediation. Springer, Cham, pp 441–452

Bissessur R (2020) Chapter-18, Nanomaterials applications. In: Polymer science and nanotechnology. Elsevier, pp 435–453. https://doi.org/10.1016/b978-0-12-816806-6.00018-2

Carvalho PN, Basto MCP, Almeida CMR, Brix H (2014) A review of plant–pharmaceutical interactions: from uptake and effects in crop plants to phytoremediation in constructed wetlands. Environ Sci Pollut Res 21(20):11729–11763

Cristaldi A, Conti GO, Jho EH, Zuccarello P, Grasso A, Copat C, Ferrante M (2017) Phytoremediation of contaminated soils by heavy metals and PAHs. A brief review. Environ Technol Innovation 8:309–326

Ding N, Han M, He Y, Wang X, Pan Y, Lin H, Yu G (2021) Advances in application of nanomaterials in remediation of heavy metal contaminated soil. In: E3S Web of Conferences, vol 261. EDP Sciences, pp 1–4

Ebrahimbabaie P, Meeinkuirt W, Pichtel J (2020) Phytoremediation of engineered nanoparticles using aquatic plants: mechanisms and practical feasibility. J Environ Sci 93:151–163

Forte J, Mutiti S (2017) Phytoremediation potential of Helianthus annuus and Hydrangea paniculata in copper and lead-contaminated soil. Water Air Soil Pollut 228(2):77–88

Gerhardt KE, Huang X-D, Glick BR, Greenberg BM (2009) Phytoremediation and rhizoremediation of organic soil contaminants: potential and challenges. Plant Sci 176(1):20–30

Gomes MVT, de Souza RR, Teles VS, Araújo Mendes É (2014) Phytoremediation of water contaminated with mercury using Typha domingensis in constructed wetland. Chemosphere 103:228–233

Gul I, Manzoor M, Hashim N, Shah GM, Waani SPT, Shahid M et al (2021) Challenges in microbially and chelate-assisted phytoextraction of cadmium and lead – a review. Environ Pollut 287:1–13

Jesitha K, Harikumar PS (2018) Application of nano-phytoremediation technology for soil polluted with pesticide residues and heavy metals. In: Ansari A, Gill S, Gill R, Lanza G, Newman L (eds) Phytoremediation. Springer, Cham, pp 415–439. https://doi.org/10.1007/978-3-319-99651-6_18

Kamal M (2004) Phytoaccumulation of heavy metals by aquatic plants. Environ Int 29(8):1029–1039

Karn B, Kuiken T, Otto M (2009) Nanotechnology and in situ remediation: a review of the benefits and potential risks. Environ Health Perspect 117(12):1823–1831

Khan AG (2020) Promises and potential of in situ nano-phytoremediation strategy to mycorrhizo-remediate heavy metal contaminated soils using non-food bioenergy crops (Vetiver zizinoides & Cannabis sativa). Int J Phytorem 22(9):900–915. https://doi.org/10.1080/15226514.2020.1774504

Khan AG (2021) Nano-phytoremediation of heavy metals contaminated wastewater ecosystems and wetlands by constructed wetlands planted with waterlogging-tolerant mycorrhizal fungi and vetiver grass. Environ Sci Proc 6(1):25. https://doi.org/10.3390/iecms2021-09385

Khan I, Saeed K, Khan I (2017) Nanoparticles: properties, applications and toxicities. Arab J Chem 12(7):908–931

Klimkova S, Cernik M, Lacinova L, Filip J, Jancik D, Zboril R (2011) Zero-valent iron nanoparticles in treatment of acid mine water from in situ uranium leaching. Chemosphere 82(8):1178–1184

Kumar L, Ragunathan V, Chugh M (2021) Nanomaterials for remediation of contaminants: a review. Environ Chem Lett 19:3139–3163

Liang S, Jin Y, Liu W, Li X, Shen S, Ding L (2017) Feasibility of Pb phytoextraction using nanomaterials assisted ryegrass: results of a one-year field-scale experiment. J Environ Manag 190:170–175

Liu Z, Chen B, Wang L, Urbanovich O, Nagorskaya L, Li X, Tang L (2020) A review on phytoremediation of mercury contaminated soils. J Hazard Mater 400:1–47

Luo J, Yang D, Qi S, Wu J, Gu XS (2018) Using solar cell to phytoremediate field-scale metal polluted soil assisted by electric field. Ecotoxicol Environ Saf 165:404–410

Mahar A, Wang P, Li R, Zhang Z (2015) Immobilization of lead and cadmium in contaminated soil using amendments: a review. Pedosphere 25(4):555–568

Mahar A, Wang P, Ali A, Awasthi MK, Lahori AH, Wang Q, Zhang Z (2016) Challenges and opportunities in the phytoremediation of heavy metals contaminated soils: a review. Ecotoxicol Environ Saf 126:111–121

Mendoza-Hernández JC, Vázquez-Delgado OR, Castillo-Morales M, Varela-Caselis JL, Santamaría-Juárez JD, Olivares-Xometl O et al (2019) Phytoremediation of mine tailings by Brassica juncea inoculated with plant growth-promoting bacteria. Microbiol Res 228:1–8

Muhammed Shameem M, Sasikanth SM, Annamalai R, Ganapathi Raman R (2021) A brief review on polymer nanocomposites and its applications. Mater Today Proc 45:2536–2539

Mukherjee R, Kumar R, Sinha A, Lama Y, Saha AK (2015) A review on synthesis, characterization, and applications of nano zero valent iron (nZVI) for environmental remediation. Crit Rev Environ Sci Technol 46(5):443–466

Nagendran R, Selvam A, Joseph K, Chiemchaisri C (2006) Phytoremediation and rehabilitation of municipal solid waste landfills and dumpsites: a brief review. Waste Manag 26(12):1357–1369

Nedjimi B (2021) Phytoremediation: a sustainable environmental technology for heavy metals decontamination. SN Appl Sci 3(3):286–304

Nwadinigwe AO, Ugwu EC (2018a) Overview of nano-phytoremediation applications. In: Newman L (ed) Phytoremediation. Springer, Cham, pp 377–382. https://doi.org/10.1007/978-3-319-99651-6_15

Nwadinigwe AO, Ugwu EC (2018b) Overview of nano-phytoremediation applications. In: Ansari A, Gill S, Gill R, Lanza G, Newman L (eds) Phytoremediation. Springer, Cham, pp 377–382. https://doi.org/10.1007/978-3-319-99651-6_15

Padmavathiamma PK, Li LY (2007) Phytoremediation technology: hyper-accumulation metals in plants. Water Air Soil Pollution 184:105–126

Palani G, Arputhalatha A, Kannan K, Lakkaboyana SK, Hanafiah MM, Kumar V, Marella RK (2021) Current trends in the application of nanomaterials for the removal of pollutants from industrial wastewater treatment—a review. Molecules 26(9):2799–2815

Patil SS, Shedbalkar UU, Truskewycz A, Chopade BA, Ball AS (2016) Nanoparticles for environmental clean-up: a review of potential risks and emerging solutions. Environ Technol Innovation 5:10–21

Pulford I (2003) Phytoremediation of heavy metal-contaminated land by trees—a review. Environ Int 29(4):529–540

Qian Y, Qin C, Chen M, Lin S (2020) Nanotechnology in soil remediation – applications vs. implications. Ecotoxicol Environ Saf 201:1–13

Ramanjaneyulu AV, Giri G (2006) Phytoremediation – a review. Agric Rev 27:216–222

Razmi B, Ghasemi-Fasaei R, Ronaghi A, Mostowfizadeh-Ghalamfarsa R (2021) Investigation of factors affecting phytoremediation of multi-elements polluted calcareous soil using Taguchi optimization. Ecotoxicol Environ Saf 207:1–9

Rehman MZ, Rizwan M, Ali S, Ok YS, Ishaque W, Nawaz MF, Akmal F, Waqar M (2017) Remediation of heavy metal contaminated soils by using Solanum nigrum: a review. Ecotoxicol Environ Saf 143:236–248

Romeh AA, Ibrahim Saber RA (2020) Green nano-phytoremediation and solubility improving agents for the remediation of chlorfenapyr contaminated soil and water. J Environ Manag 260:1–9

Ryz NR, Remillard DJ, Russo EB (2017) Cannabis roots: a traditional therapy with future potential for treating inflammation and pain. Cannabis Cannabinoid Res 2(1):210–216

Shang Y, Hasan MK, Ahammed GJ, Li M, Yin H, Zhou J (2019) Applications of nanotechnology in plant growth and crop protection: a review. Molecules 24(14):2558–2580

Shojaei TR, Salleh MAM, Tabatabaei M, Mobli H, Aghbashlo M, Rashid SA, Tan T (2019) Applications of nanotechnology and carbon nanoparticles in agriculture. In: Synthesis, technology and applications of carbon nanomaterials. Elsevier, pp 247–277. https://doi.org/10.1016/b978-0-12-815757-2.00011-5

Shrirangasami SR, Rakesh SS, Murugaragavan R, Ramesh PT, Varadharaj S, Elangovan R, Saravana Kumar S (2020) Phytoremediation of contaminated soils—a review. Int J Curr Microbiol Appl Sci 9(11):3269–3283

Singh A (2016) Nanoparticles for environmental clean-up: an overview. Int J Appl Chem 12(3):175–181

Song B, Xu P, Chen M, Tang W, Zeng G, Gong J, Ye S (2019) Using nanomaterials to facilitate the phytoremediation of contaminated soil. Crit Rev Environ Sci Technol 49(9):791–824. https://doi.org/10.1080/10643389.2018.1558891

Srivastav A, Yadav KK, Yadav S, Gupta N, Singh JK, Katiyar R, Kumar V (2018) Nano-phytoremediation of pollutants from contaminated soil environment: current scenario and future prospects. In: Ansari AA et al (eds) Phytoremediation. Springer Nature Switzerland AG, pp 383–401. https://doi.org/10.1007/978-3-319-99651-6_16

Tripathi DK, Singh VP, Prasad SM, Chauhan DK, Dubey NK (2015) Silicon nanoparticles (SiNp) alleviate chromium (VI) phytotoxicity in Pisum sativum (L.) seedlings. Plant Physiol Biochem 96:189–198

Van Aken B (2008) Transgenic plants for phytoremediation: helping nature to clean up environmental pollution. Trends Biotechnol 26(5):225–227

Vangronsveld J, Herzig R, Weyens N, Boulet J, Adriaensen K, Ruttens A, Mench M (2009) Phytoremediation of contaminated soils and groundwater: lessons from the field. Environ Sci Pollut Res 16(7):765–794

Vasavi A, Usha R, Swamy PM (2010) Phytoremediation – an overview review. J Ind Pollut Control 26(1):83–88

Wahla IH, Kirkham MB (2008) Heavy metal displacement in salt-water-irrigated soil during phytoremediation. Environ Pollut 155(2):271–283

Wang X, Shan X, Zhang S, Wen B (2004) A model for evaluation of the phytoavailability of trace elements to vegetables under the field conditions. Chemosphere 55(6):811–822

Wei Z, Van Le Q, Peng W, Yang Y, Yang H, Gu H, Sonne C (2020) A review on phytoremediation of contaminants in air, water and soil. J Hazard Mater 403:1–8

Yan W, Lien HL, Koel BE, Zhang WX (2013) Iron nanoparticles for environmental clean-up: recent developments and future outlook. Environ Sci Processes Impacts 15(1):63–77

Yan H, Gao Y, Wu L, Wang L, Zhang T, Dai, CHe, Z. (2019) Potential use of the Pteris vittata arsenic hyperaccumulation-regulation network for phytoremediation. J Hazard Mater 368:386–396

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 11:359–373

Zhang W, Sun R, Xu L, Liang J, Wu T, Zhou J (2019) Effects of micro−/nano-hydroxyapatite and phytoremediation on fungal community structure in copper contaminated soil. Ecotoxicol Environ Saf 174:100–109

Zheng K, Setyawati MI, Leong DT, Xie J (2018) Antimicrobial silver nanomaterials. Coord Chem Rev 357:1–17

Zhou Y, Kumar M, Sarsaiya S, Sirohi R, Awasthi SK, Sindhu R et al (2022) Challenges and opportunities in bioremediation of micro-nano plastics: a review. Sci Total Environ 802:1–15

Zhu Y, Xu F, Liu Q, Chen M, Liu X, Wang Y et al (2019) Nanomaterials and plants: positive effects, toxicity and the remediation of metal and metalloid pollution in soil. Sci Total Environ 662:414–421

Chapter 17
Potentials and Frontiers of Nanotechnology for Phytoremediation

Garima Pandey, Prashant Singh, Bhaskara Nand Pant, and Sangeeta Bajpai

Abstract Organic and inorganic contaminants persisting in the environment pose a threat to eco-balance and human health. Various technologies have been observed to identify and adopt a systematic approach to remove the contaminants from the environmental matrices. Phytoremediation, in combination with nanotechnology, is one such method that has the potential to be a sustainable and efficient alternative to on-site and off-site remediation. The nanomaterials and nanotools for phytoremediation are selected on the grounds of the nature and site of the contamination. Nanomaterials can assist the course of phytoremediation either by direct removal of the contaminants or by stimulating the growth of the plants. The selection of an appropriate nanoparticle for phytoremediation is of utmost importance because nanomaterials can behave both as a stimulant and a toxic material for microorganisms. The major objective of this chapter is to investigate the principles, technologies, possibilities, regulatory aspects, challenges, and future prospects of nano-mediated phytoremediation for sustainable bioremediation.

Keywords Contaminants · Nanomaterial · Phytoremediation · Sustainability

---

G. Pandey (✉)
SRM-Institute of Science and Technology, Delhi-NCR Campus, Modinagar,
Ghaziabad, UP, India

P. Singh · B. N. Pant
Department of Chemistry, Atma Ram Sanatan Dharma College, University of Delhi,
New Delhi, India

S. Bajpai
AMITY School of Applied Sciences, Amity University, Lucknow, UP, India

L. Newman et al. (eds.), *Phytoremediation*, https://doi.org/10.1007/978-3-031-17988-4_17

17.1 Introduction

The rapid increase of global industrialization and urbanization is increasing the concerns toward the growing environmental contamination all over the world (Dhote et al. 2012; Bhatia et al. 2015; El-Ramady et al. 2017; Pandey 2018a, b, 2019). Phytoremediation is an excellent and highly accepted method for treating contaminated sites. Phytoremediation is a method that makes use of plants for the degradation, stabilization, and removal of contaminants. It can be used as a green technology alternative to the conventional methods of air, soil, and water remediation (Fernández et al. 2018; Pandey 2018c). The utilization of plants in the degradation of pollutants is known as phytoremediation. Several studies have been performed to augment the effectiveness of phytoremediation through various approaches. Nanotechnology is extensively used for sorting various environmental and human health issues, and nanomaterials with novel characteristics have been utilized for the remediation of the contaminated sites (Cadotte et al. 1988; Baglieri et al. 2013; Brandl et al. 2015; Poorva et al. 2013). Various nano-enabled remediation methods like nano-phytoremediation, bio-nanoremediation, and electro-nanoremediation use nanoparticles, nano-hybrids, nanomachines, nanosensors to degrade-dissipate and adsorb the contaminants from the contaminated sites. Nano-mediated phytoremediation is one of the promising methods for facilitating the treatment of contaminated soil and groundwater (Cecchin et al. 2017). Among the several options being explored and adopted for remediation of the contaminants, phyto-nanoremediation has emerged as one of the sustainable methods. The characteristic feature of large surface area, presence of a large number of reactive sites, and high adsorption capacity of nanomaterials (Nzila et al. 2016; Kica and Wessel 2017; Pandey et al. 2021) makes them a potential solution in combination with phytoremediation for remediation of the contaminated sites (Sozer and Kokini 2009; Srivastav et al. 2018). Nano-phytoremediation is an eco-friendly, cost-effective, and enduring solution to remove contamination from polluted sites, which has the potential to degrade mineral and biological contaminants like trinitrotoluene (Simeonidis et al. 2016; Song et al. 2018). However, this promising technology of nano-phytoremediation is still in its nascent phase, and further studies are still needed to adopt and fully adapt to this method (Rizwan et al. 2014; Savage and Diallo 2015). Along with this, the complete assessment and management of all the impending environmental and health (Rafique et al. 2019; Ramírez-García et al. 2019) consequences of nano-phytoremediation should be extensively analyzed, and proper rules, regulations, and guidelines are required to govern such emerging technologies.

17.2 What Is Nano-phytoremediation?

Remediation is considered a discipline of removing or reducing contaminants from the environment by biological, physical, or chemical methods. Nanotechnology is the science of designing, creating, and utilizing ultrafine particles in nanoscale

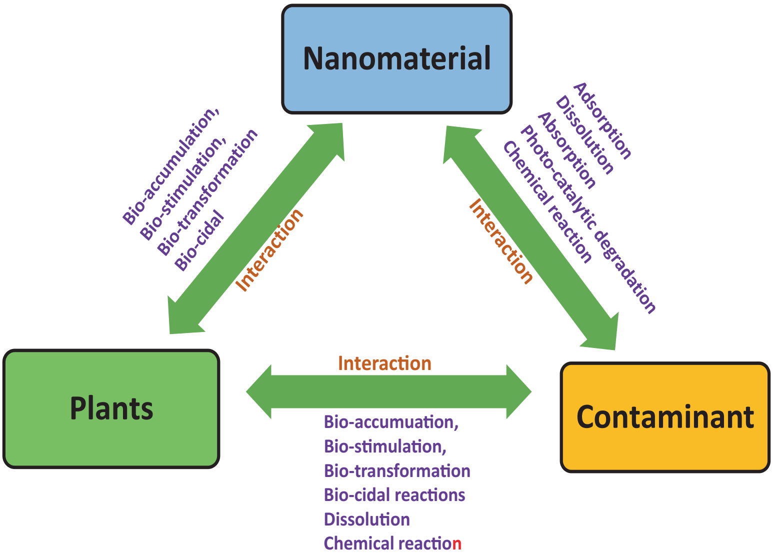


Fig. 17.1 Interaction of plants, contaminants, and environment in nano-phytoremediation

dimensions (Karn 2004). Phytoremediation is a bioremediation method that utilizes plants to eliminate, relocate, obliterate, and/or stabilize the contaminants in the environment of soil, sediments, ground, and surface water. Nano-phytoremediation is an amalgamation of phytoremediation and nanotechnology for environmental remediation (Fig. 17.1). The employment of nanomaterials for phytoremediation of the environment is growing rapidly (Karn et al. 2009; Yadav et al. 2017a, b). As nanomaterials have proven their worth in phytoremediation, it is required to extract them naturally or synthesize them in the laboratory (Watlington 2015).

17.2.1 Synthesis of Nanoparticles

Nanoparticles can be synthesized through numerous biological (green), chemical, and physical routes (Fig. 17.2). The physical scheme of the synthesis is an expensive method, while the chemical schemes pose grave environmental concerns along with sluggish growth rates and varying structures of designed nanoparticles. Synthesis of nanomaterials involves following two approaches.

(i) The bottom-up approach: this is a cost-effective approach that starts with initiating units at the atomic level. This method can be used for large-scale production of nanoparticles.
(ii) The top-down approach: this is a slow and costly approach that begins with initiating units at the macroscopic level. This method is not very beneficial for the large-scale production of nanoparticles.

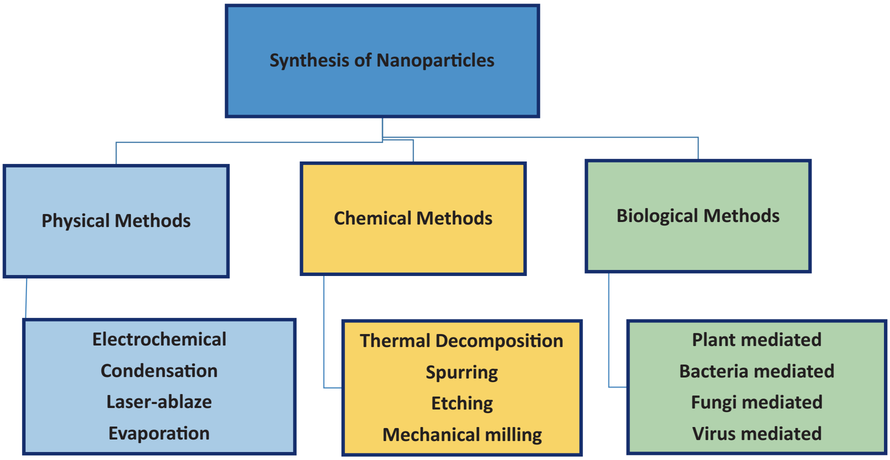


Fig. 17.2 Methods for synthesizing nanoparticles

The non-sustainability of physiochemical methods of synthesizing nanoparticles has made researchers look for an economically beneficial, greener, and more sustainable route for nanoparticle synthesis (Ingale and Chaudhari 2013; Kharissova et al. 2013). Green synthesis of nanoparticles comprises the reaction between an appropriate quantity of specific metal-ion with plant extracts, bacteria, fungi, and viruses under essential reaction conditions.

17.2.2 Phytoremediation

Phytoremediation is a sustainable and cost-effective method used to decontaminate the environment from metals, crude oils, pesticides, solvents, explosives, and various other contaminants (Cunningham et al. 1997; Badr et al. 2012; Chaudhry et al. 2005). Certain plant species with hyper-accumulation characteristic property are planted at the contaminated site, and these plants remove the contaminants or convert them into harmless or less harmful forms through degradation, extraction, bioaccumulation, or immobilization (Yavari et al. 2015; Das 2018; De Gisi et al. 2017). This is a promising technology en route to sustainable remediation of the environment (Verma and Jaiswal 2016). Phytoremediation involves the following main strategies (Fig. 17.3):

- Phyto-sequestration/phyto-extraction/phyto-absorption/phyto-accumulation: In this method, roots of plants absorb contaminants along with the nutrients from the soil and thereafter transform/accumulate them in the harvestable parts of plants. This method has principally been used to remove metalloids and metallic wastes like Se, As, Pb, Ni, Cu, Zn, and Cd (Wang et al. 2009, 2014a, b).

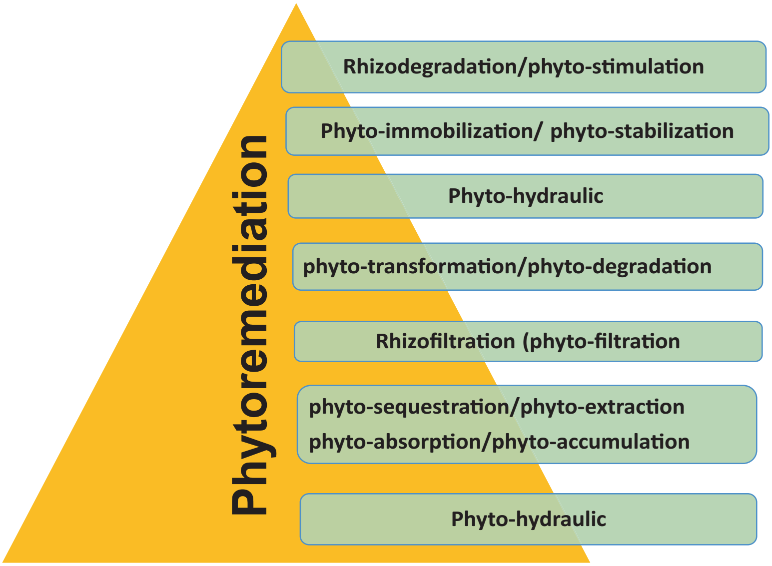


Fig. 17.3 Strategies of phytoremediation

- Phyto-transformation/phytodegradation: In this type of remediation, plants break down the contaminants into simpler compounds within the plant tissues. They are used for the remediation of nitro-aromatics, anilines, chlorinated solvents, and pesticides (Wang et al. 2016a, b).
- Rhizofiltration (phyto-filtration): In this method, the plants used for remediation are hydroponically cultivated in greenhouses. This scheme is utilized for the ex-situ remediation of groundwater, where plants take pollutants through their roots to precipitate/concentrate them. Normally the hydroponic systems use a synthetic soil medium, for example, a mixture of sand with vermiculite/perlite. When the roots of plants get saturated with pollutants, the plants are discarded and disposed of. This technique is principally employed for removing radioactive and metallic pollutants.
- Phyto-hydraulic/hydraulic barriers: This route involves the indirect remediation of pollutants by large trees. Trees control the movement of groundwater through their roots and indirectly control the movement and absorption of pollutants. Along with this, pollutants present in the absorbed water are metabolized by the plant enzymes.
- Phyto-immobilization/phyto-stabilization: Here the plants restrain the movement of contaminants and reduce their diffusion in the soil environment. This method is principally used to remove metals and organic pollutants (Roy et al. 2015).
- Rhizodegradation/phyto-stimulation: Here the plants discharge natural compounds through their roots, and these compounds work as nutrients for soil microorganisms. Microbes present in the soil augment the biodegradation of pollutants. This method is limited to the removal of organic pollutants.

- Phyto-volatilization: here plants absorb the contaminated water, convert the pollutants into their nontoxic form, and discharge them into atmosphere through the leaves. This method is generally utilized for the elimination of metalloids, heavy metals (e.g., Hg, As, Se, and Hg), and organic pollutants (Wang et al. 2012).

17.3 Contribution of Nanoparticles in Nano-phytoremediation

Nano-phytoremediation can be employed for remediating metallic, radioactive, chemical (volatile and semi-volatile organic compounds, pesticides, insecticides), contaminants found in soil, ground, and surface water systems (Kim et al. 2012; Köber et al. 2014; Kumar and Gopinath 2009; Kumari and Singh 2016) as presented in Fig. 17.4. Various studies are in progress to identify the contribution of nano-phytoremediation for remediating perchlorate, which is found to persist in the ground and surface water reservoirs. Contaminants that have been remediated using nano-phytoremediation are given in Table 17.1 (Le et al. 2015; Mahadik 2017).

The selected nanoparticles for nano-phytoremediation must have the below-mentioned characteristics (Vázquez-Núñez et al. 2020; VázquezNúñez and de la Rosa-Álvarez 2018):

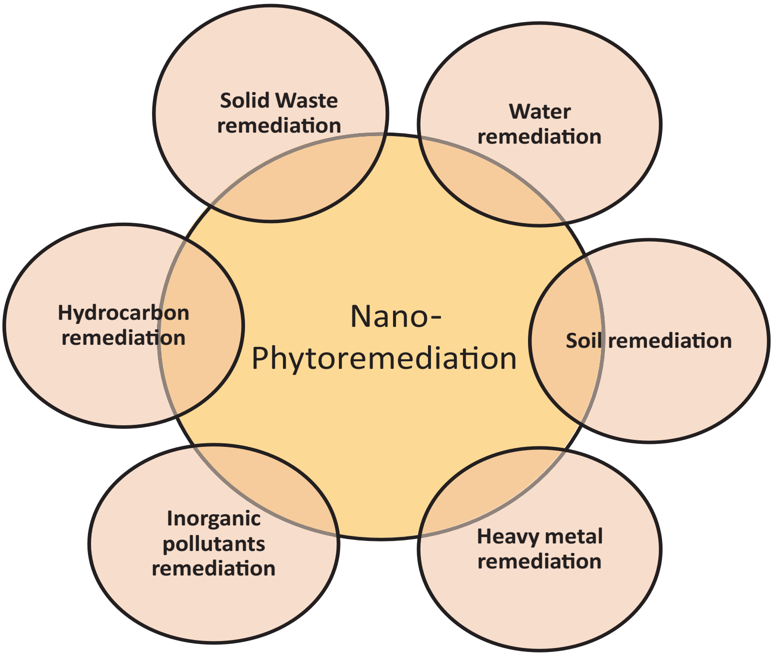


Fig. 17.4 Nano-phytoremediation

Table 17.1 Contaminants being remediated by using nano-phytoremediation

Site of contamination	Name of contaminant
Groundwater, surface water, soil	Heavy metals (cobalt, lead, copper, selenium, nickel, zinc, chromium 6^+, and cadmium), volatile organic compounds, organophosphate insecticides (parathion), pesticides, radionuclides (uranium, strontium, and cesium), explosives (di and trinitrotoluene, trinitrobenzene, octogen, RDX extra), surfactants, fuels, benzene, toluene, ethylbenzene and xylenes, chlorinated solvents (tri and poly chloroethylene), polychlorinated biphenyls, polynuclear hydrocarbons

- They should be nontoxic to the plant species being utilized.
- They should have the capability to perk up the activity of growth hormones and the production of phyto-enzymes in plants.
- They should have a strong binding capacity for the contaminants.

The persistence, bioaccumulation, and toxicity of anthropogenic organic pollutants, like aromatic hydrocarbons, polychlorinated biphenyls, pesticides, insecticides, petroleum, explosives, and phenols, are prevalent in the water and soil environment, making it very critical to remove them (Jones and de Voogt 1999; Kang 2014; Tripathi et al. 2015). Many applications of carbon-based and metal- and metal-oxide-based nanomaterials for decontaminating the soil and groundwater sites (Gong et al. 2009; Singh and Lee 2016) contaminated with Ni, Zn, Pb, Cd, and Cr have effectively been carried out in the United States and Europe (Mueller and Nowack 2010; Khan and Bano 2016; Chen et al. 2017; Liang et al. 2017a, b; Vıtkova et al. 2018). The exploitation of nanotechnology and nanomaterials has been noticed to enhance the course of phytoremediation. Zerovalent nano-iron (nZVI) is a largely used nanoparticle for facilitating phytoremediation (Thijs et al. 2016; De Gisi et al. 2017; Shipley et al. 2010; Xue et al. 2018). Some examples of nano-assisted phytoremediation are demonstrated in Table 17.2.

17.4 Role of Nanomaterials in Nano-phytoremediation

The structural scheme of nano-phytoremediation involves three chief functional units: pollutants, plants, and nanomaterials (Martínez-Fernández et al. 2017; Nwadinigwe and Ugwu 2018). Nanomaterials can directly enhance the efficiency of phytoremediation by directly acting upon the plants and pollutants, or they might indirectly enhance the final efficiency by interfering in the plant–pollutant interactions (Zhang 2003; Yogalakshmi et al. 2020). Nanomaterials assist and enhance the efficiency of phytoremediation processes by playing the following roles:

- Nanomaterials may directly act on plants and pollutants
- Applied nanomaterial may facilitate the interaction between the plant and pollutant
- May increase the phyto-availability of pollutants

Table 17.2 Some studies on nanomaterials assisted phytoremediation (nano-phytoremediation)

Name of the pollutant	Name of the plant species	Name of the nanomaterial	Remediation result	References
TNT (trinitrotoluene)	Guinea grass (*Megathyrsus maximus*)	Nanoscale zerovalent iron (nZVI)	An increase from 86% to 100% in the removal of trinitrotoluene	Jiamjitrpanich et al. (2012)
Endosulfan	Malabar grass (*Cymbopogon citrates*), Kulainjan (*Alpinia calcarata*), Tulsi (*Ocimum tenuiflorum*)	Nanoscale zerovalent iron (nZVI)	Rate of removal of endosulfan increased from 65% to 85% for Malabar grass, 80–100% for Kulainjan, and 21–76% for Tulsi	Pillai and Kottekottil (2016)
Trichloroethylene	Necklace poplar (*Populus deltoides*)	Fullerene nanoparticles	30–80% increase in phyto-uptake of trichloroethylene	Ma and Wang (2010)
Lead	English ryegrass (*Lolium perenne*)	Nanocarbon black and nano-hydroxyapatite	Elimination rate of lead from the soil was found to increase from 32% to 47% in a year	Liang et al. (2017a, b)
Chromium	Pea (*Pisum sativum*)	Silicon nanoparticles	Buildup of chromium in the shoot and the root has decreased by half	Tripathi et al. (2015)
Arsenic	*Isatisca ppadocica*	Salicylic acid nanoparticles	Increased accumulation of arsenic in the roots and shoots of the plants	Souri et al. (2017)
Cadmium	Soybean (*Glycine max*)	Titanium oxide nanoparticles	Four times increase has been observed in the cadmium uptake by the plants has increased	Singh and Lee (2016)
Arsenic, cadmium, lead, and zinc	English ryegrass (*Lolium perenne*) and sunflower (*Helianthus annuus*)	Nanoscale zerovalent iron (nZVI)	50–60% decrease in the concentration of cadmium, zinc, lead, and arsenic in plants	Vıtkova et al. (2018)
Cadmium, lead, and nickel	Maize (*Zea mays*)	Silver nanoparticles	Two times increase in the accumulation concentration of lead, nickel, and cadmium has been observed	Khan and Bano (2016)

17.4.1 Directly Removing the Pollutants

Nanomaterials have the ability to eliminate the contaminants straight from the soil through redox reactions or the process of adsorption. This role of nanoparticles lessens the weight of decontamination from the plants and shortens the duration of remediation steps (Song et al. 2019; Yogalakshmi et al. 2020). Some illustrative studies highlighting the application of nanomaterials for soil remediation are given in Table 17.3.

17.4.2 Enhancing the Phyto-availability of the Pollutants

Phyto-availability of pollutants is an important aspect in determining the efficiency of phytoremediation and the phyto-availability of the pollutants mainly depends on physiological characteristics of plants, physiochemical properties of pollutants, and

Table 17.3 Illustration of direct removal of pollutants by nanomaterials

Name of nanomaterial	Name of the pollutant	Remediation mechanism	References
Nano-chlorapatite	Lead, cadmium	Precipitation as metal-phosphate	Wan et al. (2018)
Nanoscale zerovalent iron (nZVI)	Chromium	Reduction of chromium(VI) to a less toxic and more stable form	Wang et al. (2014a, b)
Carbon nanotubes	Organochlorine pesticides	In-situ remediation through adsorption	Zhang et al. (2017)
Nano-hydroxyapatite	Zinc, copper	Precipitation as metal phosphates through ion exchange and surface complexation	Sun et al. (2018)
Selenium nanoparticles	Mercury	Precipitation of mercury as mercuric selenide	Wang et al. (2017)
Ferrous phosphate nanoparticles	Cadmium	Precipitation of cadmium as cadmium phosphate	Xu et al. (2016)
Bimetallic nickel-iron nanoparticles	Polybrominated diphenyl ethers	Direct degradation (hydrogenation/de-bromination) with nickel-iron nanoparticles	Xie et al. (2014)
Bimetallic lead-iron nanoparticles	Polychlorinated biphenyls	Direct degradation (hydrogenation/dechlorination) with lead-iron nanoparticles	Chen et al. (2014)
Magnetite nanoparticles	Arsenic	Adsorption and coprecipitation	Liang and Zhao (2014)
Iron-manganese binary oxide nanoparticles	Selenium	Direct immobilization by adsorption	Xie et al. (2015)
Bimetallic iron-copper nanoparticles	Chromium	Reduction of chromium (VI) by iron-copper nanoparticles	Zhu et al. (2016)

Table 17.4 Representation of studies on the effect of nanomaterials on the growth rate of plants

Name of nanomaterials	Name of plant species	Effect on growth	References
Quantum dots, graphene	Garlic (*Allium sativum*), coriander (*Coriandrum sativum*)	Nanomaterials acted as pesticides and nutrients, enhancing the plant growth	Chakravarty et al. (2015)
Carbon nanotubes	Tomato (*Solanum lycopersicum*)	Employed nanomaterial activated the reproductive system of the plant, and an increase in fruit production was observed	Khodakovskaya et al. (2013)
Graphene	Tomato (*Solanum lycopersicum*)	Employed nanomaterial got accumulated in the root tip and reduced the production of biomass	Zhang et al. (2015)
C_{70} fullerenes (water soluble)	Thale cress (*Arabidopsis thaliana*)	Employed nanomaterial inhibited the plant growth microtubule disorganization, uncontrolled cell division, and disrupting auxin	Liu et al. (2010)
Silver nanoparticles	Kidney bean (*Phaseolus vulgaris*)	Employed nanomaterial improved plant growth by increasing the chlorophyll activity and nitrogen intake	Das et al. (2018)
Titanium oxide nanoparticles	Greater duckweed (*Spirodela polyrrhiza*)	Employed nanomaterial reduced plant growth because of the inhibition of nitrogen fixation, photosynthesis, and protein synthesis	Movafeghi et al. (2018)
Zinc oxide nanoparticles	Cotton (*Gossypium hirsutum*)	Employed nanomaterial improved plant growth because of the increase in the absorption of phosphorus and zinc	Venkatachalam et al. (2017)
Aluminum oxide nanoparticles	Wheat (*Triticum aestivum*)	Employed nanomaterial inhibited the plant growth because of the induced toxicity	Yanık and Vardar (2015)
Copper oxide nanoparticles	Indian mustard (*Brassica juncea*)	Employed nanomaterial reduced plant growth because of the deposition of lignin in plant cell	Nair and Chung (2015)
Nanoscale zerovalent iron (nZVI)	Thale cress (*Arabidopsis thaliana*)	Employed nanomaterial improved the root growth through hydroxyl-induced loosening of the cell wall	Kim et al. (2014)

their distribution in soil. The low phyto-availability usually restricts the process of phytoremediation. Nanomaterials have two different effects on the phyto-availability of pollutants in contaminated soil (Table 17.4). They might increase the bioavailability by functioning as a pollutant carrier or may decrease the bioavailability by adsorption of pollutants on their surface.

17.4.3 Promoting Plant Growth

The biomass of plants and their growth rate plays a significant role in nano-phytoremediation. Because of the poor soils composition and low tolerance toward pollutants, sluggish growth rate and stumpy plants biomass often makes plants unsatisfactory for remediation. Hence, certain approaches are used to stimulate plant growth for the phytoremediation process. One such strategy is the employment of nanomaterials, and researchers have highlighted that some nanomaterials like carbon nanomaterials, graphenes, quantum dots, silver, iron, and zinc oxide nanoparticles can augment plant growth (Table 17.4). Direct removal of pollutants using nanomaterials lessens the phytotoxicity, which is advantageous for plant growth. Nanomaterials may also surge the tolerance level of the plants toward pollutants. Nanomaterials could also escalate plant growth by aiding the intake of nutritional substances and water, improving the speed of photosynthesis, regulating the microorganism population of soil, and getting rid of the abiotic strain.

17.5 Factors Affecting the Course of Nano-phytoremediation

The chemical behavior of the pollutants, nature of environmental conditions, and physiological characteristics of plants affect the absorption and the dissemination of pollutants (Table 17.5).

17.6 Advantages, Limitations, and Concerns

The technology of nano-phytoremediation offers numerous environmental benefits, which may be classified as: (i) recognizing and discovering, (ii) treatment and remediation, and (iii) pollution prevention (Azubuike et al. 2016; Alvarez et al. 2018; Pandey and Jain 2020; Pandey 2020). Nanotechnology upsurges the efficiency of phytoremediation; therefore, nanotechnology-aided phytoremediation may be used for decontamination/remediation/treatment of water and soil contaminated with inorganic and organic contaminants. Along with various advantages, nano-phytoremediation has certain limitations and concerns, which are summed up in Table 17.6.

Table 17.5 Factors affecting nano-phytoremediation

Physiochemical properties of the compounds	Molecular weight, vapor pressure, water solubility
Environmental characteristics	Temperature, pressure, pH, moisture, and organic matter content of the soil
Plant characteristics	Nature of enzymes, type, and nature of root system

Table 17.6 Advantages, limitations, and concerns of nano-phytoremediation

Advantages	Limitations and concerns
Lesser amount of generation of secondary wastes	Toxicity and bioaccumulation of biodegradation products and disposal of the harvest containing contaminants
Nominal disturbance in the environment and the soil composition of the remediation site	Phytoremediation is effective in sites with lower contamination
Large surface area of nanoparticles makes them absorb a large number of contaminants for remediation with a higher reaction rate.	Location, weather, and climate of the contaminated site affect the results
Lesser energy consumption	Depth restrictions and requirements of larger land area
Nanoscale dimensions of nanoparticles promote the in-situ remediation, making them reach even the inaccessible areas	Not effective for highly sorbed contaminants like PCBs (polychlorinated biphenyls)
Nanotechnology facilitates the designing of contaminant-specific, highly selective, and sensitive nanosensors for the detection of contaminants	Requirement of longer time (typically quite a few growing seasons)

In the system of nano-phytoremediation, nanoparticles are purposefully introduced to transform and depollute the environment. It is recognized that several nanoparticles are harmless, while some others tend to have good health effects. The improved surface area and the greater binding capacity helps facilitate the transportation and adsorption of pollutants for longer distance and time for nano-phytoremediation. Certain nanoparticles, when breathed in, can straightforwardly get mined with the bloodstream affecting vital body organs leading to inflamed and damaged organs, protein denaturation, respiratory tract infections like asthma, and sometimes even causing cancer, resulting in the death of the organism. Nanoparticles may aggregate and enter the food chains affecting the ecological constitution of the area. Very little information about the environmental impacts of nanoparticles is found in the literature. It is necessary to extensively analyze all the aspects of the interaction of nanomaterials with biotic/abiotic components of the environment. However, the organizations working on nano-phytoremediation still do not have well-framed guidelines to govern and evaluate the environmental impacts of nanoparticles. Therefore, it is very critical to comprehensively assess the environmental impacts of nano-phytoremediation and adopt a fixed set of rules and regulations to decrease or avoid the hazards associated with nanomaterial usage in nano-phytoremediation systems.

17.7 Conclusion

The retrieval of contaminated environments is a key concern that should be given prime attention at the earliest. The traditional decontamination approaches use physical and chemical strategies, which have various constraints. The limitless potential, interdisciplinary nature, extraordinary surface properties, and environment friendliness may possibly fast-track the utmost transformational alterations in the phytoremediation of the environment. The amalgamation of nanotechnology and phyto-technology could facilitate environmental remediation cost-effectively and sustainably. Nano-phytoremediation is a somewhat new arena for the bioremediation of contaminated sites. Most of the research in this field is still in the laboratory stage. The difference in outcomes has been observed because of the difference in physiological parameters (such as pH, humidity, temperature, and nutrient content of the soil) between the laboratory conditions and the real environment. It is necessary to select the plant and nanomaterials appropriately and comprehend the mechanism involved in the transportation of nanomaterials to assess their adverse effects on the environment and plants. A proper set of rules, guidelines, risk assessment, and management strategies are also required to broaden the acceptance and omit the difference between the lab and the real site conditions and results.

References

Alvarez PJJ, Chan CK, Elimelech M, Halas NJ, Villagrán D (2018) Emerging opportunities for nanotechnology to enhance water security. Nat Nanotechnol 13:634. https://doi.org/10.1038/s41565-018-0203-2

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

Badr N, Fawzy M, Al-Qahtani KM (2012) Phytoremediation: an ecological solution to heavy-metal-polluted soil and evaluation of plant removal ability. World Appl Sci J 16(9):1292–1301

Baglieri A, Nègre M, Trotta F, Bracco P, Gennari M (2013) Organo-clays and nanosponges for acquifer bioremediation: adsorption and degradation of triclopyr. J Environ Sci Health B 48:784–792. https://doi.org/10.1080/03601234.2013.780943

Bhatia A, Singh SD, Kumar A (2015) Heavy metal contamination of soil, irrigation water and vegetables in peri urban agricultural areas and markets of Delhi. Water Environ Res 87(11):2027–2034. https://doi.org/10.2175/106143015X14362865226833

Brandl F, Bertrand N, Lima EM, Langer R (2015) Nanoparticles with photoinduced precipitation for the extraction of pollutants from water and soil. Nat Commun 6:1–10. https://doi.org/10.1038/ncomms8765

Cadotte J, Forester R, Kim M, Petersen R, Stocker T (1988) Nanofiltration membranes broaden the use of membrane separation technology. Desalination 70:77–88. https://doi.org/10.1016/0011-9164(88)85045-8

Cecchin I, Reddy KR, Thomé A, Tessaro EF, Schnaid F (2017) 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

Chakravarty D, Erande MB, Late DJ (2015) Graphene quantum dots as enhanced plant growth regulators: effects on coriander and garlic plants. J Sci Food Agric 95:2772–2778. https://doi.org/10.1002/jsfa.7106

Chaudhry Q, Blom-Zandstra M, Gupta SK, Joner E (2005) Utilizing the synergy between plants and rhizosphere microorganisms to enhance breakdown of organic pollutants in the environment. Environ Sci Pollut Res 12:34–48

Chen X, Yao X, Yu C, Su X, Shen C, Chen C et al (2014) Hydrodechlorination of polychlorinated biphenyls in contaminated soil from an e-waste recycling area, using nanoscalezerovalent iron and Pd/Fe bimetallic nanoparticles. Environ Sci Pollut Res 21:5201–5210. https://doi.org/10.1007/s11356-013-2089-8

Chen M, Zeng G, Xu P, Zhang Y, Jiang D, Zhou S (2017) Understanding enzymatic degradation of single-walled carbon nanotubes triggered by functionalization using molecular dynamics simulation. Environ Sci Nano 4:720–727. https://doi.org/10.1039/C7EN00050B

Cunningham SD, Shann JR, Crowley DE, Anderson TA (1997) Phytoremediation of contaminated water and soil. In: Kruger EL, Anderson TA, Coats JR (eds) Phytoremediation of soil and water contaminants, ACS symposium series 664. American Chem Society, Washington, DC, pp 2–17

Das P (2018) Phytoremediation and Nanoremediation: emerging techniques for treatment of acid mine drainage water. Defence Life Sci J 3(2):190–196. https://doi.org/10.14429/dlsj.3.11346

Das P, Barua S, Sarkar S, Karak N, Bhattacharyya P, Raza N et al (2018) Plant extract–mediated green silver nanoparticles: efficacy as soil conditioner and plant growth promoter. J Hazard Mater 346:62–72. https://doi.org/10.1016/j.jhazmat.2017.12.020

De Gisi S, Minetto D, Lofrano G, Libralato G, Conte B, Todaro F et al (2017) Nano-scale Zero Valent Iron (nZVI) treatment of marine sediments slightly polluted by heavy metals. Chem Eng Trans 60:139–144

Dhote J, Ingole S, Chavhan A (2012) Review on waste water treatment technologies. Int J Eng 1:1–10

El-Ramady H, Alshaal T, Abowaly M, Abdalla N, Taha HS, Al-Saeedi AH et al (2017) Nanoremediation for sustainable crop production. In: Ranjan S, Dasgupta N, Lichtfouse E (eds) Nanoscience in food and agriculture, vol 1, 1st edn. Springer, Singapore, pp 335–363

Fernández PM, Viñarta SC, Bernal AR, Cruz EL (2018) Figueroa. L.I.C. Bioremediation strategies for chromium removal: current research, scale-up approach and future perspectives. Chemosphere 208:139–148. https://doi.org/10.1016/j.chemosphere.2018.05.166

Gong JL, Wang B, Zeng GM, Yang CP, Niu CG, Niu QY et al (2009) Removal of cationic dyes from aqueous solution using magnetic multi-wall carbon nanotube nanocomposite as adsorbent. J Hazard Mater 164:1517–1522. https://doi.org/10.1016/j.jhazmat.2008.09.072

Ingale AG, Chaudhari AN (2013) Biogenic synthesis of nanoparticles and potential application: an eco-friendly approach. J Nanomed Nanotechnol 4(2):165. https://doi.org/10.4172/2157-7439.1000165

Jiamjitrpanich W, Parkpian P, Polprasert C, Kosanlavit R (2012) Enhanced phytoremediation efficiency of TNT-contaminated soil by nanoscale zero valent iron. In: 2nd International Conference on Environment and Industrial Innovation, vol 35. IACSIT Press, Singapore, pp 82–86

Jones KC, de Voogt P (1999) Persistent organic pollutants (POPs): state of the science. Environ Pollut 100(1–3):209–221. https://doi.org/10.1016/S0269-7491(99)00098-6

Kang JW (2014) Removing environmental organic pollutants with bioremediation and phytoremediation. Biotechnol Lett 36:1129–1139. https://doi.org/10.1007/s10529-014-1466-9

Karn B (2004) Nanotechnology and the environment: applications and implications. Oxford University Press, New York, p 890. https://doi.org/10.1021/bk-2005-0890

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 N, Bano A (2016) Role of plant growth promoting rhizobacteria and Ag-nano particle in the bioremediation of heavy metals and maize growth under municipal wastewater irrigation. Int J Phytoremediation 18:211–221. https://doi.org/10.1080/15226514.2015.1064352

Kharissova OV, Dias Rasika HV, Kharisov BI, Pérez BO, Pérez Jiménez VM (2013) The greener synthesis of nanoparticles. Trends Biotechnol 31:240–248

Khodakovskaya MV, Kim BS, Kim JN, Alimohammadi M, Dervishi E, Mustafa T et al (2013) Carbon nanotubes as plant growth regulators: effects on 818 B. SONG ET AL. tomato growth, reproductive system, and soil microbial community. Small 9(1):115–123. https://doi.org/10.1002/smll.201201225

Kica E, Wessel RA (2017) Transactional arrangements in the governance of emerging technologies: the case of nanotechnology. In: Bowman DM, Stokes E, Rip A (eds) Embedding new technologies into society: a regulatory, ethical and societal perspective, 1st edn. CRC Press, Boca Raton, pp 219–257

Kim YM, Murugesan K, Chang YY, Kim EJ, Chang YS (2012) Degradation of polybrominateddiphenyl ethers by a sequential treatment with nanoscale zero valentiron and aerobic biodegradation. J Chem Technol Biotechnol 240:525–532. https://doi.org/10.1002/jctb.2699

Kim JH, LeeY KEJ, Gu S, Sohn EJ, Seo YS et al (2014) Exposure of iron nanoparticles to Arabidopsis thaliana enhances root elongation by triggering cell wall loosening. Environ Sci Technol 48:3477–3485. https://doi.org/10.1021/es4043462

Köber R, Hollert H, Hornbruch G, Jekel M, Kamptner A, Klaas N et al (2014) Nanoscale zero-valent iron flakes for groundwater treatment. Environ Earth Sci 72:3339. https://doi.org/10.1007/s12665-014-3239-0

Kumar SR, Gopinath P (2009) Nano-bioremediation: applications of nanotechnology for bioremediation. In: Wang KL, Wang SM-H, Hung Y-T, Shammas NK, Chen JP (eds) Handbook of advanced industrial and hazardous wastes management, vol 1, 1st edn. CRC Press, Boca Raton, pp 27–48

Kumari B, Singh DP (2016) A review on multifaceted application of nanoparticles in the field of bioremediation of petroleum hydrocarbons. Ecol Eng 97:98–105. https://doi.org/10.1016/j.ecoleng.2016.08.006

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

Liang Q, Zhao D (2014) Immobilization of arsenate in a sandy loam soil using starchstabilized magnetite nanoparticles. J Hazard Mater 271:16–23. https://doi.org/10.1016/j.jhazmat.2014.01.055

Liang J, Yang Z, Tang L, Zeng G, Yu M, Li X et al (2017a) Changes in heavy metal mobility and availability from contaminated wetland soil remediated with combined biochar-compost. Chemosphere 181:281–288. https://doi.org/10.1016/j.chemosphere.2017.04.081

Liang S, Jin Y, Liu W, Li X, Shen S, Ding L (2017b) Feasibility of Pb phytoextraction using nano-materials assisted ryegrass: results of a one-year field-scale experiment. J Environ Manag 190:170–175. https://doi.org/10.1016/j.jenvman.2016.12.064

Liu J, Zhou Q, Wang S (2010) Evaluation of chemical enhancement on phytoremediation effect of Cd-contaminated soils with Calendula officinalis L. Int J Phytoremediation 12:503–515. https://doi.org/10.1080/15226510903353112

Ma X, Wang C (2010) Fullerene nanoparticles affect the fate and uptake of trichloroethylene in phytoremediation systems. Environ Eng Sci 27:989–992. https://doi.org/10.1089/ees.2010.0141

Mahadik S (2017) Applications of nanotechnology in water and waste water treatment. J Manag Technol 7:187–191

Martínez-Fernández D, Vítková M, Míchálková Z, Komárek M (2017) Engineered nanomaterials for phytoremediation of metal/metalloid-contaminated soils: implications for plant physiology. In: Asari A, Gill S, Gill R, Lanza G, Newman L (eds) Phytoremediation. Springer, Cham, pp 369–403. https://doi.org/10.1007/978-3-319-52381-1_14

Movafeghi A, Khataee A, Abedi M, Tarrahi R, Dadpour M, Vafaei F (2018) Effects of TiO2 nanoparticles on the aquatic plant Spirodela polyrrhiza: evaluation of growth parameters, pigment contents and antioxidant enzyme activities. J Environ Sci 64:130–138. https://doi.org/10.1016/j.jes.2016.12.020

Mueller NC, Nowack B (2010) Nanoparticles for remediation: solving big problems with little particles. Elements 6:395–400. https://doi.org/10.2113/gselements.6.6.395

Nair PMG, Chung IM (2015) Study on the correlation between copper oxide nanoparticles induced growth suppression and enhanced lignification in Indian mustard (Brassica juncea L.). Ecotoxicol Environ Saf 113:302–313. https://doi.org/10.1016/j.ecoenv.2014.12.013

Nwadinigwe AO, Ugwu EC (2018) Overview of Nano-phytoremediation applications. In: Ansari A, Gill S, Gill R, Lanza G, Newman L (eds) Phytoremediation. Springer, Cham. https://doi.org/10.1007/978-3-319-99651-6_15

Nzila A, Razzak SA, Zhu J (2016) Bioaugmentation: an emerging strategy of industrial wastewater treatment for reuse and discharge. Int J Environ Res Public Health 13:846. https://doi.org/10.3390/ijerph13090846

Pandey G (2018a) Challenges and future prospects of agri-nanotechnology for sustainable agriculture in India. Environ Technol Innov 11:299–307. https://doi.org/10.1016/j.eti.2018.06.012

Pandey G (2018b) Nanotechnology for achieving green-economy through sustainable energy. Rasayan J Chem 11(3):942–950. https://doi.org/10.31788/RJC.2018.1133031

Pandey G (2018c) Prospects of nanobioremediation in environmental cleanup. Orient J Chem 34(6):2838. https://doi.org/10.13005/ojc/340622

Pandey G (2019) Biomass based bio-electro fuel cells based on carbon electrodes: an alternative source of renewable energy. SN Appl Sci 1:408. https://doi.org/10.1007/s42452-019-0409-4

Pandey G (2020) Agri-nanotechnology for sustainable agriculture. In: Bauddh K, Kumar S, Singh R, Korstad J (eds) Ecological and practical applications for sustainable agriculture. Springer, Singapore. https://doi.org/10.1007/978-981-15-3372-3_11

Pandey G, Jain P (2020) Assessing the nanotechnology on the grounds of costs, benefits, and risks. Beni-Suef Univ J Basic Appl Sci 9:63. https://doi.org/10.1186/s43088-020-00085-5

Pandey G, Bajpai S, Tripathi S (2021) Prospects of nanotechnology as a tool to mitigate COVID-19. Rasayan J Chem 14(02):1297–1306

Pillai HP, Kottekottil J (2016) Nano-phytotechnological remediation of endosulfan using zero valent iron nanoparticles. J Environ Prot 7:734–744. https://doi.org/10.4236/jep.2016.75066

Poorva M, Arushi J, Sudha S, Nidhi G (2013) Environmental pollution and nanotechnology. Environ Pollut 2(2):49–58. https://doi.org/10.5539/ep.v2n2p49

Rafique M, Tahir MB, Sadaf I (2019) Nanotechnology: an innovative way for wastewater treatment and purification. In: Advanced research in nanosciences for water technology. Springer, Cham, pp 95–131. https://doi.org/10.1007/978-3-030-02381-2_5

Ramírez-García R, Gohil N, Singh V (2019) Recent advances, challenges, and opportunities in bioremediation of hazardous materials. In: Chandra PV, Bauddh K (eds) Phytomanagement of polluted sites, vol 1, 1st edn. Elsevier, Cambridge, MA, pp 517–568

Rizwan MD, Singh M, Mitra CK, Morve RK (2014) Ecofriendly application of nanomaterials: Nanobioremediation. J Nanopart 1:1–7. https://doi.org/10.1155/2014/431787

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. https://doi.org/10.1016/j.envint.2014.11.010

Savage N, Diallo MS (2015) Nanomaterials and water purification: opportunities and challenges. J Nanopart Res 7:331–342. https://doi.org/10.1007/s11051-005-7523-5

Shipley HJ, Engates KE, Guttner AM (2010) 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

Simeonidis K, Mourdikoudis S, Kaprara E, Mitrakas M, Polavarapu L (2016) Inorganic engineered nanoparticles in drinking water treatment: a critical review. Environ Sci Water Res Technol 2:43–70. https://doi.org/10.1039/C5EW00152H

Singh J, Lee BK (2016) Influence of nano-TiO2 particles on the bioaccumulation of Cd in soybean plants (Glycine max): a possible mechanism for the removal of Cd fromthe contaminated soil. J Environ Manag 170:88–96. https://doi.org/10.1016/j.jenvman.2016.01.015

Song Y, Hou D, Zhang J, O'Connor D, Li G, Gu Q et al (2018) Environmental and socio-economic sustainability appraisal of contaminated land remediation strategies: a case study at a mega-site in China. Sci Total Environ 610:391–401. https://doi.org/10.1016/j.scitotenv.2017.08.016

Song B, Xu P, Chen M, Tang WW, Zeng G, Gong J et al (2019) Using nanomaterials to facilitate the phytoremediation of contaminated soil. Crit Rev Environ Sci Technol 49(9):791–824. https://doi.org/10.1080/10643389.2018.1558891

Souri Z, Karimi N, Sarmadi M, Rostami E (2017) Salicylic acid nanoparticles (SANPs) improve growth and phytoremediation efficiency of Isatis cappadocica Desv., under as stress. IET Nanobiotechnol 11:650–655. https://doi.org/10.1049/iet-nbt.2016.0202

Sozer N, Kokini JL (2009) Nanotechnology and its applications in the food sector. Trends Biotechnol 27(2):82–89. https://doi.org/10.1016/j.tibtech.2008.10.010

Srivastav A, Yadav KK, Yadav S, Gupta N, Singh JK, Katiyar R, Kumar V (2018) Nano-phytoremediation of pollutants from contaminated soil environment: current scenario and future prospects. In: Ansari A, Gill S, Gill R, Lanza G, Newman L (eds) Phytoremediation. Springer, Cham. https://doi.org/10.1007/978-3-319-99651-6_16

Sun RJ, Chen JH, Fan TT, Zhou DM, Wang YJ (2018) Effect of nanoparticle hydroxyapatite on the immobilization of Cu and Zn in polluted soil. Environ Sci Pollut Res 25(1):73–80. https://doi.org/10.1007/s11356-016-8063-5

Thijs S, Sillen W, Rineau F, Weyens N, Vangronsveld J (2016) Towards an enhanced understanding of plant–microbiome interactions to improve phytoremediation: engineering the metaorganism. Front Microbiol 7:1–15. https://doi.org/10.3389/fmicb.2016.00341

Tripathi DK, Singh VP, Prasad SM, Chauhan DK, Dubey NK (2015) Silicon nanoparticles (SiNp) alleviate chromium (VI) phytotoxicity in Pisumsativum (L.) seedlings. Plant Physiol Biochem 96:189–198. https://doi.org/10.1016/j.plaphy.2015.07.026

VázquezNúñez E, de la Rosa-Álvarez G (2018) Environmental behavior of engineered nanomaterials in terrestrial ecosystems: uptake, transformation and trophic transfer. Curr Opin Environ Sci Health 6:42–46. https://doi.org/10.1016/j.coesh.2018.07.011

Vázquez-Núñez E, Molina-Guerrero CE, Peña-Castro JM, Fernández-Luqueño F, de la Rosa-Álvarez MG (2020) Use of nanotechnology for the bioremediation of contaminants: a review. PRO 8:826. https://doi.org/10.3390/pr8070826

Venkatachalam P, Priyanka N, Manikandan K, Ganeshbabu I, Indiraarulselvi P, Geetha N et al (2017) Enhanced plant growth promoting role of phycomolecules coated zinc oxide nanoparticles with P supplementation in cotton (Gossypium hirsutum L.). Plant Physiol Biochem 110:118–127. https://doi.org/10.1016/j.plaphy.2016.09.004

Verma JP, Jaiswal DK (2016) Book review: advances in biodegradation and bioremediation of industrial waste. Front Microbiol 6:1–2. https://doi.org/10.3389/fmicb.2015.01555

Vıtkova M, Puschenreiter M, Komarek M (2018) Effect of nano zero-valent iron application on As, Cd, Pb, and Zn availability in the rhizosphere of metal(loid) contaminated soils. Chemosphere 200:217–226

Wan J, Zeng G, Huang D, Hu L, Xu P, Huang C et al (2018) Rhamnolipid stabilized nano-chlorapatite: synthesis and enhancement effect on Pb-and Cd-immobilization in polluted sediment. J Hazard Mater 343:332–339. https://doi.org/10.1016/j.jhazmat.2017.09.053

Wang H, Jia Y, Wang S, Zhu H, Wu X (2009) Bioavailability of cadmium adsorbed on various oxides minerals to wetland plant species Phragmites australis. J Hazard Mater 167(1–3):641–646. https://doi.org/10.1016/j.jhazmat.2009.01.012

Wang J, Feng X, Anderson CWN, Xing Y, Shang L (2012) Remediation of mercury contaminated sites. J Hazard Mater 221:1–18. https://doi.org/10.1016/j.jhazmat.2012.04.035

Wang C, Liu H, Chen J, Tian Y, Shi J, Li D et al (2014a) Carboxylated multi walled carbon nanotubes aggravated biochemical and subcellular damages in leaves of broad bean (Viciafaba L.) seedlings under combined stress of lead and cadmium. J Hazard Mater 274:404–412. https://doi.org/10.1016/j.jhazmat.2014.04.036

Wang Y, Fang Z, Kang Y, Tsang EP (2014b) Immobilization and phytotoxicity of chromium in contaminated soil remediated by CMC-stabilized nZVI. J Hazard Mater 275:230–237

Wang P, Lombi E, Zhao F-J, Kopittke PM (2016a) Nanotechnology: a new opportunity in plant sciences. Trends Plant Sci 21:699–712

Wang X, Liu Y, Zhang H, Shen X, Cai F, Zhang M et al (2016b) The impact of carbon nanotubes on bioaccumulation and translocation of phenanthrene, 3-CH3-phenanthrene and 9-NO2-phenanthrene in maize (Zea mays) seedlings. Environ Sci Nano 3:818–829. https://doi.org/10.1039/C6EN00012F

Wang X, Zhang D, Pan X, Lee DJ, Al-Misned FA, Mortuza MG, Gadd GM (2017) Aerobic and anaerobic biosynthesis of nano-selenium for remediation of mercury contaminated soil. Chemosphere 170:266–273. https://doi.org/10.1016/j.chemosphere.2016.12.020

Watlington K (2015) Emerging nanotechnologies for site remediation and wastewater treatment. United States Environmental Protection Agency, Washington, DC, p 47. www.epa.gov

Xie Y, Fang Z, Cheng W, Tsang PE, Zhao D (2014) Remediation of polybrominated diphenyl ethers in soil using Ni/Fe bimetallic nanoparticles: influencing factors, kinetics and mechanism. Sci Total Environ 485–486:363–370. https://doi.org/10.1016/j.scitotenv.2014.03.039

Xie W, Liang Q, Qian T, Zhao D (2015) Immobilization of selenite in soil and groundwater using stabilized Fe–Mn binary oxide nanoparticles. Water Res 70:485–494. https://doi.org/10.1016/j.watres.2014.12.028

Xu Y, Yan X, Fan L, Fang Z (2016) Remediation of Cd(II)-contaminated soil by three kinds of ferrous phosphate nanoparticles. RSC Adv 6:17390–17395. https://doi.org/10.1039/C5RA23299F

Xue W, Huang D, Zeng G, Wan J, Zhang C, Xu R et al (2018) Nanoscale zero-valent iron coated with rhamnolipid as an effective stabilizer for immobilization of Cd and Pb in river sediments. J Hazard Mater 341:381–389. https://doi.org/10.1016/j.jhazmat.2017.06.028

Yadav KK, Gupta N, Kumar V, Singh JK (2017a) Bioremediation of heavy metals from contaminated sites using potential species: a review. Ind J Environ Prot 37(1):65–84

Yadav KK, Singh JK, Gupta N, Kumar V (2017b) A review of nanobioremediation technologies for environmental cleanup: a novel biological approach. J Mater Environ Sci 8(2):740–757

Yanık F, Vardar F (2015) Toxic effects of aluminum oxide (Al2O3) nanoparticles on root growth and development in Triticum aestivum. Water Air Soil Pollut 226:296

Yavari S, Malakahmad A, Sapari NB (2015) A review on phytoremediation of crude oil spills. Water Air Soil Pollut 226:1–18. https://doi.org/10.1007/s11270-015-2550-z

Yogalakshmi KN, Das A, Rani G, Jaswal V, Randhawa JS (2020) Nano-bioremediation: a new age technology for the treatment of dyes in textile effluents. In: Bioremediation of industrial waste for environmental safety. Springer, Singapore

Zhang W (2003) Nanoscale iron particles for environmental remediation: an overview. J Nanopart Res 5:323–332. https://doi.org/10.1023/A:1025520116015

Zhang M, Gao B, Chen J, Li Y (2015) Effects of graphene on seed germination and seedling growth. J Nanopart Res 17:78

Zhang J, Gong JL, Zeng GM, Yang HC, Zhang P (2017) Carbon nanotube amendment for treating dichlorodiphenyltrichloroethane and hexachlorocyclohexane remaining in Dong-ting Lake sediment: an implication for in-situ remediation. Sci Total Environ 579:283–291. https://doi.org/10.1016/j.scitotenv.2016.11.105

Zhu F, Li L, Ma S, Shang Z (2016) Effect factors, kinetics and thermodynamics of remediation in the chromium contaminated soils by nanoscale zero valent Fe/Cu bimetallic particles. Chem Eng J 302:663–669. https://doi.org/10.1016/j.cej.2016.05.072

Chapter 18
Nanotechnology in Management of Environmental Contaminants

Ammara Saeed, Haram Javed, Hussein Alserae, Rida Nawaz, Zia Ur Rahman Farooqi, Sobia Riaz, and Humaira Nawaz

Abstract Nanotechnology has emerged as a critical and important area in the scientific world in recent decades because of its interdisciplinary nature. Environmental remediation has traditionally relied on a variety of methods (such as adsorption, absorption, chemical reactions, photocatalysis, and filtration) to remove pollutants from various parts of the environment. However, the traditional techniques of nanoparticle manufacturing, such as physical and chemical processes, are harmful to the environment. To address this issue, scientists have shifted their attention to eco-friendly techniques for environmental remediation. These techniques are devoid of hazardous precursors and difficult process conditions, making them cost-effective approaches. Nanomaterials, such as nanoparticles (NPs), have improved characteristics that make them a feasible choice for a variety of applications in many areas. Nanoparticles have a wide variety of uses in environmental biotechnology, including pollution reduction, water treatment, remediation, dye degradation, and the development of water purification. In this chapter, the authors have tried to give an overview of nanotechnology, its types, uses, and advantages in the remediation of environmental pollutants.

Keywords Nanotechnology · Environmentally friendly · Pollutants remediation · Heavy metals · Organic and in-organics

---

A. Saeed · H. Javed · R. Nawaz · Z. U. R. Farooqi (✉) · S. Riaz
Institute of Soil and Environmental Sciences, University of Agriculture Faisalabad,
Faisalabad, Pakistan

H. Alserae
Institute of Soil and Environmental Sciences, University of Agriculture Faisalabad,
Faisalabad, Pakistan

Department of Soil Sciences and Water Resourses, College of Agricultural Engineering
Science, Baghdad University, Baghdad, Iraq

H. Nawaz
College of Earth and Environmental Sciences, Quaid-e-Azam Campus,
University of the Punjab, Punjab Lahore, Pakistan

L. Newman et al. (eds.), *Phytoremediation*, https://doi.org/10.1007/978-3-031-17988-4_18

18.1 Introduction

Nanotechnology is a multidisciplinary field that brings together chemistry, physics, biology, material science, healthcare, pharmacy, and engineering. Environmental cleanup, medication delivery, electronics, biotechnology, catalysis, cosmetics, aviation industry, cancer therapy and anticancer drug delivery, and materials science are all uses of nanotechnology and nanomaterials (Thangadurai et al. 2020). Nanotechnology is the capacity to examine and comprehend microscopic particles with a significant surface area (average size of 1100 nm) (Oke et al. 2017). The ultra-small size, form (sheets, rods, tubes, and wires), and size distribution of these particles have attracted interest owing to their unusual morphological and physicochemical features (Tyagi et al. 2018). They also possess magnetic, optical, thermal, and mechanical properties. Nanoparticles (NPs) are generally classified as the type of material from which these are synthesized, i.e., carbon, metals, ceramic, polymers, lipids, etc. Metals and carbon-based NPs are commonly used in environmental remediation. Environmental contaminants such as heavy metals, nutrient pollutants, and organics like pesticides and other related contaminants are effectively remediated through these NPs in an eco-friendly way (Torrens and Castellano 2019; Sohail et al. 2021; Farooqi et al. 2021). Because of its biological toxicity and nondegradability, heavy metal contamination in water has become a major worldwide issue for human health and the environment. Chemical precipitation, adsorption, photocatalysis, and membrane filtration are among the main methods suggested for removing heavy metals from wastewater. Among them, adsorption as an economically viable technique for heavy metal wastewater treatment has gotten a lot of attention. Carbon materials, chitosan, clays, zeolites, and silica were created for the absorption of heavy metal ions, among other natural and man-made materials (Shao et al. 2020). This chapter highlights the significance of nanotechnology in the management of environmental contaminants.

18.2 Environmental Contamination

Chemicals that enter the environment by mistake or on purpose, typically but not usually as a consequence of human activity, are known as environmental pollutants. Many substances in the environment are very persistent in nature and may cause serious health hazards to animals, plants, and human health. These substances are found above permissible limits of their concentrations hence called environmental pollutants. Rapid industrialization and the unjudicial use of agrochemicals are the major causes of environmental contamination. These pollutants are either organic (pesticides, polycyclic aromatic hydrocarbons (PAHs) (Ilic et al. 2021a, b, c), polychlorinated biphenyls (PCBs) (Ilic et al. 2020), organic solvents, and pharmaceutical dyes and other pharmaceuticals) and inorganic nature (heavy metals and metalloids). Such contaminants may be solid, liquid, or gaseous contaminants that are a result of intensive short-term benefitted human economic activities by compromising over long-term environmental gains of mankind. The contaminants could be both natural and anthropogenic in nature. Natural sources include weathering of the earth's crust, volcanoes, storms, cyclones, floods, forest fires, rising sea levels, and warmer oceans. Anthropogenic sources include industrial effluents, transportation, manufacturing, electricity generation, microplastics, food and beverages, and heavy metals released from point and non-point sources. Major sources of environmental contaminants are industrial emissions, effluents, other industrial accidents, oil spilling, polychlorinated hydrocarbons, heavy metals, organic and inorganic solvents, pesticides, mining, instruments of war, and ammunitions. The unintentional release of such contaminants into the environment may cause an eruption of new diseases in humans as well as mortality on a larger scale. The Environmental Protection Agency reported that approximately 4.7 billion pounds of environmental contaminants were released into the atmosphere in 2002 by 24,379 US facilities. Almost 72 million pounds of environmental contaminants were known as carcinogens. A research study determined that environmental contaminants are causing 23% of death worldwide (Tilley and Fry 2015).

There is three main routes of exposure, gastrointestinal, pulmonary, and dermal. Some factors determined the dose to target the organism. These are absorption of environmental contaminants, distribution to tissues, metabolism, and excretion. The fate of environmental contaminants is when transported in the blood, where they are either free or bound with blood plasma proteins. During distribution majority of these contaminants are present in the kidney and liver, while some contaminants are released in unchanged form. Environmental contaminants' movements and distribution depend mainly on molecular size, solubility, stability, and reactivity. At the same time, organisms are affected by the amount of dose, the route of entry, the timing of exposure, and the sensitivity of organisms. Contaminants are released or excreted by different routes of excretion from the liver in the form of feces, kidneys in the form of urine and lungs, mammary glands, salivary glands, and sweating (Fig. 18.1).

Various remediation techniques are employed for the removal of contaminants from the environment, including physical remediation, chemical remediation, and biological remediation. Nanotechnology has recently emerged as an effective technique that has attracted the interest of environmental scientists for the removal of various toxins from soil because of its low cost, high reactivity, and environmentally friendly properties. Nanoscience allows materials to be manipulated at the atomic and molecular level, and these materials have special capabilities that can identify a specific contaminant in a mixture.

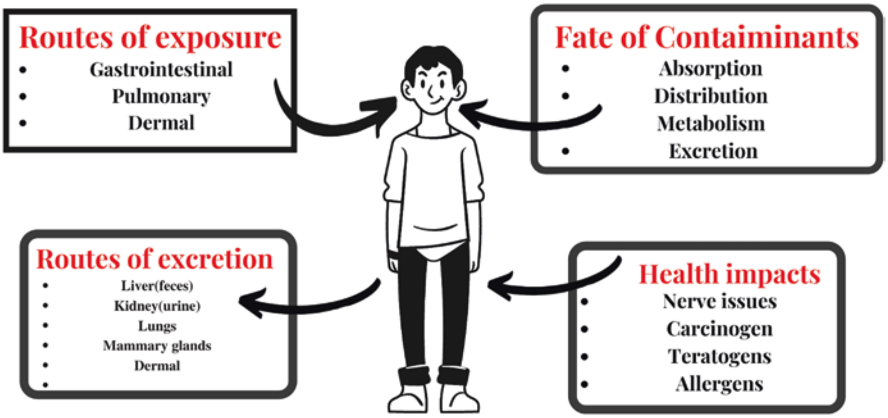


Fig. 18.1 Fate and impacts of environmental contaminants on human health

18.3 Nanotechnology: Origin and Types

Nanotechnology is a recent field of extensive research that is now used in all disciplines of study; it was first depicted by Nobel laureate Richard P. Feynmen in his famous lecture "There is plenty of room at the bottom." He brings revolutionary advancement in the field of science by exploring material things at a very small scale with dimensions of less than 100 nm (Laurent et al. 2008). Nanotechnology comprises nanoparticles and various nanomaterials having unique physical, biochemical, and morphological properties that impart distinguishing features from other microsize materials. On the basis of overall shape, they are classified into 0D, 1D, 2D, and 3D dimensions (Khan et al. 2019). Nanotechnology employs the use of nanomaterial in various industries as well as in different technologies, including wastewater treatment systems (Vaseghi et al. 2018), environmental remediation (Yirsaw et al. 2016), biomedical (Somanathan et al. 2016), and photocatalytic activities. (Ong et al. 2018).

Nanotechnology has the potential to improve the environment through the direct application of nanomaterials to detect, monitor, prevent, and eliminate contaminants. Indirectly, it also involves the production of environment-friendly products formed through better industrial design that are in sync with the environment and are cost-effective. The reactivity of the nanomaterials and nanoparticles is manyfold because of their enhanced surface area and small size. Nanotechnology efficiently lessens the entry of waste material into the environment that generates through anthropogenic activities by changing the way of their consumption (Taran et al. 2021). Nanoparticles have a more effective surface area than larger particles, making them capable of better interacting with the chemical agents to enhance their affinity with the desired molecules. These properties of nanoparticles are used as an effective tool to treat the contaminant water and enhance the absorption of the pollutants (Safaei et al. 2020).

18.4 Classification of NPs/Types of NPs

Nanoparticles are classified into various groups or categories depending upon their sizes, composition, morphological features, effective diameter, and biochemical properties to impart unique characteristics. Nanoparticles possess distinctive properties having high surface area and effective size that are different from bulk material. Following are the broad categories of nanoparticles.

18.4.1 Carbon-Based NPs

In nanotechnology, the most widely studied materials are carbon-based, have low intrinsic toxicity, are more efficient, have the least cost of mass production, have a high surface area, and multifunctional (Panwar et al. 2019). There are various carbon nanoparticles such as carbon nanotubes (single-walled and multiwalled), graphene, carbon quantum dots and fullerene, and nano wires that are also known as quantum wires. Because of their extraordinary unique characteristics of thermal, mechanical, biological, morphological, and physical properties, they are extensively used in all modern technologies. They are easily accessible to the electrolyte by possessing increased contact of surface area and excellent electrical conductivity. They are used in a wide range of applications because of containing pure carbon that is highly stable and environmentally friendly (Yan et al. 2016). They are extensively examined for wastewater treatment and heavy metal scavenging due to more stable distribution of pores, mono-dispersed, enhanced surface area, high reactivity, and more chemical stability under diverse environments. Besides these, carbon nanoparticles have a broad range of environmental applications, such as environmental sensors, sorbents, pollution prevention strategies, depth filters, renewable energy technologies, and antimicrobial agents (Mauter and Elimelech 2008).

18.4.2 Metal-Based NPs

Metal nanoparticles are mainly prepared from precursors of metal. They are also synthesized by photochemical, chemical, and electrochemical methods. These have a wide range of applications in the area of research, detection, environmental remediation, imaging of biomolecules, and bioanalytical applications. Because of their high surface activity, they are capable of absorbing smaller molecules. The most commonly used metal nanoparticles are titanium oxide (TiO_2), nano zerovalent (nZVI), aluminum oxide (Al_2O_3), and silicon dioxide (SiO_2). They are excellent sorbents, highly stable, reusable, and have a high surface area. Some of them are used as individuals or may be used as a component of other nanocomposites. Some metal nanoparticles are magnetic such as iron oxide, and they are widely known because of their exceptional properties such as low cost, easy separation, high reactivity, reusability, high relative abundance, and environment friendly (Das et al. 2017).

18.4.3 Semiconductor NPs

The semiconductor NPs possess the properties between metals and nonmetals. They are important nanostructured materials having unique physical, mechanical, optical, chemical, and electronic properties. They play a vital role in photocatalysis, electronic devices, and optics (Krishnan and Alivisatos 1999). At the same time, the photocatalytic property of semiconductors is widely used for degrading organic pollutants. They are used in a wide range of diversified fields such as agriculture, electronics, food processing, health, environmental catalysis, and sustainable energy (Nayak et al. 2017).

18.4.4 Ceramic Nanoparticles

Ceramic nanoparticles are nonmetallic, solid particles comprised of carbonates, oxides, phosphates, and carbides. They are synthesized through successive heating and cooling. Because of their high resistance to heat and chemical inertness, they are used in photodegradation, drug delivery, photocatalysis, and imaging applications. Because of the intensive attention of the researchers, they are found in polycrystalline, hollow, amorphous, and dense forms (Thomas et al. 2015). Besides these, they are also employed in transportation, supply and storage of energy, communication, and biomedical field. Ceramic nanoparticles combined with other inorganic ions, such as iron and silica, vary in size, shape, properties, and porosity. As they are inorganic, they are more stable over a wide range of temperatures and pH (Kumar et al. 2014a, b).

18.4.5 Polymeric nanoparticles

Polymeric nanoparticles are nano-capsular and nano-spheric structured and organic in nature (Mansha et al. 2017). They are soft, biodegradable, environment-friendly, and biocompatible materials. Through chemical transformation, they have the potential for surface modification. Polymeric nano-adsorbents are also found. Dendrites are the synthetic molecules of polymeric nanoparticles. They have a multivalent surface, and that is why they are used as excellent adsorbents for pollutants of wastewater, both organic and inorganic (Chen et al. 2011).

18.4.6 Lipid-Based Nanoparticles

The synthesis of lipid-containing nanoparticles is a special field of nanotechnology, and it has been effectively used in the biomedical discipline. They have a wide range of medical applications such as carrier and delivery of drugs, while in cancer therapy, they are used as RNA releasers. They are also used in various industries, including pharmaceuticals and cosmetics, because of their potential to break inside the cells (Gujrati et al. 2014).

18.4.7 Nanomaterials

According to international standardization, material that are manufactured, agglomerated having internal surface structure of nanoscale, whereas their external surface confined to the range of 1and 100 nm, are called as nanomaterial (Khan 2020). These chemical materials are used and manufactured at a very small scale to exhibit peculiar features such as enhanced surface activity, immense chemical reactivity, and high strength compared to the same material that is not developed on the nanoscale. Various forms of nanomaterial are manufactured to impart novel characteristics such as nanofibers, carbon-nanotubes, nanowires, quantum dots, and nanosorbents.

The effective and high surface area of the nanomaterial is due to their reduced size and smaller radius of curvature that increased their reactivity many folds than ordinary material; these characteristics are used to scavenge and deteriorate the pollutants of the air and water (Sánchez et al. 2011). A wide range of nanomaterials varies in their forms, shapes, morphological composition, and chemical properties to improve the quality of water, air, and water in the environment (Diallo and Savage 2005).

Globally, pollution is increasing rapidly due to industrialization, an alarming rate of urbanization, and changing habits of people that jeopardize the environment. Under these emerging conditions, providing clean air, water, and environment is a major challenge nowadays. The unique fabrication, functionalities, features due to high surface-to-volume ratio of nanotechnology provide the immense opportunity to treat the waste pollutant and remediate the environment. Nanomaterials are extensively used in the treatment of wastewater, soil sediments, natural and industrial wastewater, as well as domestic polluted water and polluted atmosphere. Table 18.1 describes the classification of the nanomaterials and their uses.

Table 18.1 Important uses of various nanomaterials

Nanomaterials	Uses	References
Carbon nanotubes	Water purification system Removal of natural organic contaminants Desalinization process Chemical sensors Environmental remediation Sorbent of pollutants	Negi et al. (2021), Saeed and Khan (2016), Nasrollahzadeh et al. (2019b)
Nanofibers	Sensors to access the harmful biological and chemical agents Removal of pollutants and heavy metals by filtration Filtration: automatic oil filters, ultra-low particulate air filters, heat ventilators, and air filtration Medical application: drug delivery, tissue engineering, implantation of material, component of artificial organ, wound dressing Textile: rainwear, sports shoes, apparel Energy: membrane fuel cells, batteries, polymer electrolytes	Li and Xia (2004)
Nanowires	Electrical appliances Transistors Junction diodes Fabrication of logic gates Electrochemical sensor	Stortini et al. (2015)
Nanosorbents	Purification of water Removal of hazardous metals Disinfection of mining industries Decontamination of wastewater Removal of organic and inorganic pollutants	Bora and Dutta (2014)
Dendrimers	Environmental remediation Ideal absorbent of organic, inorganic pollutants, and heavy metals	Chen et al. (2011)
Fullerene	Photocatalytic reactors Solar disinfector system	Qu et al. (2013a, b)
Quantum dots	Optical detection Sensing and monitoring Electrocatalysis Bioimaging	Nasrollahzadeh et al. (2019a), Vaseghi and Nematollahzadeh (2020)

(continued)

Table 18.1 (continued)

Nanomaterials	Uses	References
Nanometals	Electrical appliance Photocatalyst Antimicrobial process Coating of nanocomposites Waste disinfection systems	Sohail et al. (2021)
Nanometal oxide	Disinfection of water Antimicrobial agent Biomedical applications Absorptive filter media Transformation of the contaminant in air and water (both organic and inorganic) Photocatalysis to decompose organic pollutants Removal of malodorous chemicals and airborne microbes	Qu et al. (2013a, b)
Nanocomposite membranes	Extensively used in the filtration process, water purification, reverse osmosis, ultrafiltration, discriminating process of pollutants, forward osmosis	Homaeigohar and Elbahri (2014)

18.5 Remediation of Major Environmental Contaminants Via Nanotechnology

Remediation is described as the process which is meant for removing, minimizing, or neutralizing contaminated water. Traditional soil and water remediation methods are not proven efficient enough, so nanotechnology is an emerging, multifunctional, highly efficient technology being exploited in the current era because of its high performance and cost-effectiveness (Qu et al. 2013a, b). Various forms of nanomaterials have been developed, which include nanotubes, nanoparticles, nanowires, and quantum dots.

18.5.1 Heavy Metals

One of the main environmental problems is the pollution of soil and water by various heavy metals released from urban and industrial waste. Heavy metals are generally described as elements that have a high density of more than 4–5 g/cm^3 and are considered harmful to human health even at very low concentrations and are chromium, mercury, iron, lead, arsenic, copper, cobalt, zinc, aluminum, and cadmium. The term metal (loid)s refers to a chemical element that has certain properties of metals and certain properties of nonmetals. Heavy metals are released into the soil through natural and human activities. They are naturally found in the soil through weathering the underlying bedrock during the soil-forming processes. Heavy metals exist in rocks in various chemical forms. As ores, these metals can be extracted as minerals (Fuge et al. 1991). The man-made sources of soil heavy metal pollution include ore refining and mining, paper industry, fertilizer industry, pesticides, batteries, tannery, solid waste treatment including sewage sludge, sewage irrigation, and automobile exhaust. The physicochemical properties also play a key role in the accumulation of heavy metals in the soil environment. Soil is the direct route through which vegetables and cultivated plants are contaminated via heavy metals (loids) by absorption through roots (Pierart et al. 2015). Since the activity of heavy metals in the soil is determined by the adsorption–desorption reaction with other soil components, a large number of additives are used to control the bioavailability of heavy metals and their diffusion in the soil to induce various adsorption processes. In recent years, NPs have attracted great interest in fixing, stabilizing, and adsorbing heavy metals in soil and groundwater. A colloidal solution or aqueous slurry of nanoparticles may be injected or sprayed into polluted soil using pressure or gravity. When nanoparticles are injected into the soil, they establish a treatment zone and stay floating in the air (Noubactep et al. 2012).

Water is being contaminated by heavy metals through various pathways such as agricultural runoff, mining, wastewater from industries, and domestic uses. Heavy metals such as lead, zinc, copper, mercury, etc. could cause life-threatening conditions because of their accumulation in the food chain. Various natural and anthropogenic sources are responsible for the entry of heavy metals into the aquatic environment. Natural sources include soil weathering and volcanic eruptions, while anthropogenic sources include effluents from industrial areas and mining. Heavy metal contamination in water is classified into two groups point and nonpoint sources**.** A point source is due to pollution from a single source that can be identified, but nonpoint sources are due to intermingled sources that cannot be identified. Heavy metals adversely affect the life of aquatic animals as heavy metals are being absorbed into the body tissues of fish which is, in return, consumed by humans as the source of protein and omega-3 so, through various direct and indirect ways they are heavy metals are affecting aquatic life and causing the increase in mortality rate among them (Olojo et al. 2005). Adsorption is considered a promising approach for the remediation of heavy metals in contaminated water because of its high efficiency and low operational cost. Adsorption is defined as the surface phenomenon in which any substance from a liquid solution is adsorbed onto the solid surface through various physiochemical bonds. It consists of three steps: first, the contaminant is transferred to the solid adsorbent surface; second, it is adsorbed; and lastly, it is transported within the solid surface.

Over past decades, nanotechnology has been exploited for remediation of heavy metals in the water environment, which includes the use of nanotubes, NPs, nanowires, and nanomembranes. The materials used to remediate contaminated soil can be broadly divided into two categories: absorbent materials and reactive materials according to different remediation mechanisms. Adsorptive materials remove impurities by adsorption on the surface and internal structure. Chemical changes such as acid-base, ion exchange, redox, precipitation/dissolution, and photocatalytic processes are examples of reactive substances. Adsorption is one of the most promising and effective technologies for removing heavy metals from soil. There are several nanomaterials that can be used to remove metal contaminants, such as zerovalent iron nanoparticles, iron sulfide nanoparticles, iron phosphate nanoparticles, iron oxide nanoparticles, allophones, and carbon black (Rabbani et al. 2016).

Environmental remediation technologies based on iron are rapidly being developed and tested in the lab and on-site. Iron has many advantages, including being the most plentiful element on the planet, being nontoxic and ecologically benign, and being able to be utilized in polluted soil. Zerovalent iron nanoparticles (ZVI) are extremely small, allowing them to penetrate into contaminated areas; they also have a large surface area, allowing for close contact with pollutants and improving purification efficiency. They have higher reactivity than their mass counterparts. They have very good adsorption and reduction properties, enabling them to react with heavy metals. Because ZVI nanoparticles have a significant propensity to agglomerate, their applications are limited. Various modifications have been made to the ZVI nanoparticles to overcome their aggregation tendency and improve their mobility and ability to be introduced into the soil. In general, modified nanoparticles offer some additional benefits in terms of removing contaminants when compared to bare nanoparticles.

Heavy metals such as mercury (Hg) have been immobilized, and the dispersion of nanoparticles in soil and groundwater has been improved using iron sulfide (FeS) nanoparticles stabilized with carboxymethyl cellulose (CMC). Mercury may be coupled with CMC-FeS nanoparticles by three different reaction mechanisms throughout the remediation process: adsorption, structural bonding, and precipitation, and then fixed in the soil and sediments. CMC-FeS nanoparticles have been shown to be viable options for mercury fixing in soil and sediments.

Heavy metals are also removed from polluted soil with the help of iron oxide nanoparticles. For heavy metals, iron oxide (FeO) has a high adsorption capability. Zr-FeO is chemically more stable than FeO, has a higher binding affinity, and has a high adsorption capacity across a broad pH range. On a laboratory scale, Almaroai et al. (2014) used iron-rich nanomaterials such as iron oxide (FeO) and zirconia iron (Zr-FeO) to repair arsenic and lead polluted agricultural soils. The increasing number of iron oxide nanoparticles in this method boosted the adsorption rate of heavy metals in the soil. These findings suggest that iron-rich nanomaterials can effectively repair arsenic and lead in soil.

Allophane is a copper adsorbent that is made up of nanoscale hydrous aluminosilicate. On a laboratory scale, Yuan (2004) showed the adsorption and removal of copper from soil using the natural nanomaterial allophane. Copper adsorption on the allophane happens due to the cation exchange process and the particular complexation between the copper ion and the $(OH)Al(OH_2)$ group. Allophane may be used to remediate copper in polluted soil since it is an ecologically favorable substance. Silica nanoparticles have outstanding surface characteristics for heavy metal cleanup in damaged aquatic environments (Mahmoud et al. 2016).

Because it has a high affinity for heavy metals, surface-modified carbon black is employed to remove them through adsorption. On a laboratory scale, Cheng et al. (2014) used surface-modified nanosize carbon black to repair soil polluted with copper and zinc. Adsorption and complexation have been hypothesized as strategies for removing certain metals. Carbon black was oxidized with HNO_3 to introduce functional groups that improve surface cation exchange and carbon black complexing. As a result, it was discovered that modified carbon black might efficiently repair copper and zinc-contaminated soil.

18.5.2 Organic Pollutants

Organic pollutants such as pesticides, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), organic solvents, and pharmaceuticals enter the soil through the use of organic waste, improper disposal, the release of harmful chemicals, and accidental spillage. Many organic pollutants are toxic, lipophilic, hydrophobic, and/or difficult to biodegrade in the soil. Organic pollutants in the soil can harm the environment and human health. They can be absorbed by edible plants and accumulate through the food chain, thereby causing risk to human health. Nanotechnology has shown great potential in environmental cleanup and reduction of organic pollution. It is worth noting that recently manufactured nanoparticles are being studied as new and effective tools for removing organic pollutants from water and sediments (Crane and Scott 2012).

Surface-modified carbon black is used to remove heavy metals by adsorption since it has a high affinity for them. Surface-modified nanosize carbon black are used to repair copper and zinc-polluted soil in the lab. Adsorption and complexation have been proposed as removal techniques for specific metals. HNO_3 was used to oxidize carbon black, resulting in functional groups that increase surface cation exchange and carbon black complexing. As a consequence, it was revealed that modified carbon black might effectively heal soil that has been polluted with copper and zinc.

A number of studies have confirmed that nZVI can significantly degrade PCBs and PAHs. These pollutants are resistant to the environment, have strong carcinogenicity, and are soluble in fat. nZVI particles are also used to decompose organic solvents, such as trichloroethylene (TCE), which has contaminated large areas of soil in the United States and other industrialized countries in the past three decades. Bimetallic iron nanoparticles represent another type of nano-iron that are usually synthesized by adding freshly prepared nanometals (such as nZVI) to an organic solvent containing another precious metal, which results in a nanometal with a higher reactivity than the metal alone. Nano-titanium dioxide ($nTiO_2$) has attracted great interest due to its semiconductor properties, photocatalytic activity, and environmental friendliness. These particles show high performance in degrading organic pesticides in the soil through a redox reaction, photocatalysis, and thermal destruction under irradiation (Makarova et al. 2000). $nTiO_2$ can also effectively decompose PAHs.

A large number of new nanocarbon materials, such as fullerene, carbon nanotubes (CNT), and graphene, are of great significance for soil remediation due to their high hydrophobicity and large adsorption capacity. As a carrier of pollutants, fullerene (C60) can promote the transportation of hydrophobic organic compounds in the soil. Carbon nanotubes (CNT) are nanoparticles with a diameter of 4–30 nm and a length of 1 μm. They are composed of 2–50 coaxial tubular graphite plates. According to the number of carbon atoms, carbon nanotubes are divided into single-walled (SWCNT) and multiwalled carbon nanotubes (MWCNT). Carbon nanotubes have a high affinity for organic pollutants. Surface functional groups (such as hydroxyl, carbonyl, and carboxyl) generated during the synthesis and purification of carbon nanotubes can enhance the adsorption capacity. The adsorption of organic compounds by carbon nanotubes is determined by noncovalent interactions, such as -π interactions, hydrogen bonds, hydrophobic interactions, and electrostatic interactions (Ren et al. 2011).

Graphene is a new type of carbon nanoparticle with a large specific surface area and two-dimensional structure. Due to the strong π-π attractive force, graphene has high adsorption to organic compounds, thereby improving the transport of hydrophobic organic substances. Graphene functionalized with oxygen-containing groups (i.e., graphene oxide nanoparticles (GONPs) can enhance the adsorption capacity of graphene for organic pollutants.

Despite the benefits of nanocarbon, its potential toxicity to plants and soil microorganisms is the main challenge for its application in soil remediation. Carbon nanoparticles functionalized with tiny hydrophilic groups such as hydroxyl and carboxyl groups, which may enhance the solubility and biocompatibility of carbon nanoparticles, are especially troublesome in terms of biotoxicity. Another issue restricting field testing and implementation is high manufacturing and application expenses.

Other types of NPs, such as silver, gold, and palladium, also show a high ability to purify soil organic pollutants. Palladium nanoparticles have high catalytic reactivity. Unfortunately, their high cost and difficulty in recycling hinder their application in large-scale soil remediation. It has been observed that bimetallic palladium-gold nanoparticles with Au core and Pd shell structures catalyze the degradation of perchloroethylene, trichloroethylene, and other chlorinated substances. The degradation rate of Pd/Au nanoparticles to organic solvents is about 20 times higher than that of pure Pd nanoparticles. Unfortunately, the need for unconventional methods of synthesizing gold nanoparticles prevents their widespread application (Magureanu et al. 2007).

Renewable amphiphilic polymer nanoparticles have a high capacity to bind aromatic molecules. They may be made by utilizing a mechanical stirrer to emulsify polymeric precursor chains in deionized water. Amphiphilic polymer nanoparticles have a hydrophobic interior, which is conducive to the adsorption of organic pollutants and a hydrophilic outer surface, which can improve the transport of particles in the soil. The affinity between nanoparticles and organic pollutants increases with the increased size of the hydrophobic backbone (Kim et al. 2004).

Nanofiltration using nanomembranes is a new technique and is being explored recently and is a promising approach for water remediation. They are considered to have high efficiency in extracting metal ions. Benefits of this technique include environmental protection, simple equipment, energy conservation, high separation efficiency, ease of operation, and no phase change required. But some limitations in their use involve pretreatment, fouling properties, complexity in the process, and low recovery.

18.5.3 Pesticides

Pesticides are organic materials manufactured to control crop-destroying pests and weeds. Many of them are called broad-spectrum pesticides, which are used to destroy a variety of crop-damaging organisms, i.e., pests, weeds, rodents, etc. As they are widely used in the agriculture sector to protect crops against different fungal and bacterial diseases and insect pests, these pesticides can be classified according to the following criteria: (a) source or chemical formula; (b) type of targeted organism or disease. Among all kinds of pesticides, chemical pesticides have a wide range of uses in agriculture. However, in up to 90% of cases, the overuse of pesticides can contaminate the environment and cause more damage compared to its non-application. The most harmful types of pesticides to humans and the environment are chemical-based pesticides, like di-chloro di-phenyl trichloro ethane (DDT), parathion, di-chloro diphenyl dichloroethylene (DDE), malathion, atrazine, chlordane, etc. Their adverse effects include a decline in biodiversity, threats to endangered species, reduction in pollinating insect populations, and destruction of bird habitats (Rawtani et al. 2018).

Higher dosages of these herbicides harm the soil and water resources. These chemicals may harm the neurological system, mimic hormones, cause cancer, and even kill people in extreme situations. Many technologies based on surface adsorption, membrane filtering, and biodegradation have been developed recently to minimize pesticide content in the environment, particularly in soil and water. However, these treatments are focused on a range of contaminants in the environment, which significantly impacts their performance.

In recent years, with the emergence of new technologies, these pesticides have reached the limit of health risks at the molecular level. Only a few molecules of such pesticides are enough to threaten people's health. Therefore, techniques for detecting and decomposing these pesticides at the molecular and atomic levels are needed. Nanotechnology is an area where this goal can be achieved. It entails manipulating atoms and molecules to create materials with nanometer-scale dimensions (Tharmavaram et al. 2018). As we all know, nanotechnology-based technologies for pesticide detection and degradation are incredibly specific. Countless approaches have been used to study various forms of nanomaterials, such as nanoparticles, nanocomposites, and nanotubes, for the detection, degradation, and removal of various pesticides. These particles exhibit distinct chemical, physical, and biological characteristics as compared to their mass equivalent. The tiny size, distinctive shape, and enhanced surface area of NPs are responsible for these properties (Zhang et al. 2008). The major kinds of nanoparticles employed by different researchers to detect and break down pesticides include metal nanoparticles, bimetallic nanoparticles, and metal oxide nanoparticles.

In the realm of environmental remediation, nanoparticles of different metals, particularly precious metals such as gold (Au), silver (Ag), platinum (Pt), and palladium (Pd), have been frequently employed. In addition to noble metal nanoparticles, transition metal nanoparticles such as iron (Fe), copper (Cu), and zinc (Zn) have been used in various research. Low reagent costs, easy production methods, and selective, quick, and delicate responses are among the benefits of NPs. The decomposition of harmful pesticides into smaller and less toxic organic molecules is also aided by redox reactions on the surface of nanoparticles.

Metal oxide nanoparticles are also widely used in the field of environmental remediation, mainly due to their superconducting properties of nanoparticles. The superconducting properties of the NPs endow them with high efficiency and specific photocatalytic activity and have been used in various research projects to detect and remediate pesticides. Different types of metal oxide NPs, such as silicon dioxide (SiO_2-NP), titanium oxide (TiO_2 NP), zinc oxide (ZnO-NP), and iron oxide (Fe_2O_3 or Fe_3O_4-NP), are used for detection, degradation, and removal of pesticides from various sources.

Bimetallic nanoparticles are made up of atoms from two distinct metals united into a single particle. Many researchers across the globe are interested in this kind of nanoparticle because the combination of two metals may yield a variety of surprising and unique features. The synergistic impact of the coupled metals is responsible for these novel features of bimetallic NPs (Zaleska-Medynska et al. 2016). The distribution of metal atoms in these nanoparticles determines their shape and function. Pesticides have been degraded using bimetallic nanoparticles, particularly iron/nickel nanoparticles.

Nanocomposites are composites made up of various materials having nanometer-scale dimensions. Nanocomposites are created by combining the qualities of several materials to create new forms of nanomaterials with superior physical and chemical capabilities. Nanocomposites have a greater surface area and a higher surface area-to-volume ratio than standard composite materials. These composite materials have piqued the interest of environmental scientists, particularly for pesticide degradation. For pesticide cleanup, graphene oxide (GO) is often utilized to form nanocomposites with a variety of metal and metal oxide nanoparticles. The explanation underlying GO's significant adsorption behavior for many pesticides is the strong P-P interaction between organic contaminants and graphene aromatic rings (Zhang et al. 2015). The electrostatic interaction of nanocomposites with pesticides aids in the adsorption and removal of pesticides.

Carbon nanotubes are members of the fullerene structure family, cylindrical hollow nanostructures (NS) composed of single or multiple graphene layers. Due to their layering, carbon nanotubes are classified as single-walled carbon nanotubes (SWCNTs) or multi-walled carbon nanotubes (MWCNTs). It has been reported that carbon nanotubes CNT can specifically adsorb and mask ionizable organic compounds (for example, drugs and pesticides) due to low-barrier charge-assisted hydrogen bonding and cation-π-assisted π-π interactions (Kah et al. 2017).

Halloysite nanotubes (HNTs) have also started to pique people's interest in pesticide detection and degradation. HNTs remarkable adsorption activity aids in the removal and degradation of a wide range of pesticides. HNT is a nanotube-shaped clay mineral with aluminosilicate as its chemical form. They've lately acquired popularity as a result of their enormous surface area, non-toxicity, biocompatibility, and inexpensive cost, and they've been employed in a variety of applications all over the globe (Yuan et al. 2015). Pollutants in HNTs, on the other hand, may alter the adsorption of numerous compounds. As a result, pollutants must be eliminated from HNTs before they can be utilized for pesticide remediation applications

18.6 Conclusion and Future Research Directions

In addition to the advantages, there are some points that are needed to be studied about the application, effects, and fate of NPs in the environment:

(a) The fate and transport of NPs in the environment should be studied.
(b) The reaction mechanisms of NPs are not fully understood due to their diverse reaction capabilities with the specific sites and their variable morphology.
(c) The toxicological effects of NPs are not extensively studied.
(d) More research focus is required to use biowastes as feedstock for the synthesis of NPs.
(e) Studies about the life cycle assessment of the NPs are less and need to be executed.
(f) There should be a method which is internationally acceptable standardized method by all the NPs should be synthesized along with their characterization to fully understand their mechanistic pathways of action.

References

Almaroai YA, Vithanage M, Rajapaksha AU, Lee SS, Dou X, Lee YH, Ok YS (2014) Natural and synthesised iron-rich amendments for As and Pb immobilisation in agricultural soil. Chem Ecol 30(3):267–279

Bora T, Dutta J (2014) Applications of nanotechnology in wastewater treatment—a review. J Nanosci Nanotechnol 14:613–626

Chen P, Yang Y, Bhattacharya P, Wang P, Ke PC (2011) A tris-dendrimer for hosting diverse chemical species. J Phys Chem C115:12789–12796

Cheng JM, Liu YZ, Wang HW (2014) Effects of surface-modified nano-scale carbon black on Cu and Zn fractionations in contaminated soil. Int J phytorem 16(1):86–94

Crane RA, Scott TB (2012) Nanoscale zero-valent iron: future prospects for an emerging water treatment technology. J Hazard Mater 211:112–125

Das R, Vecitis CD, Schulze A, Cao B, Ismail AF, Lu X, Chen J, Ramakrishna S (2017) Recent advances in nanomaterials for water protection and monitoring. Chem Soc Rev 46:6946–7020

Diallo MS, Savage N (2005) Nanoparticles and water quality. Kluwer Academic Publishers

Farooqi ZUR, Qadeer A, Hussain MM, Zeeshan N, Ilic P (2021) Characterization and physicochemical properties of nanomaterials. In: Nanomaterials: synthesis, characterization, hazards and safety. Elsevier, pp. 97–121

Fuge R, Laidlaw I, Perkins WT, Rogers KP (1991) The influence of acidic mine and spoil drainage on water quality in the mid-Wales area. Environ Geochem Heal 13(2):70–75

Gujrati M, Malamas A, Shin T, Jin E, Sun Y, Lu Z-R (2014) Multifunctional cationic lipid-based nanoparticles facilitate endosomal escape and reduction-triggered cytosolic sirna release. Mol Pharm 11:2734–2744

Homaeigohar S, Elbahri M (2014) Nanocomposite electrospun nanofiber membranes for environmental remediation. Materials 7:1017–1045

Ilić P, Nišić T, Farooqi ZUR (2020) Occurrence of specific polychlorinated biphenyls congeners in an industrial zone. Pol J Environ Stud 30(1):635–643

Ilić P, Markić DN, Bjelić LS, Farooqi ZUR (2021a) Polycyclic aromatic hydrocarbons in different layers of soil and groundwater-evaluation of levels of pollution and sources of contamination. Pol J Environ Stud 30(2):1191–1201

Ilić P, Ilić S, Markić DN, Bjelić LS, Farooqi ZUR, Sole B, Adimalla N (2021b) Source identification and ecological risk of polycyclic aromatic hydrocarbons in soils and groundwater. Ecol Chem Eng Soc 28(3):355–363

Ilić P, Nišić T, Farooqi ZUR (2021c) Polycyclic aromatic hydrocarbons contamination of soil in an industrial zone and evaluation of pollution sources. Pol J Environ Stud 30(1):1–8

Kah M, Sigmund G, Xiao F, Hofmann T (2017) Sorption of ionizable and ionic organic compounds to biochar, activated carbon and other carbonaceous materials. Water Res 124:673–692

Khan FA (2020) Nanomaterials: types, classifications, and sources. In: Applications of nanomaterials in human health. Springer, pp. 1–13

Khan I, Saeed K, Khan I (2019) Nanoparticles: properties, applications and toxicities. Arab J Chem 12:908–931

Kim YG, Oh SK, Crooks RM (2004) Preparation and characterization of 1− 2 nm dendrimer-encapsulated gold nanoparticles having very narrow size distributions. Chem Mater 16(1):167-172.

Krishnan K, Alivisatos A (1999) Science 2001, 291, 2115.[crossref],[pubmed],[cas], google scholar (c) sun, s.; murray. J Appl Phys 85:4325

Kumar N, Kumar R, Kumar N, Kumar R (2014a) Nano-based drug delivery and diagnostic systems. In: Nanotechnology and nanomaterials in the treatment of life-threatening diseases, pp. 53–107

Kumar R, Khan MA, Haq N (2014b) Application of carbon nanotubes in heavy metals remediation. Crit Rev Environ Sci Technol 44:1000–1035

Laurent S, Forge D, Port M, Roch A, Robic C, Vander Elst L, Muller RN (2008) Magnetic iron oxide nanoparticles: synthesis, stabilization, vectorization, physicochemical characterizations, and biological applications. Chem Rev 108:2064–2110

Li D, Xia Y (2004) Electrospinning of nanofibers: reinventing the wheel? Adv Mater 16:1151–1170

Magureanu M, Mandache NB, Hu J, Richards R, Florea M, Parvulescu VI (2007) Plasma-assisted catalysis total oxidation of trichloroethylene over gold nano-particles embedded in SBA-15 catalysts. Appl Catal B 76(3-4):275–281

Mahmoud ME, Fekry NA, El-Latif MM (2016) Nanocomposites of nanosilica-immobilized-nanopolyaniline and crosslinked nanopolyaniline for removal of heavy metals. Chem Eng J 304:679–691

Makarova OV, Rajh T, Thurnauer MC, Martin A, Kemme PA, Cropek D (2000) Surface modification of TiO2 nanoparticles for photochemical reduction of nitrobenzene. Environ Sci Technol 34(22):4797–4803

Mansha M, Khan I, Ullah N, Qurashi A (2017) Synthesis, characterization and visible-light-driven photoelectrochemical hydrogen evolution reaction of carbazole-containing conjugated polymers. Int J Hydrog Energy 42:10952–10961

Mauter M, Elimelech M (2008) Environmental applications of carbon-based nanomaterials. Environ Sci Technol 42:5843–5859

Nasrollahzadeh M, Sajadi SM, Sajjadi M, Issaabadi Z (2019a) Applications of nanotechnology in daily life. Interface Sci Technol 28:113–143

Nasrollahzadeh M, Sajadi SM, Sajjadi M, Issaabadi Z (2019b). An introduction to nanotechnology. In: Interface science and technology. Elsevier, pp. 1–27

Nayak MK, Singh J, Singh B, Soni S, Pandey VS, Tyagi S (2017) Introduction to semiconductor nanomaterial and its optical and electronics properties. In: Metal semiconductor core-shell nanostructures for energy and environmental applications. Elsevier, pp. 1–33

Negi S, Batoye S, Singh K, Waraich JS (2021) Environmental pollution, its causes and impact on ecosystem. In: New frontiers of nanomaterials in environmental science, pp. 1–22

Noubactep C, Caré S, Crane R (2012) Nanoscale metallic iron for environmental remediation: prospects and limitations. Water, Air, Soil Pollu 223(3):1363–1382

Oke AE, Aigbavboa CO, Semenya K (2017) Energy savings and sustainable construction: examining the advantages of nanotechnology. Energy Procedia 142:3839–3843

Olojo E, Olurin K, Mbaka G, Oluwemimo A (2005) Histopathology of the gill and liver tissues of the African catfish Clarias gariepinus exposed to lead. Afr J Biotechnol 4:117–122

Ong CB, Ng LY, Mohammad AW (2018) A review of zno nanoparticles as solar photocatalysts: synthesis, mechanisms and applications. Renew Sust Energ Rev 81:536–551

Panwar N, Soehartono AM, Chan KK, Zeng S, Xu G, Qu J, Coquet P, Yong K-T, Chen X (2019) Nanocarbons for biology and medicine: sensing, imaging, and drug delivery. Chem Rev 119:9559–9656

Pierart A, Shahid M, Sejalon-Delmas N, Dumat C (2015) Antimony bioavailability: knowledge and research perspectives for sustainable agricultures. J Hazard Mater 289:219–234

Qu X, Alvarez PJ, Li Q (2013a) Applications of nanotechnology in water and wastewater treatment. Water Res 47:3931–3946

Qu X, Brame J, Li Q, Alvarez PJ (2013b) Nanotechnology for a safe and sustainable water supply: enabling integrated water treatment and reuse. Acc Chem Res 46:834–843

Rabbani M, Rafiee F, Ghafuri H, Rahimi R (2016) Synthesis of Fe3O4 nonoparticles via a fast and facile mechanochemicl method: Modification of surface with porphyrin and photocatalytic study. Mater Lett 166:247–250

Rawtani D, Khatri N, Tyagi S, Pandey G (2018) Nanotechnology-based recent approaches for sensing and remediation of pesticides. J Environ Manag 206:749–762

Ren X, Chen C, Nagatsu M, Wang X (2011) Carbon nanotubes as adsorbents in environmental pollution management: a review. Chem Eng J 170(2-3):395–410

Saeed K, Khan I (2016) Preparation and characterization of single-walled carbon nanotube/nylon 6, 6 nanocomposites. Instrum Sci Technol 44:435–444

Safaei M, Taran M, Jamshidy L, Imani MM, Mozaffari HR, Sharifi R, Golshah A, Moradpoor H (2020) Optimum synthesis of polyhydroxybutyrate-co3o4 bionanocomposite with the highest antibacterial activity against multidrug resistant bacteria. Int J Biol Macromol 158:477–485

Sánchez A, Recillas S, Font X, Casals E, González E, Puntes V (2011) Ecotoxicity of, and remediation with, engineered inorganic nanoparticles in the environment. TrAC Trends Anal Chem 30:507–516

Shao P, Liang D, Yang L, Shi H, Xiong Z, Ding L et al (2020) Evaluating the adsorptivity of organo-functionalized silica nanoparticles towards heavy metals: quantitative comparison and mechanistic insight. J Hazard Mater 387:121676

Sohail MI, Ayub MA, ur Rehman MZ, Azhar M, Farooqi ZUR, Siddiqui A et al (2021) Sufficiency and toxicity limits of metallic oxide nanoparticles in the biosphere. In: Nanomaterials: synthesis, characterization, hazards and safety. Elsevier, pp 145–221

Somanathan T, Krishna VM, Saravanan V, Kumar R, Kumar R (2016) Mgo nanoparticles for effective uptake and release of doxorubicin drug: Ph sensitive controlled drug release. J Nanosci Nanotechnol 16:9421–9431

Taran M, Safaei M, Karimi N, Almasi A (2021) Benefits and application of nanotechnology in environmental science: an overview. Biointerface Res Appl Chem 11:7860–7870

Thangadurai D, Sangeetha J, Prasad R (2020) Nanotechnology for food, agriculture, and environment. Springer International Publishing

Tharmavaram M, Pandey G, Rawtani D (2018) Surface modified halloysite nanotubes: a flexible interface for biological, environmental and catalytic applications. Adv Colloid Interface Sci 261:82–101

Thomas S, Kumar Mishra P, Talegaonkar S (2015) Ceramic nanoparticles: fabrication methods and applications in drug delivery. Curr Pharm Des 21:6165–6188

Tilley SK, Fry RC (2015) Priority environmental contaminants: understanding their sources of exposure, biological mechanisms, and impacts on health. In: Systems biology in toxicology and environmental health. Academic Press, pp. 117–169

Torrens F, Castellano G (2019) Green nanotechnology: an approach towards environment safety. In: Advances in nanotechnology and the environmental sciences. Apple Academic Press, pp. 85–92

Tyagi S, Rawtani D, Khatri N, Tharmavaram M (2018) Strategies for nitrate removal from aqueous environment using nanotechnology: a review. J Water Process Eng 21:84–95

Vaseghi Z, Nematollahzadeh A (2020) Nanomaterials: types, synthesis, and characterization. In: Green synthesis of nanomaterials for bioenergy applications, pp. 23–82

Vaseghi Z, Nematollahzadeh A, Tavakoli O (2018) Green methods for the synthesis of metal nanoparticles using biogenic reducing agents: a review. Rev Chem Eng 34:529–559

Yan Q-L, Gozin M, Zhao F-Q, Cohen A, Pang S-P (2016) Highly energetic compositions based on functionalized carbon nanomaterials. Nanoscale 8:4799–4851

Yirsaw BD, Megharaj M, Chen Z, Naidu R (2016) Environmental application and ecological significance of nano-zero valent iron. J Environ Sci 44:88–98

Yuan G (2004) Natural and modified nanomaterials as sorbents of environmental contaminants. J Environ Sci Heal, Part A 39(10):2661–2670

Yuan P, Tan D, Annabi-Bergaya F (2015) Properties and applications of halloysite nanotubes: recent research advances and future prospects. Appl Clay Sci 112:75–93

Zaleska-Medynska A, Marchelek M, Diak M, Grabowska E (2016) Noble metal-based bimetallic nanoparticles: the effect of the structure on the optical, catalytic and photocatalytic properties. Adv Colloid Interface Sci 229:80–107

Zhang L, Gu FX, Chan JM, Wang AZ, Langer RS, Farokhzad OC (2008) Nanoparticles in medicine: therapeutic applications and developments. Clin Pharmacol Therap 83(5):761–769

Zhang Y, Li T, Zeng B, Zhang H, Lv H, Huang X, Azad AK (2015) A graphene based tunable terahertz sensor with double Fano resonances. Nanoscale 7(29):12682–12688

Chapter 19
Nanotechnologies and Phytoremediation: Pros and Cons

Alessia Corami

Abstract The request for resources is increasing day by day because of population growth. Modern agricultural practices are primarily based on pesticides and fertilizers to increase yields, which have become primary factors in *soil pollution*. Similarly, the emission of toxic gaseous materials from industries and vehicles has resulted in *air pollution* and the accumulatlon of industrial chemicals, organic sludge, heavy metals, and residential waste in oceans and rivers has resulted in *water pollution*. Environmental remediation of all of these problems is carried out on different environmental media, with the choice of a remediation method depending on the kind and the extent of the pollution. In particular, water remediation is a process to remove pollutants from water. Soil pollution results in the losso of fertility and leads to contamination and soil remediation invloves the revitalization of the soil. In situ remediation means treating soil pollutants in situ, without removing soil medium, as would occur in ex situ remediation. Conversely, bioremediation is considered a simply and natural method to treat a large number of samples and media.

Keywords Nanotechnology · Phytoremediation · Nano-zero valent iron · Soil pollution · Wastewater · Contaminants · Fertilizers · Pesticides · Remediation · Toxicity · Metals · Sustainability · Dechlorination · Plants · Bio-degradation

19.1 Introduction

Generally, researchers have found that environmental applications of nanotechnology could be used in the case of environmental and/or sustainable products (e.g. green chemistry or pollution prevention), the remediation of hazardous substances, and sensors for environmental agents (Tratnyek and Johnson 2006; Masciangioli and Zhang 2003; Karn 2005). Within this field, the process of nanobioremediation

---

A. Corami (✉)
MIUR, Ministry of University and Research, Rome, Italy

L. Newman et al. (eds.), *Phytoremediation*, https://doi.org/10.1007/978-3-031-17988-4_19

is considered a new emerging technology for contaminant remediation by biosynthetic nanoparticles, and it is currently regardedas an area for extensive research.

Environmental nanotechnologies contribute to the achievement of sustainability while simultaneously protecting the environment. Effective methods for drinking water purification and groundwater or wastewater treatments are currently under development. Stabilized nanoparticles present a number of advantages, including a broad specific surface area, major activity, and soil deliverability, and better soil transportability; moreover, nanoparticles can be distributed into contaminated soil or deep aquifers (Gong et al. 2018; Cai et al. 2020).

One potential risk could arise from the products of water treatment, which might be more toxic than the original contaminants; these compounds can entry into the environment and/or could form new class of toxins (Rickerby 2008; Masciangioli and Zhang 2003; Rajan 2011). Watlington (2005) has highlighted some concerns about the misuse and/or negative effects of the use of nanotechnology because nanotechnology means the formation of substances with peculiar properties, and worker exposure and accidental release could pose future threats. Nanomaterials (NM) have always been present in the environment, meaning that human exposure is not a "new" problem, but from the time of the industrial revolution, there has been an increase in the use of NMs and thus in our level of contact with them. These newer NMs have an anthropogenic origin and human beings could be exposed to ingestion, inhalation, injection, and dermal exposure (Oberdorster et al. 2005). The fundamental point is the level of the exposure to these materials and also their safe handling, according to Raloff (2005). In this regard, Watlington (2005) has suggested an increasing in the number of studies focusing on the ecological impact of nanotechnologies used in production as well as in remediation technologies. Horne (2009) has pointed out that nanoscale science is a key technology frontier and that the risks involved are due to our limited knowledge. Improving policy with regard to the use of these materials could reduce the risks to consumers, workers, and the environment, and simultaneously increasing innovation and the market.

19.2 Phytoremediation

Bioremediation (biodegradation) means the breakdown of organic compounds by living organisms and the formation of carbon dioxide and water or methane. Biodegradation could be divided into two forms: aerobic (in which oxygen is used as an electron acceptor) and anaerobic (which is carried out without oxygen) (Corami 2017). Phytoremediation involves the use of plant sites to mitigate the toxic effects of contaminants in polluted media through physical, biochemical, biological, chemical, and microbiological interactions. Several mechanisms, such as accumulation or extraction, degradation, filtration, stabilization, and volatilization have been employed in phytoremediation (Corami 2017; Gudeppu et al. 2019). By contrast, phytoextraction means contaminants are uptaken by roots and translocated into the shoots. Through the harvesting of the plants, contaminants are removed. The biomass produced through this process could be either disposed of or re-used (Ali et al. 2013). The process of phytoextraction can be divided into continuous phytoextraction (using hyperaccumulator plants) and induced phytoextraction (the chemically induced accumulation of metals to crop plants) (Corami 2017; Fitz and Wenzel 2002). Heavy metals are adsorbed and/or absorbed by plant roots via xylem and phloem tissues and then HMs arrive in the harvestable part of the plant. Rhizofiltration is the use of plant roots to absorb, concentrate, and precipitate heavy metals from polluted effluents (Corami 2017; Dushenkov et al. 1995). It occurs in the rhizosphere and water must be in contact with roots. Phytostabilization means contaminant immobilization in soil by roots through absorption and accumulation, adsorption onto roots, or precipitation within the root zone of plants, and the prevention of contaminant migration via wind and water erosion, leaching, and avoiding metals entry into the food chain. Through such processes HMs are converted to a less toxic state by special redox enzymes excreted by plants (Ali et al. 2013; Corami 2017). The choice of which plants to use is a decisive aspect of phytostabilization-based techniques. (Rizzi et al. 2004; Corami 2017). Phytotransformation or phytodegradation means the rupture of pollutants through metabolic processes within the plant. The degradation might occur outside the plant because of the release of compounds that cause the transformation; conversely degradation caused by microorganisms is considered rhizodegradation. Phytotransformation might occur in an environment free of microorganisms, and also in sterile soils where biodegradation could not occur. Unfortunately, toxic intermediate products may form (e.g. Pentachlorophenol (PCP) was metabolized to tetrachlorocatechol). Organic contaminants, after their uptake, might be translocated to other plant tissues and then volatilized, or they might be degraded, or bound in non-available forms (Salt et al. 1998; Corami 2017). Few organic contaminants appear to be mineralized; in general, a small amount of these pollutants are fully transformed into water and CO_2. Phytostimulation or rhizodegradation is the breakdown of organic contaminants in soil by microorganisms in the rhizosphere. Groundwater movement may be induced by the transpiration of plants so that contaminants in the groundwater might reach the rhizosphere. Plants' roots produce exudates, such as sugars, amino acids, organic acids, fatty acids, and sterols, which could increase the number of microorganisms. These exudates differ according to the type of plants. Roots might increase soil aeration and soil moisture, and therefore the conditions for biodegradation by microorganisms are more favourable (EPA 2000; Corami 2017). Furthermore, rhizospheric microorganisms may accelerate the processes through the volatilizing of contaminants (Salt et al. 1998; Corami 2017).

The process of phytovolatilization is the release of the contaminant to the atmosphere, the contaminant is uptaken by the plant metabolism, and transpiration is released. The released contaminants may be also subject to photodegradation in the atmosphere.

19.3 Nanotechnology

The concept of nanotechnology was initially postulated by Richard Feynman in 1959 (Roco 2005; Watlington 2005). Nanotechnology seems likely to provide a good contribution to the enhancement of NM properties to be used very well in soil remediation technologies. Masciangioli and Zhang (2003) classified the areas to apply nanotechnology into three categories: treatment and remediation; sensing and detection; and pollution prevention. Treatment and remediation have felt the first impacts in nanotechnology applications (Watlington 2005).

Nanotechnology provides to be more sensitive and also to be a cost-effective technology for the detection of pollution in the ground, water, and air (Rose-Pehrsson and Pehrsson 2005). NMs in remediation may remove heavy metals from soil and water, cause the degradation of dyes in industrial wastewater, and degradation and the removal of hydrocarbons (Das et al. 2019; El-Ramady et al. 2020).

It is clear that NMs can decrease pollution and could revolutionise remediation technologies.

In situ remediation by NMs results are less destructive, cost-effective, and proactive against pollutants, thereby cutting down the remediation time frame and reaching contaminant plumes in deep aquifers (Karn et al. 2009; Zhao et al. 2016; Cai et al. 2020). Zhang (2003) confirmed the features of NMs to remediate more material and a wide range of contaminants at a higher rate and with a lower generation of hazardous byproducts. For example, processes such as nano-zerovalent iron (nZVI), bi-metallic nanoscale particles (BNPs), and emulsified zerovalent iron (EZVI) may diminish pollutants such as perchloroethylene (PCE), TCE, cis-1, 2-dichloroethylene (c-DCE), vinyl chloride (VC), and 1-1-1-tetrachloroethane (TCA), along with polychlorinated biphenyls (PCBs), halogenated aromatics, nitroaromatics, and metals such as arsenic or chromium (Otto 2009). Engineered nanoparticles (NPs), zero-valent iron nZVI, carbon nanotubes, and iron oxide NPs are generally utilized to remove heavy metals from potable water.

NMs will prove of benefit in the areas of agriculture and environmental remediation. Masciangoli and Zhang (2003) wrote about the opportunity to use NMs to provide fertilizers and pesticides, at the same time avoiding excess. Unfortunately, it seems that nanoparticles may not reach a wide distribution in the subsurface because of the agglomeration phenomenon before finishing the dispersion within the soil or groundwater matrix. Passivation is another factor, which can reduce the efficacy of NMs such as iron nanoparticles. In the case of nZVI being used, an iron, which is unsuitable for management, can result in an oxidized and passivated phenomenon before reacting with the pollutants (Otto 2009). Rajan (2011) stated that there are data on the potential of nanoparticle accumulation in environmentally important species and few studies on the consequences of nanoparticles on environmental microbial communities.

Bioremediation techniques are many and result efficiently in restoring sites with the help of microorganisms. The diversity, abundance, and community structure in contaminates environments are very effective in the fate of any bioremediation technique supplied from other environmental factors. Phytoremediation is also a prominent method in the removal of contaminants from the soil and aqueous systems. Nanotechnology seems cost-effective in remediating hazardous waste sites and in approaching demanding site conditions, such as where dense nonaqueous-phase liquids (DNAPLs) are found in polluted aquifers. Nanoscale iron is already in use in full-scale projects with success.

19.4 Nanomaterial

Many nanosized structures, such as weathered minerals, are naturally present in the environment (Masciangioli and Zhang 2003), but they are not considered to be nanomaterials. The requisites for defining a nanomaterial are that compounds must hold exclusive physical, chemical, and/or biological properties, which are different from those found in the same material on a large scale. A nanomaterial (NM) is defined as a material whose size lies between 1 and 100 nm, called nanocrystalline material. At this size, the surface shows defects or altered electronic structure; such materials can be crystalline, amorphous, or polymeric, with physical and chemical properties that could be altered at the nanometre scale (Thangadurai et al. 2019; Suryanarayana 1995; Gleiter 1989). Thanks to these specific physical and chemical features, nanoparticles have high reactivity with the contaminated area; therefore nanomaterials are used in different forms in bioremediation processes like nanoiron, nanofibres, nanorods, nanotubes, nanoribbons, nanocomposites, nanoporous materials, nanofoam, and nanocrystalline materials (Gudeppu et al. 2019; Otto 2009; Masciangioli and Zhang 2003).

Nanomaterials (NMs) could be used in a wide variety of applications: health care, insulations, lubricants, additives, biosensing, bioimaging, tumor diagnosis, insulation, lubrificants, and so on (Gudeppu et al. 2019). One example is the nanotechnology used in developing membranes for water treatment, desalination, and water reclamation (Theron et al. 2008). For example, injecting nano-zero valent iron (nZVI) particles into areas within aquifers, the origin of chlorinated hydrocarbon contamination, seems to be very speedy and efficient in groundwater cleanups when compared to classical cleanup methods (Otto 2009). Masciangioli and Zhang (2003) have suggested that nanoparticles deployed in ex-situ slurry reactors are effective in treating contaminated soils, sediments, and solid wastes. It is also suggested they could be in a solid zeolite matrix for treating water, wastewater, or gaseous process streams. In particular, they have highlighted the use of carbon nanotubes for air and water pollution control. The great advantage of using nanomaterial (NM) in the bioremediation process is that NMs possess a high surface area per unit mass and a higher reactivity with the surrounding material of contaminated area. Thanks to its very little size and wide surface area, NMs simply go into the polluted zone, something which is not possible with micro-particles; they show elevated reactivity toward redox-amenable pollutants and low activation energy is necessary to make the chemical reactions achievable. A dendrimer is a polymer with a huge size (a large molecule) and little molecules inside. The structure of these dendrimers comprises three components: a central core; interior branch cells/radial symmetry; and terminal branch cell/peripheral symmetry.

The peculiar and tunable properties of carbon nanotubes (CNTs) and nanocrystals, synthesized mainly from carbon, entitled new technologies for a broad range of environmental applications: high-flux membranes, depth filters, sorbents, antimicrobial agents, environmental sensors, pollution prevention strategies, and renewable energy technologies (Mauter and Elimelech 2008). Single-wall nanotubes (SWNTs) can act as sensors of electrical resistance changes in the presence of a targeted pollutant, such as nitrogen dioxide (Kamat et al. 2002). Carbon nanotubes (CNT) have shown great adsorption properties; due to their functional group they have an increased affinity towards contaminants such as Cr^{3+}, Pb^{2+}, Zn^{2+} arsenic compounds, organics, biological impurities, dioxin, and volatile organic compounds; they also maintain water quality (Li et al. 2003; Rao et al. 2007; Agnihotri et al. 2005; Savage and Diallo 2005). Generally, this process is used in multi-walled carbon nanotubes (MWCNTs) and to increase the efficiency of absorption it is oxidized with nitric acid. CNTs are functionalized with functional groups (Bianco et al. 2008; Sayes et al. 2004) to increase solubility and biocompatibility so that they could be highly dispersed in water and easily separated in order to be re-used.

Enzymes are a mixture of proteins, which are very specific and efficacious, and act as biocatalysts in bioremediation. Silica nanoparticles have been applied for environmental remediation to reduce radioactive compounds and also the levels of heavy metals in soil and water (Jeelani et al. 2020; El-Ramady et al. 2020).

Biogenic uraninite, because of its defined size, biological origin, and dominant bioremediation strategies, became of great concern to geoscientists. Based on the past researches, the chemical and structural features of these fundamental natural NMs were increasingly understood, and their uses in bioremediation of subsurface uranium (VI) contamination were assessed (Bargar et al. 2008).

These special characteristics of NMs make them well suited to dealing with matters of waste and toxic material degradation, thanks to the presence of microorganisms and also enhance their effectiveness by protecting them from pollutants, making them nonreactive.

Multiple combinations of contaminants are often present in wastewater, brownfield, or polluted soil and cannot be restored simultaneously with only one technique due to their different needs for reagents, reaction conditions, and time. Properly designed NMs can adsorb or degrade specific pollutants without being depleted by water, or being mixed up with native soil constituents, contaminants may be transformed into less toxic forms readily biodegradable (Zhang et al. 2019).

19.5 Nano Zero-Valent Iron (nZVI)

Nanoparticles which contain zero-valent iron (nZVI) are one of the most outstanding examples of technology with remarkable benefits. nZVI seems to be a solution for groundwater pollution, in particular against volatile organic compounds (VOCs) and metals. It has been found that nZVI can move with groundwater far from the injection site, so they could treat larger areas in a contaminated aquifer. Macé et al. (2006) and Karn et al. (2009) confirmed the reduction of VOCs in fractured bedrock and a steadier decrease in primary porosity aquifers. It is also observed that BNP is more effective, whereas nZVI shows a longer effect. Furthermore, no important changes have been observed in the microbial community, after the use of NMs. Iron nanoparticle technology is defined as the first generation of nanoscale environmental technologies (Sun et al. 2006), being used as a reactive material due to its great ability in reducing and stabilizing different types of ions. The appeal of nZVI for remediation is that the science of contaminant remediation is well-developed and this has led to a fast transfer from preliminary laboratory testing to pilot-scale demonstrations in the field (Tratnyek and Johnson 2006; Zhang 2003; Wang and Zhang 1997; Elliot and Zhang 2001; ITCR 2005).

The nano-zerovalent iron particles show low toxicity, high iron source availability, high reactivity, and attractive magnetic properties (magnetic adsorbents), which may support the adsorption through remediation (El-Ramady et al. 2020). Galdames et al. (2020) classified nZVI into three groups: (1) bimetallic iron-based nanoparticles (BNP); (2) emulsified iron nanoparticles (EZVI); and (3) polymer-coated (NZVI). The two different metals in the bi-metallic nanoscale particles induce a synergic effect enhancing the degradation of different contaminants (Zhang and Elliott 2006; USEPA 2008). Bimetallic particles are made of iron (or zinc) and noble metals such as palladium (Pd), platinum (Pt), nickel (Ni), silver (Ag), or copper (Cu); these noble metals could facilitate contaminant degradation. The second metal is generally less reactive and it is supposed to promote Fe oxidation or electron transfer (Karn et al. 2009; USEPA 2008).

EZVI could deliver nZVI in an oil–water emulsion, making it easy the transport into the polluted zones and reducing the nZVI's degradation. Emulsion droplets, consisting of an oil–liquid membrane, are formed and they surround nZVI particles in water (Reinhart et al. 2003; Singh and Misra 2016; O'Hara et al. 2006; Galdames et al. 2020).

Nanoparticles present a high reactivity due to their large surface area, allowing a rapid degradation of contaminants; conversely, nZVI presents a lack of stability, rapid passivation, and limited mobility because of the rapid tendency to aggregate. Moreover, nZVI has a high affinity for oxygen causing passivation of the nanoparticles in contact with the air or an aqueous medium (Saleh et al. 2008), to avoid these problems, a coating polymer has been used to increase nZVI dispersion. Indeed, polymer-stabilized nanoparticles show great stability and soil transportability, also increasing the remediation capability. One problem to consider is biocompatibility and/or biodegradability to avoid the worsening of the environmental problem. In particular, biopolymers could be a nutrient source for microorganisms (Shi et al. 2015), since nZVIs have been coated with a biodegradable polymer, in order to increase both the dispersion of nanoparticles and their stability. Coating polymers avoid nanoparticle aggregation; in some cases, they are food or energy for microorganisms during remediation processes such as bioremediation or phytoremediation (Galdames et al. 2020); on the contrary, nanoparticles coated with natural polymers don't show consequences because these polymers are biodegradable.

Lien and Zhang (2007) have reported on the palladium (Pd) properties for hydrodechlorination by nanoscale zero-valent iron particles. Kinetic data allow researchers to infer that the nZVI-mediated dechlorination, whereas if Pd is absent, nanoscale Fe particles show a very slow degradation rate. It is inferred from XRD that Pd is deposited onto the iron surface as nanoparticles, and it is observed in the dissolution of water by nZVI and the formation of a layer of atomic hydrogen on the Pd surface. Successively, atomic hydrogen degrades chlorinated hydrocarbons (es. PCE) through a surface-mediated process. It is suggested that PCE dechlorination, through nanoscale Pd/Fe particles, is a catalytic reaction and Pd is the catalyst. Satapanajaru et al. (2003) have confirmed the dechlorination from nZVI on atrazine. Unfortunately, atrazine could travel far from the application sites, leaching into rivers, lakes, and groundwater. The results confirm that nZVI is useful in remediating atrazine contamination in water and soil. The main process is reductive dechlorination, nZVI can promote rapid abiotic degradation and, in particular, coated Pd-nZVI is more effective. Gillham and O'Hannesin (1994) have observed that generally in aerobic conditions, oxygen is the usual electron acceptor. In anaerobic conditions, from the reaction of ZVI with water, the released electron can be coupled with chlorinated and nitroaromatic compounds. They confirm the catalyst role for Pd as already written. Indeed in anaerobic conditions, Pd can absorb hydrogen causing dechlorination of lindane and atrazine molecules. In aerobic conditions, Pd behaves as an electron donor (Joo and Zhao 2008). It is observed a decreasing in pH values with atrazine degradation, the decrease of pH allows the removal of passivating layers from the ZVI core and these layers are free to react with halogenated molecules (Satapanajaru et al. 2003; Dombek et al. 2001). nZVIs increase this phenomenon. It is inferred that atrazine destruction is due to two processes: reductive dechlorination and acid hydrolysis Satapanajaru et al. (2003) determined the effectiveness of NZVI to dechlorinate atrazine in soils, which could run off into surface water and groundwater. Pd was used as a catalyst, the optimum pH is determined and also the possible effects due to the presence of Fe and Al salts. In particular, dechlorination was found to be the main process (Gillham and O'Hannesin 1994). In aerobic conditions, oxygen is the electron acceptor. In anaerobic conditions, electrons released from the reaction between ZVI and water can be joined to the reaction of chlorinated and nitroaromatic compounds, promoting rapid abiotic degradation. Decreasing the pH from 9 to 4 increases the kinetic rates of atrazine destruction and the presence of Pd increases this phenomenon.

Some uncertainties of this process have been highlighted because of the formation of the microsized cluster during the aggregation of nanoparticles, the risk to the environment and to human beings, and a lack of studies on the long-term effect of the process (Patil et al. 2016; Bardos et al. 2018; Qian et al. 2020). Galdames et al. (2020) suggest five points to improve the efficiency of this remediation method: the management of nZVI; the evaluation of the effect on living organisms; ageing effects; effects among the soil and/or water and nZVIs; and the use of nanoremediation in combination with other remediation technology such as phytoremediation.

Barnes et al. (2010) reported that iron nanoparticles are cytotoxic to bacterial cells in the case of the presence of chlorinated aliphatic hydrocarbons (CAH); they could show a negative impact on exposed microbial communities. They suggested the combination of a two-step process to degrade CAH; first stimulating TCE biodegradation through acetate and then adding bimetallic nanoparticles (Ni/Fe) to degrade the remaining cis-1,2-DCE and VC. According to Barnes et al. (2010), bioremediation is a cost-effective approach, which requires less energy; more importantly, it removes contaminants trying to maintain the original environmental condition to allow microbial growth. Unfortunately, Fe nanoparticles were inhibitory to the indigenous reducing bacterial community, and TCE degradation diminished to 0.01–0.1 g/L Fe nanoparticle concentration; this is definitively inhibited at a concentration above 0.3 g/L. From the experiments carried out, it is inferred that CAH biological and chemical reduction could not occur simultaneously. It is suggested that the CAH biological reduction in groundwater is achieved through the process of increasing the concentration of degradation products. Subsequently, to reach TCE biodegradation, later bimetallic nanoparticles could reduce all of the groundwater CAHs. This two-step process allows the injection of fewer Fe nanoparticles avoiding the negative impact on indigenous microbial communities under anaerobic conditions.

Jagupilla et al. (2009) have compared nZVI, EZVI, and MZVI for the remediation of TCE and Cr (VI) in groundwater. Tests show nZVI is better than the other two NMs and, in some samples, the reduction is biologically mediated. Cr (VI) and TCE are common contaminants; generally, during a remediation process, the highly mobile Cr (VI) is reduced to a less soluble Cr (III); similarly, TCE is reduced to ethane and chloride with great results. The amount of Cr (VI) decreased gradually; conversely, in the case of nZVI. EZVI performance was peripheral in tests, MZVI performed badly with respect to the other two reductants. It is inferred that Cr (VI) was suddenly removed and not biologically mediated, because no differences are shown in the test results between sterilized and non-sterilized samples. In particular, nZVI achieved a complete reduction of TCE, a complete removal did not occur to EZVI even after 28 days. Moreover, TCE reduction was biologically mediated for nZVI. Üzum et al. (2008) have already carried out a study about a fast uptake and huge capacity of Co^{2+}removal from nZVI. In particular, actual uptake is inferred even after several repetitive trials. Increasing pH, it is observed an increase in Co^{2+} uptake. The experiments were carried out to investigate the consequences of the *V*/*m* ratio (volume of solution/mass of sorbent), to define the time required to achieve the equilibrium of uptake, and to determine the extent of desorption. The nZVI particles appear to have the characteristic chain-like morphology, these particles possess a core-shell structure, in which the shell is the oxidised FeO part surrounding the core and preserving it against further oxidation. Iron nanoparticles have widely preserved their reactivity towards Co^{2+} ions, even 40 days after preparation. In particular, it is highlighted that the extent of reactivity loss with ageing, is closely related to the uptake mechanism. According to Li and Zhang (2006), the sorption mechanisms are electrostatic adsorption, complex formation, reduction, and precipitation. Each depends on the metal ion standard electrode potential and experimental conditions, mainly medium pH. Li and Zhang (2007) have reported that the uptake is by oxidation-reduction mechanism and it is effective for ions such as Pb^{2+}, Cr^{6+}, Ni^{2+},

As^{3+}, As^{5+}, Cu^{2+}, $Ni^{2+,}$ and Ag^{+}. In this case, Üzum et al. (2008) suggest that Co^{2+} is sorbed by hydroxyl groups on the surface of the nZVI shell or that it precipitates on that surface forming $Co(OH)_2$. The uptake mechanism seems to depend on the speciation oxihydroxyl superficial group on the nZVI surface and neither redox mechanism evidence is observed.

Another great and deep problem is the number of radionuclides in soil and groundwater because of their long-term environmental concerns and the strong bearing on the potential for site redevelopment (Crane et al. 2015). Unfortunately, soluble radionuclides could contaminate groundwater, compromising drinking water sources and they could spread contamination over long distances. With regard to other elements, the oxidation state is the most important chemical property in groundwater. In the environment, plutonium can exist as one of the following, Pu^{3+}, Pu^{4+}, $Pu^{5+,}$ or Pu^{6+}, the first two in oxidising conditions, whereas the last two in reducing conditions. Interaction between aqueous plutonium and iron minerals are well known (Triay et al. 1997). Plutonium forms complexes with various organic ligands, such as acetate, citrate, formate, fulvate, humate, lactate, oxalate, and tartrate, with many inorganic ligands, such as hydroxyl, carbonate, nitrate, sulphate, phosphate, chloride, bromide and fluoride, and with many synthetic organic ligands, e.g. EDTA and 8-hydroxyquinoline derivatives. Plutonium and actinide ions generally form extremely stable aqua-complexes with carbonate and bicarbonate, which are common anions in natural water systems (Clark et al. 1995). Indeed Pt is often included in plutonium carbonate complexes. It has been observed a fast and important decrease in aqueous concentrations, Pt uptake onto the nZVI has been observed by XPS analysis (X-ray phoelectron spectroscopy). According to Dickinson and Scott (2010), first, there is a sorption mechanism, and later a chemical reduction that is surface-mediated. Crane et al. (2015) stated the opportunity to use nZVI in remediating contaminated solutions with plutonium and uranium. It was observed a fast and high decrease in aqueous concentrations of actinide species. In particular, they have recorded low aqueous contaminant concentrations for these systems until the first week of reaction. Additionally, XPS analysis carried out on extracted nanoparticulate solids, confirmed contaminant uptake onto nZVI, indicating, for actinide species, first a sorption mechanism and later a chemical reduction on nZVI surfaces.

Gonçalves (2016) carried out experiments with nZVI in an industrial complex, used for the production of fertilizers and sulfuric acid (from massive polymetallic sulphides), in this site there was a high concentration of zinc, copper, lead, arsenic, sulphates, and nitrates. In particular, the products from the transformation of Fe(0) nanoparticles are iron oxide (mainly magnetite – Fe_3O_4). Regarding groundwater flow direction, nZVI was injected in the middle between the upstream and downstream monitoring points. A sharp decrease was observed for some major pollutants in the first; this effect is assumed to be due to the reactivity, which took place in the soil after the injection so that this effect also took place in the aquifer. He observed a stabilization in the concentration of the metals with a reducing efficiency of nZVI. About two months later, the metal concentration showed values over 60% but below the baseline. This effect seems due to the hydrogeological system; it was found that the sulfate concentration in the aquifer is also decreased thanks to nZVI. Gonçalves (2016) wrote the precipitation of metals as sulfides followed sulfate ion reduction; in particular, the ongoing Fe particle oxidation and, consequently, precipitation of Fe (III) hydroxide. It is inferred that this methodology, applied in soils and groundwater, reduces the available concentration of these metals. He observed, first, a huge concentration decrease in heavy metals, a contaminant stabilization reflecting a stabilization due to the reducing effect by nZVI itself. pH increase is caused by nZVI's reductive action; nZVI does not act as metals-reducing agent, but it does facilitatehydrogen production. Hence it is suggested that the pH should be increased by adding $Ca(OH)_2$ or Na(OH), which will increase the cost but create a good environment for efficient remediation. The use of nZVI is a good and cost-effective new approach to reach this goal.

Kanel et al. (2006) have already affirmed the efficiency of nZVI as an adsorbent, in particular for the removal of As(III) and As(V) in the subsurface environment (Manning et al. 2002; Su and Puls 2001a, b; Farrell et al. 2001; Leupin and Hug 2005; Lackovic et al. 2000; Bang et al. 2005; Kanel et al. 2006). It has been suggested to use nZVI because of the huge increase in water consumption in countries such as Bangladesh, India, Nepal, and Indo region and the high level of As in groundwater. It used nZVI as a colloidal reactive barrier for in situ groundwater remediation (Elliot and Zhang 2001; Kanel et al. 2006; Cantrell and Kaplan 1997). After the application of nZVI, the researchers observed two shell-like layers and the formation of a chain-like structure. Moreover, as is taken away by nZVI in a few minutes, whereas micron ZVI needs hours or days by adsorption and precipitation. It was also inferred that both nZVI and ZVI show similar generation mechanisms for iron oxide precipitates and an ageing process (Kanel et al. 2006), confirming that the larger surface area is more effective. This study confirmed the possible use of nZVI as an effective NM in a permeable barrier for groundwater remediation.

In addition, Kanel et al. (2005) has already written the good results from the use of nZVI to treat polluted water. It was highlighted that nZVI favoured anaerobic microbial growth in the subsurface with the rise of pH, the reduction of redox potential, the production of hydrogen gas, and the emission of ferrous iron ions. It was also stated that in a large range of pH, As (III) is firmly sorbed on nZVI, while it the co-precipitation of As (III) and As (V) on Fe (III) oxide/hydroxide was also observed and corrosion products are embroiled. Finally, it was suggested that there might be an opportunity to use nZVI for As (III) treatment as an efficient material and it was suggested that it could be used in a permeable reactive barrier or ex-situ groundwater treatment.

Rajan (2011) has carried out experiments on polluted groundwater, confirming that nZVI is highly efficacious in transforming and detoxifying many contaminants in water, such as chlorinated organic solvents, organochlorine pesticides, and polychlorinated biphenyls. The efficiency arises from the wide specific surface area; in particular, the efficiency is higher in removing arsenic from groundwater as already stated by Kanel et al. (2006).

The reactivity of nZVI for the reduction of an oversaturated uranyl solution was provided by Riba et al. (2008). It has been stated that metaschoepite is the main solid phase at pH $\geq$ 4.2, but it has been also observed that metaschoepite precipitation is significant after 7 days. It is suggested that the adsorption and precipitation of uranium phase on the surface of nanoparticles are triggered by nZVIs; it has not been observed U precipitation in control experiments under the same conditions and with no nZVIs. Conversely, the precipitation of uranium is observed on nZVI and this phenomenon prolongs their lifetime by hindering their dissolution. The removal of uranium at this pH condition occurred by precipitation and reductive precipitation, validating Fe(II) as a reducing agent and it may cause reduction from U (VI) to U (IV) (White and Peterson 1996; Charlet et al. 1998; Liger et al. 1999; Scott 2005; Scott et al. 2005). Popescu et al. (2013) confirmed the use of iron zero valent nanoparticles (INP)[1] to remove U (VI) from water. In particular, it was compared the use of carboxy-methyl-cellulose (CMC) and carboxy-methyl-cellulose with iron nanoparticles (CMC-INP). CMP is used as a "delivery vehicle" to facilitate nanoparticle mobility within porous networks. The presence of INP allows for to the removal about twice of U (VI). It was inferred that the removal of aqueous uranium was higher at pH 5, and that it decreased with the increase in pH. Contact time were also compared; after 30 hours, increasing the contact time does not make any differenc to the adsorption process. Therefore the uranyl ions' adsorption on the CMC–INP (nZVI) material is inferred to ensure a mechanism embroiling a redox precipitation (UO_2), chemisorption (by the CMC), and physical adsorption (by the formed iron oxyhydroxides).

Rajan (2011) has posed a question about the risk of a negative effect to human health from nanoparticles, as they could be inhaled or absorbed through the skin (Kreyling et al. 2006). However, he has also highlighted that greater mobility is increasing the remediation with the opportunity to use nanomaterials migration into wells or aquifers, and possibly a dangerous discharge in surface water. It has been suggested that these manufactured nanoparticles may be dangerous in the environments where they are used (Handy et al. 2008; Karn et al. 2009) because these materials are designed with properties that are not likely to find in nature. These properties could enhance possible toxicologic properties; some of these effects have been reported on microbes, plants, and fish. Boxall et al. (2007) and Colvin (2003) suggested that the effects on the environment and human health could be low. Conversely, Tratnyek et al. (2006) said that in laboratory conditions nanoparticles could aggregate and build up to micrometer size, so they could be more likely colloids.

There is a wide debate about the pro and cons of using nanomaterials in the environment (Ruffini Castiglione and Cremonini 2009). They have underlined three points:, the source, transformation, and fate of nanoparticles; the biotransformation between engineered nanoparticles and the environment; and the toxicity of engineered nanoparticles, and the possibilities of them entering the food chain. It is suggested that is is important to understand the ways in which nanoparticles are transported and penetrated into plants to determine the possible benefits, pointing out the ecosystem detriment due to particulate deposition because of competition

---

[1] In Popescu et al. 2013 nZVI are called INP (iron nano particle)

pattern alteration among the species, resulting in an extreme effect on plant biodiversity. Lin and Xing (2007) have reported that root growth inhibition change among nanoparticles and plants and that this also seems to be caused by nanoparticle concentration. Racuciu and Creanga (2007) noted that the enzymatic structures, engaged in the different stages of photosynthesis, might be magnetically influenced by iron-based nanoparticles.

Actually, in a culture medium when it adds a small concentration of aqueous ferrofluid the result is a stimulating effect on the growth of the plantlets; conversely, increasing the concentration of the result is an inhibitory effect.

Jośko and Oleszczuk (2014) have carried out experiments to value the risk due to engineered nanoparticle presence. They compared methods to assess nano-ZnO, nano-TiO2, and nano-Ni ecotoxicity and their behaviour; furthermore, they studied how NMs are applied to the soil. In particular, nano-ZnO and nano-TiO2 could prove a significant deep threat to the environment because of their extensive use and because the European Union has requested by the year 2018 an ecotoxicological characterization if the production is over 1 m^3ton/year (European Parliament and European Council 2006a, b), thus it is essential to assess the potential phytotoxicity. It is supposed that particle sizes, preparation methods, and test designs caused differences in the individual studies, and, more importantly, how NMs are applied, affecting the distribution of NMs themselves and consequently the toxicity effect in soil. Two of the studied parameters have been germination inhibition and root elongation inhibition. NMs have been applied with three different methods: as a powder; as a water suspension with dried soil; and, thirdly, as a water suspension without drying the soil. No correlations have been inferred between the concentration and the observed toxic effect, probably due to the test design; perhaps filter presence in the experiment reduces the toxicity in the first method for all of the three NMs. With an increase in concentration the root growth inhibition also increased. The three NMs show different toxicity behaviour according to their concentration and the method as they have been applied. Only in one case was an elongation of the observed, using nano-Ni with the first two application methods. It is therefore suggested that controls should be placed on how nanoparticles are applied to the soil because of the important effect on toxicity levels. This study strongly suggests that NMs have different effects on the plants according to the methods used for their introduction. The application method concerns many variables, such as the kind of environmental nanoparticles, concentration, and the matrix. This means that erroneous estimations about the NMs' potential could be achieved by suggesting a validation method.

Ruttkay-Nedecky et al. (2017) have discussed the interactions of nanomaterials and vascular plants, because plants react with the soil, water, and atmosphere; nanoparticles could penetrate live plant tissue and, consequently, could enter into the food chain. In particular, it is underlined fate and transportation of nanoparticles, if nanoparticles could cause physical and/or chemical toxicity to plants (Jeyasubramanian et al. 2016; Alidoust and Isoda 2013; Lee et al. 2012; Mirzajani et al. 2013). Toxic effects are not shown in all plants treated with nanoparticles (Husen and Siddiqi 2014; Ruffini Castiglione and Cremonini 2009; Ma et al. 2010;

Rico et al. 2011; Arruda et al. 2015). Ruttkay-Nedecky et al. (2017) have carried out some phytotoxicity tests during germination. During the germination time (preferably at least four days) and seedling, growth seeds are exposed to the solution test, and root/shoot elongation and dry weight are often modified, assessing the harmful substance effect on plants (Wang and Freemark 1995). Indeed they assessed that nanoparticle phytotoxicity is mainly affected by the shape, size, chemical composition, and the material composition of the coating material. Sometimes, nanoparticle phytotoxicity is due to the toxicity of the substance which is used for its preparation. According to plant composition, shape, size of the nanoparticle, and anatomy, plant roots uptake nanoparticles and transport them through the vascular system into the above-ground part of the plants.

Ruttkay-Nedecky et al. (2017) have found that micro-sized particles of ZnO are less inhibitory to fungal growth than ZnO NPs. It is observed that ZnO NPs show positive effects in terms of promoting germination, stem and root growth, an increase in phosphorus-mobilizing enzymes, phosphorus uptake, and antifungal properties.,They have reviewed many studies about ZnO toxicity suggesting high acute toxicity of ZnO NPs (in the low mg L-1 levels) to environmental species, suggesting test species affect toxicity, material physicochemical properties, and test methods. Gogos et al. (2012) correlate CuNPs' stimulatory effects to the induction of antioxidant activity, and Cu nanoparticles on vines are 8%more effective by than against a phytopathogenic fungus. It is inferred that CuNPs interfere with the uptake of micro- and macronutrients such as Na, P, S, Mo, Zn, and Fe. CuNPs can trigger important metabolic changes in leaves and root exudates, revealing a protection mechanism against CuNPs, with a root length decrease, root biomass reduction, and Cu bioaccumulation in roots. Nanoscaled iron particles exhibit a different behaviour, high absorbency and a response to external magnetic fields. Fe_2O_3 NPs enhance root length, plant height, and biomass. Finally, Ruttkay-Nedecky et al. (2017) have observed that nanoparticles of iron oxides and manganese oxides are less phytotoxic.

Actually, Verma et al. (2019) have written about the concerning impacts on the health and safety of workers who use nanotechnology in green technology. It is suggested that greater value should be placed on risk assessment, risk management, and finally risk communication; planning worker protection from harm, and providing all the benefits of green nanotechnology for society (Palaniselvam et al. 2016; Drasler et al. 2017; Laux et al. 2018; Becker et al. 2011; Iavicoli et al. 2014).

19.6 Nano-phytoremediation

Nano-phytoremediation is the term given to nanotechnology applied to phytoremediation. This nano-remediation depends on nanomaterials to remove contaminants in soils and water through nano-bioremediation and nano-phytoremediation (Verma et al. 2019; Yadav et al. 2017). Nano-phytotechnology allows a decrease in the retention time and the cost of nanotechnology. According to Vázquez-Núñez et al. (2020), using nano-bioremediation and nano-phytoremediation reduces cost and negative effects when groundwaters and wastewaters, heavy metal pollution, hydrocarbons, the organic and inorganic compound in soils are treated (Rizwan et al. 2014; Yogalakshmi et al. 2020; De Gisi et al. 2017; Bharagava et al. 2020). It is important to take into consideration that nanoparticles are used in detecting contaminants and, consequently avoiding pollution. Nanoremediation concurs with sustainability offering many advantages and being costly-effective compared to other technologies.

The most important nanomaterials that have the potential in removing pollutants from contaminated soils and water are nano-silica, nano-zero-valent iron, nano-sized iron sulfide particles, nano-ZnO, and others. Most experiments have been carried out using nZVI with good results. Some questions have been opened, the most rigorous is if these nanomaterials will be stable in new environmental conditions if they could enter the food chain, and/or if these materials make remediation more efficient, environment friendly, and less expensive. Phytoremediation could be enhanced by microbes, and plants give shelter and nutrients/food to their adjacent endophytic and rhizospheric microbes; meanwhile, microbes support plants degrading pollutants. Nanotechnology could support the phytoremediation process by increasing the germination, seedling, root and shoot elongation, biomass production, and the capability to bind contaminants (Nwadinigwe and Ugwu 2018; Kumar et al. 2020; El-Ramady et al. 2020). The challenge is how to stock the contaminated biomass considering that this biomass is a toxic waste (Verma and Rawat 2021; Bhati and Rai 2018). Karn et al. (2009) have written that NMs, and in particular nZVI, have site-specific requirements to be effective.

It is deeply important that site characterization is carried out, with information about site location, geology, concentration, and type of contaminants, also including groundwater gradient, flow velocity, hydrogeologic conditions, and geochemical properties. All of this information is important in valuing the behaviour and efficiency of NMs in soil and/or groundwater. Rajan (2011), confirmed that all of these factors have affected these nanomaterials in nanoremediation and most important is to consider the safety and caution when experiments are carried out. The study highlights the enormous potential to clean-up large contaminated sites in situ, the reduced clean-up time, and, most importantly, the effectiveness of this technology in reducing the concentration of contaminants.

Ding et al. (2017) have carried out some tests on artificially Pb-contaminated soils using nanohydroxyapatite (NHAP) and ryegrass. NHAP is better than hydroxyapatite in immobilizing metals because of its high sorption capacity, low water solubility, high stability, and cost-effectiveness. Ryegrass has been chosen because it is simply to make grow and manage, and produce a high amount of biomass; therefore, it is cost-effective for phytoremediation (Sarma 2011). The aim was to investigate the effects of NHAP on Pb in soil and Pb accumulation in ryegrass. Metals have been divided into three groups: bioavailable, potentially bioavailable, and bio-unavailable. Pb is transformed from non-residual to residual fractions in the presence of NHAP. First, NHAP was dissolved in a soil solution releasing phosphate ions and producing a low solubility of lead phosphate. In the case of ryegrass a Pb decrease was observed in the roots and the shoots. It is inferred that NHAP reduces Pb mobility and bioavailability.

Moreover, Jiamjitrpanich et al. (2012) have carried out some experiments on soil contaminated by trinitritoluene (TNT). It has been used nZVI and purple guinea grass (*Panicum maximum*) as a hyperaccumulation plant. Nano-phytoremediation is more effective in removing TNT-contaminated soil than either nanotechnology or phytoremediation.

In particular, it is shown that the half-life of TNT decreased from 100 days in a sample with no treatment, to 30 days with only hyperaccumulator, and in the sample with nZVI and *Panicum maximum,* the half-life is greatly reduced, to just 1.5 days. Nano-phytoremediation results are very promising for the removal of contaminated soil and water.

Khan and Bano (2016) evaluated the growth of a plant in presence of rhizobacteria (PGPR) and Ag nanoparticle on the growth and metabolism of maize irrigated with municipal wastewater. In particular, municipal wastewater contains microorganisms, and different PGPR show a different survival efficiency to the proliferation of heavy metals. Heavy metals and nutrients in wastewater affect plants and soils, e.g. Ag nano-particles augmented PGPR with an increase in the root area and root length; they suppressed the CFU (colony forming unit) of all the PGPR. Ag nanoparticles enhance their bioremediation potential for Pb, Cd, and Ni, increasing the root area and root length by PGPR isolates and reducing the growth-promoting potential of PGPR. It is also inferred that plants produce antioxidant enzymes to protect themselves from metal toxicity in metal-stressed soils acting as a scavenger for the toxicity of reactive oxygen species.

Sarkar et al. (2021) stated that nano-phytoremediation could be an economic process and ecologically useful. They highlight the importance to study nanoparticles and their effect on the plant to avoid any kind of risk and to enhance the sustainable development of nano-phytoremediation. According to them, it is fundamental to reduce the number of contaminants in the environment; this allows the reduction of the number of toxic metals in agricultural soils and also avoids the presence of toxic metals in crops. Nano-phytoremediation is an innovative and encouraging technology and could be a supporting biological clean-up technique increasing the sustainability. Sen et al. (2015) have already written that nano-phytoremediation is a strong means for Indian agriculture because of the high amount of heavy metals, shrinking arable land, and the contamination of water. They have confirmed that nanoparticles can influence pollutant fate and uptake during phytoremediation treatments. Srivastav et al. (2019) affirmed that air pollution is a big challenge directly affecting human health. The development of phyto-technologies for the removal of pollutants from the environment is necessary to ameliorate the quality of life. They also suggested that among the nanoparticles are included nano-fertilizers which help to regulate nutrient release in the soil system. It is highlighted that studies about nano-phytoremediation are scarce; in particular, only microcosm experiments have been carried out rather than long-term experiments. These are more important in seeing the actual effects of nano-particles in soils, water, their toxicity, and soil fertility. It is suggested that a better understanding of contaminant uptake will support agro-mining and the opportunity for the extraction of contaminants from harvestable plant biomass.

Finally, nano-phytoremediation is technology including nanoscale materials used to adsorb pollutants and degrade plant-accumulated contaminants. Nanomaterials and phytoremediation can increase the decontamination effect both efficiently and sustainably.

19.7 Conclusion

The application of nanotechnology to phytoremediation enhance physico-chemical properties of NMs in green and sustainable applications, being energy-efficient as well as cost-effective. These solutions may reduce the use of raw materials and, most importantly, re-use wastes according to the circular economy principles, to be more safe, efficient, and sustainable in the remediation of soil, water, and air and providing an improved quality of ecosystem and livelihood.

These positive aspects of nano-phytoremediation should be level-headed with the critical aspect concerning human health and safety. Unfortunately, NMs could show important dangerous characteristics because of their physicochemical properties, posing risks for human beings and also the environment. Therefore, studying the impact of NMs to value risk assessment and risk management through scientific research, technological, governmental and workforce efforts is fundamental; to reach valid results for in-situ remediation treatments by nanomaterials with other technologies. This would provide helpful information and guidance to write a policy considering appropriate preventive and protective measures for the exposed populations. This chapter aims to highlight and maximize this promising remediation technology, increasing the environmental benefits with the aim of a sustainable future. Nowadays sustainability of remediation approaches is an important consideration.

References

Agnihotri S, Rood MJ, Rostam-Abadi M (2005) Adsorption equilibrium of organic vapors on single walled carbon nanotubes. Carbon 43:2379–2388

Ali H, Khan E, Sajad MA (2013) Phytoremediation of heavy metals—concepts and applications. Chemosphere 91(7):869–881

Alidoust D, Isoda A (2013) Effect of gamma Fe_2O_3 nanoparticles on photosynthetic characteristic of soybean (Glycine max (L.) Merr.): foliar spray versus soil amendment. Acta Physiol Plant 35:3365–3375

Arruda SCC, Silva ALD, Galazzi RM, Azevedo RA, Arruda MAZ (2015) Nanoparticles applied to plant science: a review. Talanta 131:693–695

Bang S, Johnson MD, Korfiatis GP, Meng X (2005) Chemical reactions between arsenic and zero-valent iron in water. Water Res 39:763–770

Bardos P, Merly C, Kvapil P, Koschitzky H-P (2018) Status of nanoremediation and its potential for future deployment: risk–benefit and benchmarking appraisals. Remediat J 28:43–46

Bargar JR, Bernier-Latmani R, Giammar DE, Tebo BM (2008) Biogenic uraninite nanoparticles and their importance for uranium remediation. Elements 4(6):407–402

Barnes RJ, Riba O, Gardner MN, Singer AC, Jackman SA, Thompson IP (2010) Inhibition of biological TCE and sulphate reduction in the presence of iron nanoparticles. Chemospher 80:554–562

Becker H, Herzberg F, Schulte A, Kolossa-Gehring M (2011) The carcinogenic potential of nanomaterials, their release from products and options for regulating them. Int J Hyg Environ Health 214:231–238

Bharagava RN, Saxena G, Mulla SI (2020) Introduction to industrial wastes containing organic and inorganic pollutants and bioremediation approaches for environmental management. In: Springer (ed) Bioremediation of industrial waste for environmental safety. Singapore

Bhati M, Rai R (2018) Nano-phytoremediation application for water contamination. In: Ansari AA et al (eds) Phytoremediation. Springer, Switzerland, pp 441–452

Bianco A, Kostarelos K, Partidos CD, Prato M (2008) Biomedical applications of functionalized carbon nanotubes. Chem Commun 1:571–577

Boxall ABA, Tiede K, Chaudhry Q (2007) Engineered nanomaterials in soils and water: how do they behave and could they pose a risk to human health? Nanomedicine 2(6):919–917

Cai Z, Zhao X, Duan J, Zhao D, Dang Z, Lin Z (2020) Remediation of soil and groundwater contaminated with organic chemicals using stabilized nanoparticles: lessons from the past two decades. Front Environ Sci Eng 14(5):84–90

Cantrell KJ, Kaplan DI (1997) Zero-valent iron colloid emplacement in sand columns. J Environ Eng 123:499–495

Charlet L, Liger E, Gerasimo P (1998) Decontamination of TCE- and U-rich waters by granular iron: role of sorbed Fe(II). J Environ Eng 124:25–30

Clark DL, Hobart DE, Neu MP (1995) Actinide carbonate complexes and their importance in actinide environmental chemistry. Chem Rev 95:25–48

Colvin VL (2003) The potential environmental impact of engineered nanomaterials. NatBiotechnol 21:1166–1170

Corami A (2017) Soil pollution and phytoremediation. In: IIT Roorkee Executive (ed) Environmental science and engineering

Crane RA, Dickinson M, Scott TB (2015) Nanoscale zero-valent iron particles for the remediation of plutonium and uranium contaminated solutions. Chem Eng J 262:319–315

Das A, Kamle M, Bharti A, Kumar P (2019) Nanotechnology and it's applications in environmental remediation: an overview. Vegetos 32:227–227

De Gisi S, Minetto D, Lofrano G, Libralato G, Conte B, Todaro F, Notarnicola M (2017) Nanoscale Zero Valent Iron (nZVI) treatment of marine sediments slightly polluted by heavy metals. Chem Eng Trans 60:139–134

Dickinson M, Scott TB (2010) The application of zero-valent iron nanoparticles for the remediation of a uranium-contaminated waste effluent. J Hazard Mater 178:171–179

Ding L, Li J, Liu W, Zuo Q, Liang S-x (2017) Influence of nano-hydroxyapatite on the metal bioavailability, plant metal accumulation and root exudates of ryegrass for phytoremediation. Lead-polluted soil. Int J Environ Res Public Health 14(5):532–540

Dombek T, Dolan F, Schultz J, Klarup D (2001) Rapid reductive dechlorination of atrazine by zero-valent iron under acidic conditions. Environ Pollut 111:21–27

Drasler B, Sayre P, Steinhäuser KG, Petri-Fink A, Rothen-Rutishauser B (2017) In vitro approaches to assess the hazard of nanomaterials. Nano Impact 8:99–16

Dushenkov V, Nanda Kumar PBA, Motto H, Raskin I (1995) Rhirofiltration: the use of plants to remove heavy metals from aqueous streams. Environ Sci Technol 29(5):1239–1235

Elliot D, Zhang W-x (2001) Field assessment of nanoscale bimetallic particles for groundwater treatment. Environ Sci Technol 35:4922–4926

El-Ramady H, El-Henawy A, Amer M, El-Dein Omara A, Elsakhawy T, Salama A-M, Ezzat A, El-Shereif A, El-Mahrouk M, Shalaby TA (2020) Agro-pollutants and their nano-remediation from soil and water: a mini-review. Env Biodiv Soil Security 4:361–369

EPA [Internet]: EPA/600/R-99/107 (2000). Available from: http://nepis.epa.gov/

European Parliament and European Council [internet] (2006a) Scientific Committee on Consumer Safety SCCS OPINION on Titanium dioxide (TiO_2) used in cosmetic products that lead to exposure by inhalation. Available at: https://ec.europa.eu/health/sites/default/files/scientific_committees/consumer_safety/docs/sccs_o_238.pdf

European Parliament and European Council [internet] (2006b) Scientific Committee on Consumer Safety SCCS OPINION ON Zinc oxide (nano form) Available at: https://ec.europa.eu/health/scientific_committees/consumer_safety/docs/sccs_o_103.pdf

Farrell J, Wang J, O'Day P, Coklin M (2001) Electrochemical and spectroscopic study of arsenate removal from water using zerovalent iron media. Environ Sci Technol 35:2026–2022

Fitz WJ, Wenzel WW (2002) Arsenic transformations in the soil-rhizosphere-plant system: fundamentals and potential application to phytoremediation. J Biotechnol 99:259–258

Galdames A, Ruiz-Rubio L, Orueta M, Sánchez-Arzalluz M, Vilas-Vilela JL (2020) Zero-valent iron nanoparticles for soil and groundwater remediation. Int J Environ Res Public Health 17:5817–5819

Gillham RW, O'Hannesin SF (1994) Enhanced degradatinon of halogenated aliphatics by zero-valent iron. Ground Water 32:958–957

Gleiter H (1989) Nanocrystalline materials. Prog Mater Sci 33:223–225

Gogos A, Knauer K, Bucheli TD (2012) Nanomaterials in plant protection and fertilization: current state, foreseen applications, and research priorities. J Agric Food Chem 60:9781–9782

Gonçalves JR (2016) The soil and groundwater remediation with zero valent iron nanoparticles. Procedia Eng 143:1268–1265

Gong Y, Zhao D, Wang Q (2018) An overview of field-scale studies on remediation of soil contaminated with heavy metals and metalloids: technical progress over the last decade. Water Res 147:440–450

Gudeppu M, Varier KM, Chinnasamy A, Thangarajan S, Balasubramanian J, Li Y, Gajendran B (2019) Nanobiotechnology approach for the remediation of environmental hazards generated from industrial waste. In: Springer (ed) Emerging nanostructured materials for energy and environmental science, pp 531–561

Handy RD, von der Kammer F, Lead JR, Hassellöv M, Owen R, Crane M (2008) The ecotoxicology and chemistry of manu-factured nanoparticles. Ecotoxicology 17:287–284

Horne N (2009) A comprehensive comparative regulatory policy analysis: U.S. and EU nano regulation and policy alternatives. Proceedings for the international conference on the environmental implications and applications of nanotechnology The Environmental Institute (TEI)

Husen A, Siddiqi KS (2014) Phytosynthesis of nanoparticles: concept, controversy and application. Nanoscale Res Lett 9:1–24

Iavicoli V, Leso W, Ricciardi L, Hodson L, Hoover MD (2014) Opportunities and challenges of nanotechnology in the green economy. Environ Health 13:78–77

Interstate Technology and Regulatory Council (ITRC) [internet], Permeable Reactive Barriers: Lessons Learned/New Directions, ITRC (2005). Available at: https://connect.itrcweb.org/HigherLogic/System/DownloadDocumentFile.ashx?DocumentFileKey=9cdc7633-cc17-4fe2-a7b3-c9a55cb7f65c

Jagupilla SC, Wazne M, Liu X, Rabah N, Lazar B, Su T-L, Christodoulatos C (2009) Comparative study of nano zerovalent iron, micro zerovalent iron and emulsified nano zerovalent iron for the remediation of TCE and Cr(VI) contaminated groundwater. Proceedings conference on the environmental implications and applications of nanotechnology; 2009 June 9–11; Amherst Massachusetts. p 37–43

Jeelani PG, Mulay P, Venkat R, Ramalingam C (2020) Multifaceted application of silica nanoparticles. Rev Silicon 12:1337–1334

Jeyasubramanian K, Thoppey UUG, Hikku GS, Selvakumar N, Subramania A, Krishnamoorthy K (2016) Enhancement in growth rate and productivity of spinach grown in hydroponics with iron oxide nanoparticles. RSC Adv 19:15451–15459

Jiamjitrpanich W, Parkpian P, Polprasert C, Kosanlavit R (2012) Enhanced phytoremediation efficiency of TNT-contaminated soil by nanoscale zero valent iron. 2nd international conference on environment and industrial innovation, Singapore, pp 82–86

Joo SH, Zhao D (2008) Destruction of lindane and atrazine using stabilized iron nanoparticles under aerobic and anaerobic conditions: effects of catalyst and stabilizer. Chemosphere 70:418–415

Jośko I, Oleszczuk P (2014) Phytotoxicity of nanoparticles—problems with bioassay choosing and sample preparation. Environ Sci Pollut Res 21:10215–10214

Kamat P, Huehn R, Nicolaescu R (2002) A “sense and shoot” approach for photocatalytic degradation of organic contaminants in water. J Phys Chem B 106(4):788–784

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

Kanel SR, Greneche J-M, 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

Karn B (2005) Overview of environmental applications and implications. How does nanotechnology relate to the environment? Or why are we here? In: Karn B, Masciangioli T, Zhang W-Z, Colvin V, Alivisatos P (eds) Nanotechnology and the Environment. American Chemical Society, pp 2–27

Karn B, Kuiken T, Otto M (2009) Nanotechnology and in situ remediation: a review of the benefits and potential risks. Environ Health Perspect 117(12):1813–1811

Khan N, Bano A (2016) Role of plant growth promoting rhizobacteria and Ag-nano particle in the bioremediation of heavy metals and maize growth under municipal wastewater irrigation. Int J Phytoremediation 18(3):211–211

Kreyling WG, Semmler-Behnke M, Möller W (2006) Health implications of nanoparticles. J Nanopart Res 8(5):543–542

Kumar S, Kumari N, Karmakar S, Ankit SR, Behera M, Rani A, Kumar N (2020) Advances in plant–microbe-based remediation approaches for environmental cleanup. In: Bharagava RN (ed) Emerging eco-friendly green technologies for wastewater treatment, microorganisms for sustainability 18. Springer Nature Pte Ltd, Singapore, pp 103–128

Lackovic JA, Nikolaids NP, Dobbs GM (2000) Inorganic arsenic removal by zerovalent iron. Environ Eng Sci 17:29–39

Laux P, Tentschert J, Riebeling C, Braeuning A, Creutzenberg O, Epp A, Fessard V, Haas K-H, Haase A, Hund-Rinke K, Jakubowski N, Kearns P, Lampen A, Rauscher H, Schoonjans R, Störmer A, Thielmann A, Mühle U, Luch A (2018) Nanomaterials: certain aspects of application, risk assessment and risk communication. Arch Toxicol 92:121–141

Lee S, Kim S, Lee I (2012) Effects of soil-plant interactive system on response to exposure to ZnO nanoparticles. J Microbiol Biotechnol 22:1264–1270

Leupin OX, Hug SJ (2005) Oxidation and removal of arsenic (III) from aerated groundwater by filtration through sand and zerovalent iron. Water Res 39:1729–1740

Li X-q, Zhang W-x (2006) Iron nanoparticles: the core–shell structure and unique properties for Ni(II) sequestration. Langmuir 22:4638–4632

Li YH, Dinga J, Luanb Z, Dia Z, Zhua Y, Xua C, Wu D, Wei B (2003) Competitive adsorption of Pb^{2+}, Cu^{2+} and Cd^{2+} ions from aqueous solutions by multiwalled carbon nanotubes. Carbon 41(14):2787–2782

Lien H, Zhang W-x (2007) Nanoscale Pd/Fe bimetallic particles: catalytic effects of palladium on hydrodechlorination. Appl Catal B Environ 77:110–116

Liger E, Charlet L, Van Cappellen P (1999) Surface catalysis of uranium(VI) reduction by iron(II). Geochim Cosmochim Acta 63(19–20):2939–2935

Lin D, Xing B (2007) Phytotoxicity of nanoparticles: inhibition of seed germination and root growth. Environ Pollut 150:243–250

Ma XM, Geiser-Lee J, Deng Y, Kolmakov A (2010) Interactions between engineered nanoparticles (ENPs) and plants: phytotoxicity, uptake and accumulation. Sci Total Environ 408:3053–3051

Macé C, Desrocher S, Gheorghiu F, Kane A, Pupeza M, Cernik M, Kvapil P, Venkatakrishnan R, Zhang W-x (2006) Nanotechnology and groundwater remediation: a step forward in technology understanding. Remediation 16(2):23–23

Manning BA, Hunt M, Amrhein C, Yarmoff JA (2002) Arsenic(III) and arsenic(V) reactions with zerovalent iron corrosion products. Environ Sci Technol 36:5455–5451

Masciangioli T, Zhang W-x (2003) Environmental Technologies at the Nanoscale. Environ Sci Technol 37(5):102A–108A

Mauter MS, Elimelech M (2008) Environmental applications of carbon-based nanomaterials. Environ Sci Technol 42(16):5843–5849

Mirzajani F, Askari H, Hamzelou S, Farzaneh M, Ghassempour A (2013) Effect of silver nanoparticles on Oryza sativa L. and its rhizosphere bacteria. Ecotox Environ Safe 88:48–44

Nwadinigwe AO, Ugwu EC (2018) Overview of nano-phytoremediation applications. In: Ansari AA et al (eds) Phytoremediation. Springer Nature, Switzerland, pp 377–400

O'Hara S, Krug T, Quinn J, Clausen C, Geiger C (2006) Field and laboratory evaluation of the treatment of DNAPL source zones using emulsified zero-valent iron. Remediation 16:35–36

Oberdorster G, Oberdorster E, Oberdorster J (2005) Nanotoxicology: an emerging discipline evolving from studies of ultrafine particles. Environ Health Perspect 113(7):823–829

Otto M (2009) Nanotechnology for site remediation. Proceedings conference on the environmental implications and applications of nanotechnology; 9–11 June 2009; Amherst Massachusetts. p 77–80

Palaniselvam K, Mashitah M, Yusoff G, Natanamurugaraj G (2016) Biosynthesis of metallic nanoparticles using plant derivatives and their new avenues in pharmacological applications—an updated report. Saudi Pharm J 24:473–474

Patil SS, Shedbalkar UU, Truskewycz A, Chopade BA, Ball AS (2016) Nanoparticles for environmental clean-up: a review of potential risks and emerging solutions. Environ Technol Innov 5:10–11

Popescu I-C, Filip P, Humelnicu D, Humelnicu I, Bligh Scott T, Crane RA (2013) Removal of uranium (VI) from aqueous systems by nanoscale zero-valent iron particles suspended in carboxymethyl cellulose. J Nucl Mater 443:250–255

Qian Y, Qin C, Chen M, Lin S (2020) Nanotechnology in soil remediation—applications vs. implications. Ecotoxicol Environ Saf 201:110815–110819

Racuciu M, Creanga DE (2007) TMA-OH coated magnetic nanoparticles internalized in vegetal tissues. Romanian J Phys 52:395–392

Rajan CS (2011) Nanotechnology in groundwater remediation. Int J Environ Sci Develop 2(3):182–187

Raloff J (2005) Nano hazards: exposure to minute particles harms lungs, circulatory system. Sci News 167:179

Rao GP, Lu C, Su F (2007) Sorption of divalent metal ions from aqueous solutions by carbon nanotubes: a review. Sep Purif Technol 58(1):224–221

Reinhart DR, Clausen C, Geiger CL, Quinn J, Brooks K (2003) Zero-valent metal emulsion for reductive dehalogenation of DNAPLs. U.S. Patent US7037946B1

Riba O, Scott TB, Vala K, Ragnarsdottir GC (2008) Allen reaction mechanism of uranyl in the presence of zero-valent iron nanoparticles. Geochim Cosmochim Acta 72:4047–4047

Rickerby D (2008) Nanotechnological solutions for monitoring and treatment of drinking water and groundwater. Proceedings Conference on the Environmental Implications and Applications of Nanotechnology; 2009 June 9–11; Amherst Massachusetts; 2009; p 83–86

Rico CM, Majumdar S, Duarte-Gardea M, Peralta-Videa JR, Gardea-Torresdey JL (2011) Interaction of nanoparticles with edible plants and their possible implications in the food chain. J Agric Food Chem 59:3485–3488

Rizwan MD, Singh M, Mitra CK, Morve RK (2014) Ecofriendly application of nanomaterials: nanobioremediation. J Nanopart 1:1–7

Rizzi L, Petruzzelli G, Poggio G, Vigna GG (2004) Soil physical changes and plant availability of Zn and Pb in a treatability test of phytostabilization. Chemosphere 57(9):1039–1036

Roco MC (2005) The emergence and policy implications of converging new technologies integrated from the nanoscale. J Nanopart Res 7(2–3):129–123

Rose-Pehrsson SL, Pehrsson PE (2005) Sensors and sensor systems: an overview. In: Nanotechnology and the environment: applications and implications. American Chemical Society. p 154–156

Ruffini Castiglione M, Cremonini R (2009) Nanoparticles and higher plants. Caryologia 62(2):161–165

Ruttkay-Nedecky B, Krystofova O, Nejdl L, Adam V (2017) Nanoparticles based on essential metals and their phytotoxicity. J Nanobiotechnol 15:33–40

Saleh N, Kim H-J, Phenrat T, Matyjaszewski K, Tilton RD, Lowry GV (2008) Ionic strength and composition affect the mobility of surface-modified Fe0 nanoparticles in water-saturated sand columns. Environ Sci Technol 42:3349–3345

Salt DE, Smith RD, Raskin I (1998) Phytoremediation. Annu Rev Plant Physiol Plant Mol Biol 49:643–648

Sarkar S, Enamala MK, Chavali M, Sarma GVSS, Mannam KM, Kadie A, Veeramuthu A, Chandrasekhar K, Ponvel KM, Kandikonda RK (2021) Nanophytoremediation: an overview of novel and sustainable biological advancement. Import Appl Nanotechnol 6(5):47–41

Sarma H (2011) Metal hyperaccumulation in plants: a review focusing on phytoremediation technology. Environ Sci Technol 4:118–118

Satapanajaru T, Comfort SD, Shea PJ (2003) Enhancing metolachlor destruction rates with aluminium and iron salts during zerovalent iron treatment. J Environ Qual 32:1726–1724

Savage N, Diallo MS (2005) Nanomaterials and water purification: opportunities and challenges. J Nanopart Res 7(4):331–332

Sayes CM, Fortner JD, Guo W, Lyon D, Boyd AM, Ausman KD, Tao YJ, Sitharaman B, Wilson LJ, Hughes JB, West JL, Colvin VL (2004) The differential cytotoxicity of water soluble fullerenes. Nano Lett 4(10):1881–1887

Scott TB [internet] (2005) Sorption of uranium onto iron bearing minerals. [Student thesis: Doctoral Thesis (PhD)] Available at: https://research-information.bris.ac.uk/en/studentTheses/sorption-of-uranium-onto-iron-bearing-minerals

Scott TB, Allen GC, Heard PJ, Lewis AC, Lee DF (2005) The extraction of uranium from groundwaters on iron surfaces. Proc R Soc 461:1247–1249

Sen J, Pravin P, De N (2015) Nano-clay composite and phyto-nanotechnology: a new horizon to food security issue in indian agriculture. J Global Biosci 4(5):2187–2188

Shi Z, Fan D, Johnson RL, Tratnyek PG, Nurmi JT, Wu Y, Williams KH (2015) Methods for characterizing the fate and effects of nano zerovalent iron during groundwater remediation. J Contam Hydrol 181:17–15

Singh R, Misra V (2016) Stabilization of zero-valent iron nanoparticles: role of polymers and surfactants. In: Aliofkhazraei M (ed) Handbook of nanoparticles. Cham, Springer, pp 985–1007

Srivastav A, Yadav KK, Yadav S, Gupta N, Singh JK, Katiyar R, Kumar V (2019) Nanophytoremediation of pollutants from contaminated soil environment: current scenario and future prospects. In: Ansari A, Gill S, Gill R, Lanza G, Newman L (eds) Phytoremediation. Springer, Cham, pp 383–401

Su C, Puls RW (2001a) Arsenate and arsenite removal by zerovalent iron: kinetics, redox transformation, and implications for in situ groundwater remediation. Environ Sci Technol 35:1487–1482

Su C, Puls RW (2001b) Arsenate and arsenite removal by zerovalent iron: effects of phosphate, silicate, carbonate, borate, sulfate, chromate, molybdate, and nitrate, relative to chloride. Environ Sci Technol 35:4562–4568

Sun Y, Li X, Cao XJ, Zhang W, Wang HP (2006) Characterization of zero-valent iron nanoparticles. Adv Colloid Interf Sci 120:47–46

Suryanarayana C (1995) Nanocrystalline materials. Int Mater Rev 40:41–44

Thangadurai P, Joicy S, Beura R, Kumar JS, Chitrarasu K (2019) Emerging nanomaterials in energy and environmental science: an overview. In: Rajendran S, Naushad M, Raju K, Boukherroub R (eds) Emerging nanostructured materials for energy and environmental science. Environmental chemistry for a sustainable world, vol 23. Springer, Cham

Theron J, Walker JA, Cloete TE (2008) Nanotechnology and water treatment: applications and emerging opportunities. Crit Rev Microbiol 34(1):43–49

Tratnyek PG, Johnson RL (2006) Nanotechnologies for environmental cleanup. NanoToday 1(2):44–48

Tratnyek PG, Scherer MM, Johnson TL, Matheson LJ (2003) Permeable reactive barriers of iron and other zero-valent metals. In: Tarr MA (ed) Chemical degradation methods for wastes and pollutants: environmental and industrial applications. Marcel Dekker, New York. cap 9

Triay IR, Lu N, Cotter CR, Kitten HD (1997) Iron oxide colloid facilitated plutonium transport in gound water. Abstracts of Papers of the American Chemical Society. Amer Chemical Soc, Washington, DC

U.S. EPA (2008) [internet] Nanotechnology for site remediation: fact sheet. EPA 542-F-08-009. US Environmental, Washington, DC. Available at: https://www.epa.gov/sites/default/files/2015-04/documents/nano_tech_remediation_542-f-08-009.pdf

Üzüm Ç, Shahwan T, Eroğlu AE, Lieberwirth I, Scott TB, Hallam KR (2008) Application of zero-valent iron nanoparticles for the removal of aqueous Co^{2+} ions under various experimental conditions. Chem Eng J 144:213–222

Vázquez-Núñez E, Molina-Guerrero CE, Peña-Castro JM, Fernández-Luqueño F, de la Rosa-Álvarez MaG. (2020) Use of nanotechnology for the bioremediation of contaminants: a review. Processes 8(7):826–824

Verma P, Rawat S (2021) Rhizoremediation of heavy metal and xenobiotic-contaminated soil: an eco- friendly approach. In: Shah MP (ed) Removal of emerging contaminants through microbial processes. Springer, Singapore, pp 95–113

Verma N, Zafar S, Talha M (2019) Influence of nano-hydroxyapatite on mechanical behavior of microwave processed polycaprolactone composite foams. Mater Res Exp 6(8):128–125

Wang WC, Freemark K (1995) The use of plants for environmental monitoring and assessment. Ecotoxicol Environ Saf 30(3):289–281

Wang CB, Zhang WX (1997) Synthesizing nanoscale iron particles for rapid and complete dechlorination of TCE and PCBs. Environ Sci Technol 31:2154–2156

Watlington K [internet] (2005) Emerging nanotechnologies for site remediation and wastewater treatment environmental protection agency. pp 1–55. Available at: https://citeseerx.ist.psu.edu/viewdoc/download?doi=10.1.1.134.3428&rep=rep1&type=pdf

White AF, Peterson ML (1996) Reduction of aqueous transition metal species on the surface on Fe(II)-containing oxides. Geochim Cosmochim Acta 60:3799–3794

Xq L, Zhang W-x (2007) Sequestration of metal cations with zerovalent iron nanoparticles—a study with high resolution X-ray photoelectron spectroscopy (HR-XPS). J Phys Chem C 111:6939–6936

Yadav KK, Singh JK, Gupta N, Kumar V (2017) A review of nanobioremediation technologies for environmental cleanup: a novel biological approach. JMES 8(2):740–747

Yogalakshmi KN, Das A, Rani G, Jaswal V, Randhawa JS (2020) Nano-bioremediation: a new age technology for the treatment of dyes in textile effluents. In: Saxena G, Bharagava R (eds) Bioremediation of industrial waste for environmental safety. Singapore, Springer, pp 313–347

Zhang W (2003) Nanoscale iron particles for environmental remediation: an overview. J Nanopart Res 5:323–322

Zhang W-x, Elliott DW (2006) Applications of iron nanoparticles for groundwater remediation. Remediation 16(2):7–21

Zhang T, Lowry GV, Capiro NL, Chen J, Chen W, Chen Y, Dionysiou DD, Elliott DW, Ghoshal S, Hofmann T, Hsu-Kim H, Hughes J, Jiang C, Jiang G, Jing C, Kavanaugh M, Li Q, Liu S, Ma J, Pan B, Phenrat T, Qu X, Quan X, Saleh N, Vikesland PJ, Wang Q, Westerhoff P, Wong MS, Xia T, Xing B, Yan B, Zhang L, Zhou D, Alvarez PJJ (2019) In situ remediation of subsurface contamination: opportunities and challenges for nanotechnology and advanced material. Environ Sci: Nano Issue 5:1283–1282

Zhao X, Liu W, Cai Z, Han B, Qian T, Zhao D (2016) An overview of preparation and applications of stabilized zero-valent iron nanoparticles for soil and groundwater remediation. Water Res 100:245–246

Chapter 20
Nanotechnology in Phytoremediation: Application and Future

Tayyaba Yasmin, Sameen Ruqia Imadi, and Alvina Gul

Abstract Nanotechnology is an emerging approach in the field of agriculture. Among the many aspects of nanotechnology is the enhancement of plants' capabilities of phytoremediation of the soil and water, suggesting its role in the agricultural industry. Nanoparticles have many benefits over traditional soil remediating technologies, the most important of which are their size and surface area. Due to the small size of particles, nanotechnology work wonders. This chapter focuses on the role of nanotechnology in phytoremediation, its applications, and future aspects. Different types of nanoparticles can be used in the cleaning and detoxification of different kinds of pollutants. All of these features of nanoparticles have been discussed in detail in this chapter. As further research has been conducted and different sciences have been combined, there is more to this interesting field, which is yet to be discovered. Reclamation of the planet is a difficult task, but it is expected that nanophytoremediation is the answer to all of these problems.

Keywords Nanophytoremediation · Nano zero-valent iron · Nanoparticles · Soil remediation · Detoxification

---

T. Yasmin
COMSATS University Islamabad, Islamabad, Pakistan

S. R. Imadi
Commission on Science and Technology for Sustainable Development in the South (COMSATS) Secretariat, Islamabad, Pakistan

A. Gul (✉)
Atta ur Rahman School of Applied Biosciences (ASAB), National University of Sciences and Technology (NUST), Islamabad, Pakistan

L. Newman et al. (eds.), *Phytoremediation*, https://doi.org/10.1007/978-3-031-17988-4_20

20.1 Introduction to Nanotechnology

Nanotechnology is an amazing field, which has helped in the exploration of multiple areas of industry including medicine and agriculture. Nanoparticle is a term used for very small, nano-size aggregated particles of atoms or molecules. These particles have a size as small as 1 nm to 100 nm. There are three main types of nanoparticles (NPs), which are natural nanoparticles, incidental nanoparticles, and engineered nanoparticles (Nwadinigwe and Ugwu 2019).

Nanoparticles are a wonderful addition to the enhancement of crop production technologies, because they reduce the loss of nutrients, reduce environmental stresses, and increase the yields of crops. Besides this, many different sorts of contaminants are released into the environment. These chemicals have to be remediated in order to maintain high crop productivity and enhance environmental sustainability. One of the most amazing approaches for the remediation of these chemicals is with the help of nanoparticles (Ahmad et al. 2019).

20.2 Phytoremediation

The degradation of soil due to excess pollutants is a global concern. It only has serious impacts on agricultural yield but also causes a threat to food security. Adding to this crisis are unmanageable and non-degradable pollutants like heavy metals, persistent organic pollutants, and pesticides. It also leads to the contamination of the food chain (Bakshi and Abhilash 2020). Phytoremediation is a highly advantageous technique, because it only focuses on the natural processes of plants including translocation, bioaccumulation, and evapotranspiration, which leads to the degradation of contaminants. In other words, it can be said that phytoremediation is a rapid green alternative technology to get rid of environmental pollution, especially soil and water pollution (Sarkar et al. 2021).

Phytoremediation is an environment-friendly technique to get rid of contaminants from soil. Different types of chemicals, which pollute the soil include organic chemicals, inorganic chemicals, persistent chemicals, and nonpersistent chemicals. These pollutants are a reason behind the change in structure as well as the function of a sustainable ecosystem and thus pose negative effects on human life and biodiversity (Srivastav et al. 2019). The current phytoremediation techniques have a drawback in that they are very costly, and hence they are not suitable to use on larger scales. However, research has been conducted on plant-based phytoremediation, which might be able to remediate heavy metals and contaminants from the soil (Khan 2020).

The plants which are used in the remediation of soil are usually metal tolerant and hyperaccumulators. Transgenic plants can also be used for nanophytoremediation. The selection of plants depends upon the nature of contaminants in the soil and groundwater (Sarkar et al. 2021). Phytoremediation is considered to be the most environment-friendly and cost-effective method to reclaim the soil. Many plants have shown their potential to remediate toxic metals, metalloids, petroleum compounds, herbicides, pesticides, oil spillages, and radionuclides. Phytoremediation follows an intensive mechanism to detoxify the environment. This includes phytoaccumulation, phytovolatilization, phytostabilization, and rhizofiltration (Shackira et al. 2021).

20.2.1 Nanophytoremediation

Nanobioremediation is the process of using algal, fungal, and bacterial nanoparticles for the removal of contaminants from the environment and soil, including, organic waste, inorganic waste, and heavy metals. However, if higher plants are used for this process of making nanoparticles for the removal of contaminants from the environment, the process is known as nano-phytoremediation (Ndaba et al. 2021). It is known that nanotechnology increases the efficiency of phytoremediation because the size of nanoparticles is so small that they can reach places, that are not accessible easily. Basically, nanophytoremediation enhances the degradation of complex organic compounds, which is not possible otherwise. The process is performed by the activity of microorganisms as well as plants, which are encapsulated in the enzymes within nanoparticles (Nwadinigwe and Ugwu 2019).

With phytoremediation using nanoparticles, the decontamination efficiency is increased because of a dramatic increase in the surface area of the nanoparticles (Srivastav et al. 2019). Nanoparticle-enabled remediation techniques of soil can prove to be a sustainable source for revitalizing the damaged and contaminated soil. These techniques are not only simple to perform, but they also are cost-effective (Bakshi and Abhilash 2020). Nanomaterials can function in phytoremediation by performing three actions.

- Removal of pollutants directly
- Enhancement of growth of plants
- Increase in phyto-availability of pollutants (Song et al. 2019)

Nanoparticles can be used for phytoremediation, following two types of procedures. They can be used as a helper to degrade the contaminants in soil and groundwater by immobilization, or they can be producing remediating microbial enzymes, which help in revitalizing the environment (Benjamin et al. 2019). Soil reclamation through nanophytoremediation is done by adding nanomaterials to soil, which amends its nature. NPs immobilize the pollutants in soil through different mechanisms including redox, sorption, and precipitation (Baragaño et al. 2021). The nanomaterials which are most commonly used in bioremediation or phytoremediation of soil and groundwater include nano silica, nano zero-valent iron, nano zinc oxide, and nano sized iron sulfide particles (El-Ramady et al. 2020).

Ficus iron nanoparticles, Ipomea silver nanoparticles, and Brassica silver nanoparticles were used to remediate chlorfenapyr from contaminated soil as well as contaminated water. Chlorfenapyr is an insecticide, which is used for protection of plants from mites and insects. Plantago major was also used to enhance the solubility of the particles. It was observed that the degradation rates of chlorfenapyr were enhanced by 71.22% in response to ficus iron nanoparticles, 57.32% in response to Ipomea silver nanoparticles, and 73.10% in response to Brassica silver nanoparticles. Hence, it is suggested that nanophytoremediation improves with the use of solubility-improving agents like Plantago major (Romeh and Saber 2020).

20.3 Applications of Nanophytoremediation

Nanoparticles are used in bioremediation for their known features, which include the following:

- Small size
- Consuming less time
- Cost-effective
- High number of active surface sites
- High adsorption capacities

Fig. 20.1 Features of nanoparticles making them an excellent candidate for phytoremediation

- Flexible to be used in in situ and ex situ procedures
- Increased surface area as compared to bulk compounds
- Capability to control release at target site
- Ability to selectively load a wide range of molecules
- Decreased volume that enhances reactivity
- Enhance plant's resistance to many environmental stresses (Thangadurai et al. 2020; Kumar et al. 2021; Martínez-Fernández et al. 2017; Mohammadi et al. 2019; Fig. 20.1)

20.3.1 Water Purification

Besides the remediation of soils, phytoremediation can also be used for the purification of water. Removal of contaminants enhances when phytoremediation is accompanied with nanotechnology (Bhati and Rai 2019). Wastewater has been used for crop production since centuries. Moreover, with the increasing shortage of fresh water globally, wastewater is a suitable candidate for the substitution of fresh water. Nanoparticles are a potent agent to remediate wastewater from heavy metals and contaminants. They can be used alone or can be combined with PGPR to enhance the efficiency of remediation. It has been observed that silver nanoparticles, combined with rhizobacteria enhance the efficiency of bioremediation of wastewater to be used for enhancing crop yields (Khan and Bano 2019).

Wastewater treatment is a matter of concern because the existing technologies pose toxic effects on the environment. It is suggested that nanotechnology might be the answer to wastewater treatment, because it is an efficient and clean system. It not only remediates organic pollutants, but also has a role in immobilizing and removing heavy metals, including cadmium, chromium, lead, mercury, and zinc, as well as pesticides. Besides, nanomaterials add further value in treating wastewater as they are known to possess antimicrobial properties, so they disinfect the water in all possible capacities (Singh et al. 2019a, b).

20.3.2 Organic Pollutants

Chlorinated volatile organic compounds (CVOC) are some of the organic pollutants, which pose a major threat to the sustainability of the environment. Many CVOCs are found in groundwater as well as soil. Although the use of these compounds is now restricted, a still significant amount is observed to be present in the environment. The remediation of CVOC is possible by combining different technologies to build the nanophytoremediation technique because there is no single technology present to deal with these. Bioremediation integrated with reduction by nanoscale zero-valent iron is a potent strategy to get rid of these contaminants from soil (Ebrahimbabaie and Pitchel 2021).

In a study, Triton X-100 was used in combination with nano silicon dioxide particles on the plants of *Erigeron annuus* in order to observe the phytoremediation efficiency of polycyclic aromatic hydrocarbons. It was seen that the treatment of plants with silicon dioxide nanoparticles and Tritox X-100 increases the stress of these hydrocarbons in plants predicting their role as a bioaccumulator, hence a phytoremediation candidate for contaminated soils (Zuo et al. 2020).

20.3.3 Removal of Chlorinated Pesticides

Nanophytoremediation has been used to remove endosulfan from the soil samples. The remediation was confirmed with the help of gas chromatography and mass spectrometry. For this purpose, zero-valent iron nanoparticles were used in combination with different plants. The best efficiency of nano-phytoremediation was observed to be performed by *A. calcarata,* followed by *O. sanctum,* whose efficiency is followed by *C.citratus.* The processes, which are involved in the degradation of chlorinated pesticides, involve hydrogenolysis and dehalogenation (Jesitha and Harikumar 2019).

20.3.4 Removal of Insecticides

Fipronil, a widely used insecticide, is known to cause severe neurotoxicity, endocrine-related problems, and carcinogenesis, even when taken in small amounts. It has been observed that when this insecticide is present in the soil, a small amount can be absorbed by plants, as well as it gets leached into the groundwater as a potential contaminant. The research was performed, in which silver nanoparticles in combination with different plants were used for remediation of fipronil from soil samples. The results suggested that *Brassica* silver nanoparticles reduced fipronil components from groundwater samples with an efficiency of 95.45%, followed by *Ipomoea* silver nanoparticles with an efficiency of 90.15%, which is further followed by *Camellia* silver nanoparticles having an efficiency of 63.65%. The lowest phytoremediation efficiency was found to be of *Plantago* silver nanoparticles, which is 63.48%. It was also observed that when these plants were used without silver nanoparticles, was just 18.42%. Besides, when the same combination of plants and silver nanoparticles were used on soil samples for fipronil removal, the efficiency observed is given. *Brassica*-AgNPs 68.8%, *Ipomoea*-AgNPs 54.64%, *Camellia*-AgNPs 43.75%, and *Plantago*-AgNPs 30.99%. All of these results were obtained after a treatment of samples for 2 days (Romeh 2018).

20.3.5 Heavy Metals and Metalloids

Toxic heavy metals like cadmium, arsenic, lead, chromium, and mercury can accumulate in agricultural soil. This leads to the severe contamination of the soil and groundwater by heavy metals and their metalloids, posing a serious threat to not only the natural biodiversity of soil but also to human health (Chen et al. 2021a, b; Kaur and Roy 2021). Many techniques have been used to remediate the soil of heavy metals, but since the pollution rate is too high, they become very costly, which makes them ineffective. Nanophytoremediation seems like the only potent solution for the remediation of heavy metals and metalloids from the soil and groundwater (Lodhi et al. 2020).

Research has been performed on different types of nanoparticles to remediate heavy metals and their metalloids from the soil. Some of these nanoparticles include metallic nanoparticles, magnetic nanoparticles, nanowires, nanotubes, and nano fibers (Mehrotra et al. 2021). Magnetic nanoparticles are observed to be an amazing alternative for in situ remediations of heavy metals. These nanoparticles have extensive features, like re-usability that help in reducing the costs further (Maqbool et al. 2019). It is proposed that further research should be conducted on the use of magnetic nanoparticles for the removal of heavy metals from the soil, because it has farfetched benefits.

Silver and copper oxide nanoparticles were prepared on the leaf extract of *Catharanthus roseus.* This combination was utilized to observe the efficiency of remediation of heavy metals including chromium and cadmium. It was seen that the biogenic silver nanoparticles removed the highest level of chromium that is 47.84% as well as removed the levels of cadmium which is 5.68%. the study suggests proper utilization of biogenic silver and copper oxide nanoparticles for bioremediation of soil (Verma and Bharadvaja 2021). Effects of chitosan nanoparticles on the phytoremediation ability of cadmium accumulator plant, *Datura stramonium* were studied. It was observed that the application of chitosan nanoparticles significantly enhances the ability of this plant to remediate cadmium from the soil, which makes this combination an amazing green candidate for phytoremediation of the environment (Shirkhani et al. 2021).

Heavy metal phytoremediation abilities of two aquatic plants *Eichhornia crassipes* and *Salvinia molesta* were studied in the presence of titanium oxide nanoparticles. It was observed that the system is highly efficient for the remediation of lead, cadmium, and copper from water (Harikumar and Megha 2017). Around 160 days old white willow plant pots were treated with nano zero-valent iron and rhizosphere microorganisms, to observe the effects on their remediation capabilities of heavy metals including lead, copper, and cadmium. It was observed that low doses of nano zero-valent iron and rhizosphere microorganisms result in enhanced growth of plant thus increasing the accumulation of heavy metals in roots and shoots, however high dose of nanoparticle treatment resulted in the reduction of the growth of white willow. White willow is suggested to be a potential candidate for nanophytoremediation of heavy metals (Mokarram-Kashtiban et al. 2019).

K. scoparia plants were exposed to different levels of nano zero-valent iron in order to find out the nanoparticles' effect on the efficiency of the plant to accumulate lead. It was observed that lower levels of nano zero-valent iron particles enhance the capacity of *K. scoparia* to absorb lead. The maximum capacity was observed at the treatment scale of 100 to 500 mg/kg nZVI in each pot. In these pots, lead accumulation was as higher as 857.18 micrograms per pot, which is an indicator that the system of *K.scoparia* and nano zero-valent iron is a worthy candidate for phytoremediation of lead-contaminated soils and water (Zand and Tabrizi 2021).

20.3.6 Agrochemicals

Agrochemicals are known to be the most widely present contaminants in the soil. Their presence is a risk to human health because they have the potency to cause damage to health including nervous system damage as well as cancer. An approach is required to remediate these from the soils to ensure a non-toxic agricultural system around the world. For this purpose, nanophytoremediation approach can be used. The nanoparticles immobilize agrochemicals within the soil, and the plants then accumulate these chemicals easily (Sebastian et al. 2020).

20.3.7 Fluoride

Fluoride pollution is also a very common type of pollution. More than 200 million people around the globe get affected by fluoride pollution annually. Fluoride accumulator plants *Prosopis juliflora* in combination with iron oxide nanoparticles were used in a study to observe the accumulation efficiency. The nanophytoremediation technique enables *P. juliflora* to accumulate 28.43 mg/kg of fluoride from the soil samples in shoots and 34.64 mg/kg of fluoride in roots, thus making the avenues for utilization of nanophytoremediation in fluoride removal from the soil (Kumari and Khan 2018).

20.3.8 Dyes

Interestingly, certain dyes can be removed using nanoparticles. In a study, silver nanoparticles were prepared on the aqueous leaf extracts of *Lagerstroemia speciosa.* These nanoparticles were used to observe their efficiency against two dyes methyl orange and methylene blue. It was observed that the dyes degraded at a high rate of 310 and 290 min, respectively, which gives strong evidence for remediation of contamination by dyes in the environment (Saraswathi et al. 2017). In a study, mangroves were treated with nanoparticles and their potential as a candidate for remediation of dyes from industrial waste effluent was observed. It is predicted that mangroves can play an essential role in future nanophytoremediation technologies for dyes because of their high absorption capacity (Vaish and Pathak 2020).

20.3.9 Acid Mine Drainage

Acid mine drainage is a term used for the drains of mining sites that have rich sulfur content. Acid mine drainage is a very well-known contaminant of the environment and is very hard to get rid of. It affects biodiversity as well as pollutes the atmosphere. Hyperaccumulator plants in combination with nanoparticles can be used to immobilize the acid mine drainage and degrade toxic compounds into nontoxic byproducts thus reducing the pollution of environment (Das 2018).

20.4 Types of Nanoparticles to Be Used in Phytoremediation

Based on the contaminants, which are to be remediated, there are different types of nanoparticles. The most used nanoparticles include iron oxides, zinc oxides, manganese oxides, titanium oxides, and cerium oxides (Martínez-Fernández et al. 2017).

20.4.1 Nanoscale Zero-Valent Iron

Nanoscale zero-valent iron is known to be the most studied nanoparticle for phytoremediation. It has facilitated phytoremediation in research because it can be successfully engineered on a large scale. These nanoparticles can be used for the treatment of contaminated water as well as contaminated soil. These nanoparticles can also increase the phyto-availability of pollutants in both soil and water (Song et al. 2019). In a research study, zero-valent iron nanoparticles were used in combination with boat lily (*Tradescantia spathacea*) and *Alternanthera dentate* to remediate the soil of heavy metals. It has been observed that the plants when used with nZVI were able to accumulate 73.7% lead and 71.3% Cadmium, hence making it a potent approach for soil remediation (Jesitha and Harikumar 2019). The most widely used nanoparticles for phytoremediation are nanoscale zero-valent iron. These NPs remediate by immobilizing the contaminants in the soil (Baragaño et al. 2021).

Nanoscale zero-valent iron in combination with *Lolium perenne* was used, in a study, on soil samples, which were highly toxic with lead accumulation. It was observed that with the treatment of 100 mg/kg of nZVI, the maximum lead accumulation capacity of *Lolium perenne* was 1175.40 microgram per pot, predicting an alternative treatment for lead toxicity (Huang et al. 2018). The efficiency of nano zero-valent iron in the combination of *Marjoram* and *Moringa* was observed against the soil pollutant thiamethoxam, which is a pesticide. It has been seen that the nano zero-valent iron in combination with *Marjoram* gives enhanced efficiency of thiamethoxam removal from the soil, which is 75.13%. the nano zero-valent iron with *Moringa* has an efficiency of 61.06% in remediating the soil from this pesticide. Further, if this combination of nanoparticle and plant were used with *Helianthus annuus,* the pesticide is removed more quickly from the soil, because *H. annuus* is an accumulator plant (Rady et al. 2019a).

Ficus zero-valent iron nanoparticles were used in combination with *Plantago major* to observe the efficiency of remediation of Chlorpyrifos from fresh water. It is predicted that the combination is highly effective against the contaminant and can help in getting rid of chlorpyrifos contamination from the water on a large scale (Romeh 2021). Flonicamid contaminated water can be remediated from the pollutants with the help of *Plantago major* L. plus nano zero-valent iron, as predicted by research (Rady et al. 2019b).

A very interesting strategy is to use zero-valent iron nanoparticles on ornamental plants for enhancing their phytoremediation capacity of heavy metals. In this scenario, a study was performed to clean up the urban soil from heavy metals including Arsenic, Lead, and Mercury. Nano zero-valent iron particles were applied to four different ornamental plants. It was observed that the most accumulation of toxic substances was in *Cosmos bipinnatus*, which accumulates around 41.24 mg/kg arsenic, 139.15 mg/kg lead, and 15.57 mg/kg mercury. *Impatiens balsamina* was found to be the most sensitive plant among the four varieties, and hence showed the least accumulation of the metals and most damage. *Catharanthus roseus* and *Gomphrena globose* showed the medium capacity for the accumulation of metals and metalloids. Hence it is suggested that further research should be performed on cosmos combined with nano zero-valent iron to design an efficient phytoremediation approach (Majumdar et al. 2021).

20.4.2 Titanium Oxide Nanoparticles

Titanium oxide nanoparticles were used in combination with *S. bicolor* to remediate the Antimony-contaminated soil. It was observed that the phytoextraction ability of *S. bicolor* was enhanced with the use of titanium nanoparticles, by manifolds. Soils polluted with metals and metalloids can be remediated with the use of titanium oxide nanoparticles and plants (Zand and Heir 2020). In a study, titanium oxide nanoparticles and plant growth promoting rhizobacteria were used on *Trifolium* repens for remediating the cadmium polluted soil. *T. repens* is a cadmium hyperaccumulator. It was observed that the phytoremediation capacity of *T. repens* was the highest when titanium oxide nanoparticles were used at a concentration of 500 mg/kg, which is 1235 microgram per pot. After this when the amount of nanoparticles were increased, it showed a negative effect on the plant's growth. This study suggests that an association of plant, titanium oxide nanoparticles and plant growth promoting rhizobacteria can enhance phytoremediation of soil in the best possible manner (Zand et al. 2020).

20.4.3 Functional Carbon Nanodots

Functional carbon nanodots were used in research with water hyacinths, which have hyperaccumulation capacity for heavy metals. The experiments were performed on lead and cadmium stress. Due to the reason that functional carbon nanodots have excellent abilities of absorption, it was observed that the heavy metal accumulation capacity of water hyacinths was improved. The treatment with functional carbon nanodots made sure to immobilize excessive heavy metal ions on plants and helped the plant to mitigate oxidative stress. Hence it is suggested that functional carbon nanodots be used for the remediation of cadmium and lead-contaminated water areas (Chen et al. 2021a, b).

20.4.4 Copper Oxide Nanoparticles

Salt marsh plants including *Halimione portulacoides* and *Pragmites australis* were used in a study to observe the effects of copper oxide nanoparticles on their accumulation of microbial community. It was seen that the accumulation of microbial community in *P. australis* was enhanced after treatment with copper oxide nanoparticles. However, reverse results were observed in the case of *H. portulacoides*. With this research, it is suggested that the copper nanoparticles should be used with care and only in the areas which need small-level remediation like estuaries (Fernandes et al. 2017).

20.4.5 Graphene Oxide Nanoparticles

Research was conducted in which the capacity of graphene oxide nanoparticles to accumulate heavy metals was compared with nano zero-valent iron. It was observed that the graphene oxide nanoparticles were able to efficiently immobilize copper, lead, and cadmium, however, they were unable to immobilize arsenic and phosphorus. The nano zero-valent iron was found to immobilize arsenic and lead, and somehow cadmium too. Graphene oxide nanoparticles can be considered as an alternate treatment for the immobilization of heavy metals from the soil and can be combined with plants for phytoremediation (Baragaño et al. 2020).

20.5 Benefits of Nanotechnology in Phytoremediation

Recent studies have predicted that combining phytoremediation and nanomaterials gives a better alternative for the remediation of soil by heavy metals. Moreover, organic contaminants like chlorpyrifos, atrazine, and molinate, can easily be degraded using nanotechnology. Besides, research has been conducted in which nanoparticles were successfully used to degrade the soil contaminated by TNT. Due to these reasons, many nanoparticles have been developed to be used for environmental revitalization (Verma et al. 2021).

The pollution caused due to industrial wastewater from pulp and paper mill effluent can be mitigated with the use of nanoparticles in combination with *Salvinia molesta*. The combination is found to be a potential alternative for current treatments of industrial wastewater (Bhardwaj et al. 2018). Another potential benefit of Nanobioremediation is the minimum level of toxic byproducts. The reason is that in Nanobioremediation, a very small amount of harmful chemicals is used, which increases biodegradability and hence does not let harmful substances contaminate the environment (Chauhan et al. 2020).

Nanophytoremediation is an environment-friendly approach because

- It reduces the emission of greenhouse gases.
- It minimizes the generation of waste products especially toxic substances.
- It consumes natural resources for the preparation of nanoparticles (Sarkar et al. 2021).

Research has been performed on sunflower plants for phytoremediation of cadmium, chromium, lead, and uranium. It has been observed that sunflower plants easily accumulate these heavy metals from the soil and help in remediation. Nanoparticles can be used in combination with sunflower plants to enhance their ability to phytoremediation the soil (Nguyen et al. 2021).

Nanoparticles when combined with beneficial microorganisms, are known to enhance the accumulation capabilities of plants. Acidic soils which were polluted with cadmium, zinc, and lead were planted with sweet sorghum. It was treated with nano zero-valent iron and arbuscular mycorrhizal fungi. The system shows the extensive accumulation of immobilized cadmium, lead, and zinc in the plant, predicting the role of a combination of nanotechnology and biotechnology in phytoremediation (Cheng et al. 2021).

20.6 Conclusion and Future Prospects

Nanotechnology is an effective and alternative method for the phytoremediation of contaminated soils. It not only increases the chances of sustainability of soil but can also lead to better biodiversity owing to living soil (Song et al. 2019). It can be said that nanophytoremediation is an effective technique for contaminated soils and groundwater, but the process is still under exploration, which opens many grounds for research (Song et al. 2019). Nanomaterials have proved to have great potential in phytoremediation and are known to address complex problems due to their nature of high reactivity, versatility, and selectivity (Qian et al. 2020).

There is a number of nanoparticles as well as plant species, which have been recognized for their potential in phytoremediation and reclamation of the soil and water. Biotechnology is further opening the ways to develop new techniques, which might lead to a better future for the environment. It is expected that large-scale remediation of soils and water can be possible with nanophytoremediation in near future. Eco-friendly remediation is what the planet needs, and nanotechnology is the answer to the current problems (Kumar et al. 2021).

Nanotechnology can promote sustainable agriculture. Besides nanophytoremediation, nano-fertilizers, nano-biosensors, and nano-pesticides can be used to improve the technologies for agriculture (Usman et al. 2020). Nanophytoremediation is a cutting green technology for remediating soil, water, and air from harmful contaminants. Nanotechnology, in combination with different fields of study, is expected to provide us with solutions to major environmental problems, today's world is facing. From organic pollutants to inorganic pollutants, nanophytoremediation has hidden answers to everything. The future health of the human race as well as the environment is totally dependent on nanotechnology in phytoremediation (Roberto et al. 2020).

Besides phytoremediation, nanotechnology has strengthened its roots in the agricultural industry because it helps in enhancing the quality of food, increasing food safety, reducing the energy required for the growth of plants, and enriching the soil with essential nutrients. Nanofertilizers and nanopesticides are another very important implication of nanotechnology in agriculture. Therefore, it is suggested that the era of harvesting the benefits of nanotechnology has arrived (Prasad et al. 2017). Nanophytoremediation can also be enhanced in the future by combining it with different physical, chemical, and biological approaches. Besides soil reclamation, nanotechnology has its role in the reclamation of the environment as an organism. It helps reduce pollution of different sorts, including water pollution, air pollution, and soil pollution, which will lead us towards a better atmosphere.

Every system has its pros and cons. Although plants show phytotoxicity in response to nanoparticle treatment, nanophytoremediation is considered to be the best approach for remediation of soils in the future. Our future problems of sustainability of the environment and reduction of pollution can be solved with this approach (Singh et al. 2019a, b). Research has to be performed to minimize the detrimental effects of nanoparticles on plants, in order to further enhance the usage of nanophytoremediation for the development of green remediating technologies.

References

Ahmad B, Zaid A, Jaleel H, Khan MMA, Ghorbanpour M (2019) Chapter 13 - Nanotechnology for phytoremediation of heavy metals: mechanisms of nanomaterial-mediated alleviation of toxic metals. In: Advances in phytonanotechnology from synthesis to application, pp. 315–327

Bakshi M, Abhilash PC (2020) Chapter 17 - Nanotechnology for soil remediation: revitalizing the tarnished resource. In: Nano-materials as photocatalysts for degradation of environmental pollutants challenges and possibilities, pp. 345–370

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):1–10

Baragaño D, Forján R, Sierra C, Gallego JLR (2021) Chapter 26 - Nanomaterials for soil remediation: pollutant immobilization and opportunities for hybrid technologies. In: Sorbents materials for controlling environmental pollution current state and trend, pp. 701–723

Benjamin SR, De Lima F, Florean EOPT, Guedes MIF (2019) Current trends in nanotechnology for bioremediation. Int J Environ Poll 66(1–3):19–40

Bhardwaj P, Kaushal J, Naithani V, Singh AP (2018) Phytoremediation of pulp and paper mill effluents by *Salvinia molesta* and its comparison with nanoparticles inclusive phytoremediation. Int J Basic Appl Res 8(8):338–356

Bhati M, Rai R (2019) Nano-phytoremediation application for water contamination. In: Phytoremediation. Springer, Cham, pp 441–452

Chauhan R, Yadav HOS, Sehrawat N (2020) Nanobioremediation: a new and a versatile tool for sustainable environmental clean up – overview. J Mater Environ Sci 11(4):564–573

Chen Q, Cao X, Liu B, Nie X, Liang T, Suhr J et al (2021a) Effects of functional carbon nanodots on water hyacinth response to Cd/Pb stress: implication for phytoremediation. J Environ Manag 299:113624

Chen S, Chen Y, Feng T, Ma H, Liu X, Liu Y (2021b) Application of nanomaterials in repairing heavy metal pollution soil. IOP Conf Ser 621:012123

Cheng P, Zhang S, Wang Q, Feng X, Zhang S, Sun Y et al (2021) Contribution of nano-zero-valent iron and arbuscular mycorrhizal fungi to phytoremediation of heavy metal-contaminated soil. Nano 11(5):1264

Das PK (2018) Phytoremediation and Nanoremediation: emerging techniques for treatment of acid mine drainage water. Def Life Sci J 3(2):190–196

Ebrahimbabaie P, Pichtel J (2021) Biotechnology and nanotechnology for remediation of chlorinated volatile organic compounds: current perspectives. Environ Sci Pollut Res 28:7710–7741

El-Ramady H, El-Henawy A, Amer M, Omara AE, Elsakhawy T, Salama A et al (2020) Agro-pollutants and their nano-remediation from soil and water: a mini-review. Environ Biodivers Soil Secur 4(4):361–375

Fernandes JP, Almeida CMR, Andreotti F, Barros L, Almeida T, Mucha AP (2017) Response of microbial communities colonizing salt marsh plants rhizosphere to copper oxide nanoparticles contamination and its implications for phytoremediation processes. Sci Total Environ 581-582:801–810

Harikumar PS, Megha T (2017) Treatment of cadmium, lead and copper using phytoremediation enhanced by titanium dioxide nanoparticles. Eco Chronicle 12(2):25–34

Huang D, Qin X, Peng Z, Liu Y, Gong X, Zeng G et al (2018) Nanoscale zero-valent iron assisted phytoremediation of Pb in sediment: impacts on metal accumulation and antioxidative system of *Lolium perenne*. Ecotoxicol Environ Safety 153:229–237

Jesitha K, Harikumar PS (2019) Application of nano-phytoremediation technology for soil polluted with pesticide residues and heavy metals. In: Phytoremediation. Springer, Cham, pp 415–439

Kaur S, Roy A (2021) Bioremediation of heavy metals from wastewater using nanomaterials. Environ Dev Sustain 23:9617–9640

Khan AG (2020) Promises and potential of in situ nano-phytoremediation strategy to mycorrhizo-remediate heavy metal contaminated soils using non-food bioenergy crops (*Vetiver zizinoides & Cannabis sativa*). Int J Phytoremediation 22(9):900–915

Khan N, Bano A (2019) Role of PGPR in the phytoremediation of heavy metals and crop growth under municipal wastewater irrigation. In: Phytoremediation. Springer, Cham, pp 135–149

Kumar P, Kumar A, Kumar R (2021) Phytoremediation and nanoremediation. In: New frontiers of nanomaterials and environmental sciences. Springer, Singapore, pp 281–296

Kumari S, Khan S (2018) Effect of Fe3O4 NPs application on fluoride (F) accumulation efficiency of *Prosopis juliflora*. Ecotoxicol Environ Safety 166:419–426

Lodhi RS, Das S, Zhang A, Das P (2020) Nanotechnology for the remediation of heavy metals and metalloids in contaminated water. In: Water pollution & remediation: heavy metals. Springer, Cham, pp 177–209

Majumdar A, Upadhyay MK, Ojha M, Afsal F, Giri B, Srivastava S et al (2021) Enhanced phytoremediation of Metal(loid)s via spiked ZVI nanoparticles: an urban clean-up strategy with ornamental plants. Chemosphere 288:132588

Maqbool A, Hui W, Sarwar MT (2019) Nanotechnology development for in-situ remediation of heavy metal(loid)s contaminated soil. Environ Ecosys Sci 3(2):9–11

Martínez-Fernández D, Vítková M, Michálková Z, Komárek M (2017) Engineered nanomaterials for phytoremediation of metal/metalloid-contaminated soils: implications for plant physiology. In: Phytoremediation. Springer, Cham, pp 369–403

Mehrotra T, Sinha S, Singh R (2021) Chapter 15 - Application of nanotechnology in the remediation of heavy metal toxicity: a promising approach. In: New trends in removal of heavy metals from industrial wastewater. Elsevier, pp. 359–373

Mohammadi P, Hesari M, Samadian H, Hajialyani M, Bayrami Z, Farzaei MH (2019) Chapter one - Recent advancements and new perspectives of phytonanotechnology. Compr Anal Chem 84:1–22

Mokarram-Kashtiban S, Hosseini SM, Kouchaksaraei MT, Younesi H (2019) The impact of nanoparticles zero-valent iron (nZVI) and rhizosphere microorganisms on the phytoremediation ability of white willow and its response. Environ Sci Pollut Res 26:10776–10789

Ndaba B, Bello-Akinosha M, Roopnarain A, Bamuza-Pemu E, Nkuna R, Rama H, et al (2021) Nanobioremediation of contaminated agro-ecosystems applications, challenges and prospect. In: Rhizomicrobiome dynamics in bioremediation. CRC Press

Nguyen DTC, Nguyen TT, Le HTN, Nguyen TTT, Bach LG, Nguyen TD et al (2021) The sunflower plant family for bioenergy, environmental remediation, nanotechnology, medicine, food and agriculture: a review. Environ Chem Lett 19:3701–3726

Nwadinigwe AO, Ugwu EC (2019) Overview of nanophytoremediation applications. In: Phytoremediation. Springer, Cham, pp. 377–382

Prasad R, Bhattacharyya A, Nguyen QD (2017) Nanotechnology in sustainable agriculture: recent developments, challenges, and perspectives. Front Microbiol 8. https://doi.org/10.3389/fmicb.2017.01014

Qian Y, Qin C, Chen M, Lin S (2020) Nanotechnology in soil remediation – applications vs. implications. Ecotoxicol Environ Safety. 201:110815

Rady M, Muhanna AEH, Romeh A (2019a) Remediation of soil polluted with thiamethoxam using green nano – phytotechnology. J Product Dev 24(3):595–610

Rady M, Romeh A, Muhanna AEH (2019b) Using green nano-phytotechnology for remediation of water polluted with flonicamid. J Product Dev 24(3):571–593

Roberto SCC, Andrea PM, Andrés GO, Norma FP, Hermes PH, Gabriela MP, et al (2020) Chapter 9 - Phytonanotechnology and environmental remediation. In: Phytonanotechnology challenges and prospects: micro and nano technologies. Elsevier, pp. 159–185

Romeh AAA (2018) Green silver nanoparticles for enhancing the phytoremediation of soil and water contaminated by fipronil and degradation products. Water Air Soil Poll 229:1–13

Romeh AA (2021) Synergistic effect of Ficus-zero valent iron supported on adsorbents and Plantago major for chlorpyrifos phytoremediation from water. Int J Phytoremediation 3(2):151–161

Romeh AA, Saber RAE (2020) Green nano-phytoremediation and solubility improving agents for the remediation of chlorfenapyr contaminated soil and water. J Environ Manag 260:110104

Saraswathi VS, Kamarudheen N, BhaskaraRao KV, Santhakumar K (2017) Phytoremediation of dyes using Lagerstroemia speciosa mediated silver nanoparticles and its biofilm activity against clinical strains Pseudomonas aeruginosa. J Phytochem Phytobiol B 168:107–116

Sarkar S, Enamala MK, Chavali M, Sarma GVSS, Mannam KM, Kadier A, et al. (2021) Nanophytoremediation: an overview of novel and sustainable biological advancement. In: Importance and applications of nanotechnology. MedDocs Publishers 6(5):47–61

Sebastian A, Nangia A, Prasad MNV (2020) Chapter 18 - Advances in agrochemical remediation using nanoparticles. In: Agrochemicals detection, treatment and remediation: pesticides and chemical fertilizers, pp. 465–485. Elsevier

Shackira AM, Jazeel K, Puthur JT (2021) Chapter 13 - Phycoremediation and phytoremediation: promising tools of green remediation. In: Sustainable environmental clean-up: green remediation. Elsevier, pp. 273–293

Shirkhani Z, Rad AC, Mohsenzadeh F (2021) Improving Cd-phytoremediation ability of Datura stramonium L. by chitosan and chitosan nanoparticles. Biologia 76:2161–2171

Singh DV, Bhat RA, Dervash MA, Qadri H, Mehmood MA, Dar GH et al (2019a) Wonders of nanotechnology for remediation of polluted aquatic environs. In: Fresh water pollution dynamics and remediation. Springer, Singapore, pp 319–339

Singh R, Behera M, Kumar S (2019b) Nano-bioremediation: an innovative remediation technology for treatment and management of contaminated sites. In: Bioremediation of industrial waste for environmental safety. Springer, Singapore, pp 165–182

Song B, Xu P, Chen M, Tang W, Zeng G, Gong J et al (2019) Using nanomaterials to facilitate the phytoremediation of contaminated soil. Cric Rev Environ Sci Technol 49(9):791–824

Srivastav A, Yadav KK, Yadav S, Gupta N, Singh JK, Katiyar R, Kumar V (2019) Nano-phytoremediation of pollutants from contaminated soil environment: current scenario and future prospects. In: Phytoremediation. Springer, Cham, pp. 383–401

Thangadurai D, Chakrabarty M, Sangeetha J (2020) Nanoremediation of polluted environment: current scenario and case studies. In: Handbook of nanomaterials and nanocomposites for energy and environmental applications, pp. 1–16

Usman M, Farooq M, Wakeel A, Nawaz A, Cheema SA, Rehman H et al (2020) Nanotechnology in agriculture: current status, challenges and future opportunities. Sci Total Environ 721:137778

Vaish S, Pathak B (2020) Chapter 19 - Bionano technological approaches for degradation and decolorization of dye by mangrove plants. In: Biotechnological utilization of mangrove resources. Academic Press, pp. 399–412

Verma A, Bharadvaja N (2021) Plant-mediated synthesis and characterization of silver and copper oxide nanoparticles: antibacterial and heavy metal removal activity. J Clust Sci 33:1697. https://doi.org/10.1007/s10876-021-02091-8

Verma A, Roy A, Bharadvaja N (2021) Remediation of heavy metals using nanophytoremediation. In: Advanced oxidation processes for effluent treatment plants. Elsevier, pp. 273–296

Zand AD, Heir AV (2020) Phytoremediation: Data on effects of titanium dioxide nanoparticles on phytoremediation of antimony polluted soil. Data Brief 31:105959

Zand AD, Tabrizi AM (2021) Effect of zero valent iron nanoparticles on the phytoextraction ability of *Kochia scoparia* and its response in Pb contaminated soil. Environ Eng Res 26(4)

Zand AD, Tabrizi AM, Heir AV (2020) Application of titanium dioxide nanoparticles to promote phytoremediation of Cd-polluted soil: contribution of PGPR inoculation. Biorem J 24(2–3):171–189

Zuo R, Liu H, Xi Y, Gu Y, Ren D, Yuan X et al (2020) Nano-SiO2 combined with a surfactant enhanced phenanthrene phytoremediation by *Erigeron annuus* (L.) Pers. Environ Sci Poll Res 27:20538–20544

Chapter 21
Nano-phytoremediation: The Successful Combination of Nanotechnology and Phytoremediation

Melina Borges Teixeira Zanatta, Maycon Lucas de Oliveira, and Lilian Rodrigues Rosa Souza

Abstract Environmental pollution is a recurrent problem since anthropogenic actions constantly expose the environment to toxic compounds. In view of this fact, many decontamination methodologies have been developed such as thermal treatment, oxidation, ion exchange, and others. Among these methods, phytoremediation has the advantage to be a green methodology (since it is employed plants for the remediation) and can efficiently degrade, stabilizes, or accumulates both inorganic and organic pollutants. Nowadays, nanomaterials and some microorganisms have been used combined with phytoremediation in order to improve the remediation and this new approach is called nano-phytoremediation. This chapter discusses the nanomaterials and microorganisms combined with phytoremediation besides explores the mechanisms of remediation of nano-phytoremediation for some nanomaterials combined with plants.

Keywords Nano-phytoremediation · Nanomaterials · Microorganisms · Phytoremediation · Environmental pollution · Remediation

---

Melina Borges Teixeira Zanatta and Maycon Lucas de Oliveira contributed equally with all other contributors.

M. B. T. Zanatta
Environmental Studies Center (CEA), São Paulo State University, UNESP,
Rio Claro, SP, Brazil

M. L. de Oliveira · L. R. R. Souza (✉)
Department of Chemistry, FFCLRP-USP, University of São Paulo - USP,
Ribeirão Preto, SP, Brazil
e-mail: lilianrosa@alumni.usp

L. Newman et al. (eds.), *Phytoremediation*, https://doi.org/10.1007/978-3-031-17988-4_21

21.1 Introduction

The environment is constantly being exposed to different chemical elements from natural and anthropogenic sources. Industrialization and urbanization release a wide range of toxic elements from anthropogenic sources and due to the continuous release of toxic substances, environmental contamination remains a recurrent problem (Souza et al. 2020).

Toxic metals can cause harmful effects on the environment since they can persist in the long term in soil and aquatic environment. Furthermore, they can be easily transferred from one environment to another where direct or indirect exposure can occur, and also be interconverted to different species and become more bioavailable or toxic, adversely affecting the ecosystem and human health. Due to this, a wide range of methods has been applied for the removal of toxic metals including precipitation and cementation, liquid-liquid extraction, cloud-point extraction, immobilization, adsorption methods, and phytoremediation (Souza et al. 2020; Khairy et al. 2014).

Organic pollutants also can cause toxic effects not only for the environment but also the human health. One of the most used methods for remediation of organic pollutants is the oxidation and use of the photocatalytic process (Jiang 2007; McCullagh et al. 2011).

In order to overcome this problem, which affects not only the soil, air, and aquatic environment, different strategies have been developed for environmental remediation, according to the pollutant. The methods of remediation can be divided into physical methods, chemical methods, and biological methods depending on the environment (soil, water, air) (Fig. 21.1). Physical remediation employs physical methods such as thermal treatment, and soil replacement (for soil remediation). Chemical remediation employs chemical reactions to remove the contaminants and

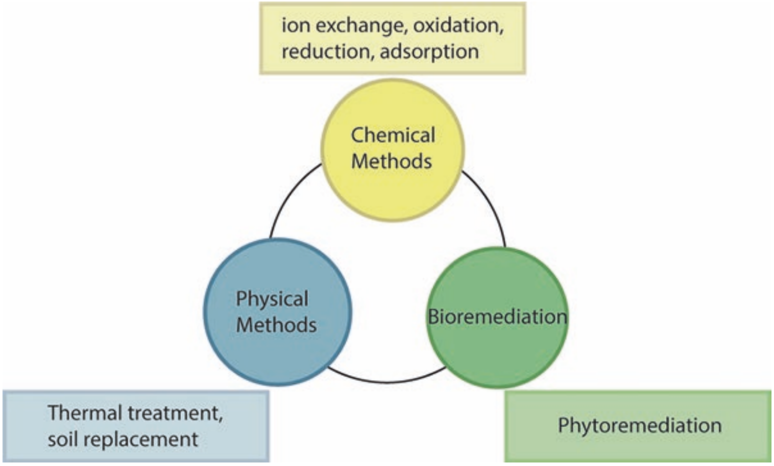


Fig. 21.1 Methods for environmental remediation (Souza et al. 2020; Song et al. 2017)

includes ion exchange, oxidation, reduction, adsorption, and catalytical methods. Biological remediation employs microorganisms and also plants (phytoremediation) in order to remove the contaminants (Song et al. 2017).

Phytoremediation is a remediation method mediated by plants that can accumulate, degrade, or stabilize pollutants such as toxic metals or organic compounds and this methodology can be applied in water, air, and soil environment (Shah and Daverey 2020).

Compared with physical and chemical remediation methods, phytoremediation has the advantage to be less expensive, and environment friendly, and it is considered a sustainable way to restore the contaminated environment (Shah and Daverey 2020), besides to (i) working with organic and inorganic compounds, (ii) it generates recyclable metal-rich plant residue, (iii) planting vegetation on a site also reduces erosion by wind and water, (iv) and practically possible and publicly accepted. On the other hand, there are some limitations such as: (i) the need for a spacious location and proper care, (ii) it can take many growing seasons to clean up a site, (iii) because of the short roots, the plants can clean up the contaminants present only in the soil or the groundwater near the surface, and (iv) plants that absorb toxic materials may contaminate the food chain (Muthusaravanan et al. 2018).

However, the phytoremediation method can be improved by using nanotechnology in order to overcome some of these disadvantages and becoming more effective for environmental remediation.

21.2 Nanotechnology for Environmental Remediation

Nanoremediation is a technology that employs different materials with a diameter of less than 100 nm for remediation of the polluted environment, such as soils, water, sediments, and air. These materials have the benefits of higher surface area and small size (Das 2018; El-Ramady et al. 2017). While several nanomaterials are synthesized, others are naturally found in the environment, including clay mineral nanoparticles (NPs) and bismuth oxide NPs. Several nanoscale materials can be applied for environment nanoremediation such as nanotubes, NPs, nanocomposites, and nanotechnology-based sensors (Borišev et al. 2020).

One of the most commonly used NPs in soil nanoremediation is nanoscale zerovalent iron (nZVI). The size range of most nZVI falls from 10 to 100 nm in diameter and they are composed of Fe, with a noble metal (often palladium) commonly added as a catalyst (bimetallic nanoparticle). When applied in soils, the second metal is useful to aid NPs mobility and distribution (Karn et al. 2011). The action modes of nanomaterials, such as nZVI, can be divided into three: (1) The *physical mode*—due to the large surface area of the materials, the contaminants can be adsorbed and immobilized. (2) The *detoxification mode*—occurs when chemical degradation of toxic compounds is induced and/or catalyzed by nanomaterials, leading to their transformation into less harmful products. (3) The *bio-cooperative mode*—here, the particles increase the bioavailability and degrading of pollutants into more bioremediate species assisting the biotic degradation (Marcon et al. 2021).

For each category of contaminant, there will be some specific material for its remediation. For example, remediation of heavy metals is basically done by adsorption on the surface of metal oxide NPs. On the other hand, redox-active inorganic anions or chlorinated compounds require reducing conditions, so nZVI (or other zero-valent metal NPs—Cu, Ni, and Co) should be applied. Polycyclic aromatic hydrocarbons (PAHs) exhibit a higher redox potential and can be degraded following oxidation reactions induced by metal oxide NPs such as CeO_2 and MnO_2. In this case, nanoremediation can be integrated with others established PAHs remediation approaches to enhance remedial efficiency (Marcon et al. 2021; Kuppusamy et al. 2017).

21.2.1 Inorganic Materials

Recalcitrant or persistent organic pollutants are compounds that are difficult to degrade and can be bioaccumulative. They have high chemical and photochemical stability and a very slow biodegradation rate. Since conventional treatment technologies are ineffective to degrade this type of pollutant, efforts have been made to reduce the level of environmental pollution (Ganie et al. 2021). Photocatalysis emerges as an eco-friendly technique for the degradation of various pollutants and is based on a photochemical process that employs a catalyst to speed up chemical reactions that requires light. In this process, the photocatalyst is activated by light (UV and/or visible light) and the electrons are promoted from the valence band to the conduction band, forming an electron/hole pair (e^-/h^+). The pair induces the formation of highly energetic and reactive species ($^{\cdot}OH$ and O_2^- radicals). Both radicals can react with organic pollutants, oxidizing them into products that are less harmful to the environmental (Ganie et al. 2021; Khan et al. 2015).

The use of nanoscale materials for photocatalysis has gained great interest in the last decade. Different nanomaterials have been developed and TiO_2 nanoparticles have great potential for environmental remediation. They are known for having high thermal stability, low cost, and good resistance. To improve the photocatalytic activity of TiO_2-based particles some modifications may be necessary, including doping TiO_2 with different metals or TiO_2 surface modification with chelating ligands (Tahir et al. 2020). The use of semiconductor nanomaterials has also been studied as nanosensors. They are defined as miniature devices capable of converting chemical interaction into an electrical signal. Ideally, it possesses high sensitivity and reproducibility, fast response, low cost, and low detection limits. These types of devices are able to quantify the composition and detect the presence or absence of a particular pollutant. To overcome some of the disadvantages of the technique, which include high cost, insensitivity, and time-consuming nature, a different method for environmental remediation is based on the fabrication of metal oxide (MO) nanosensors (Ganie et al. 2021; Shafi et al. 2019).

Another investigated material for environmental remediation is magnetic metallic nano adsorbents. The iron and iron oxide NPs are particularly interesting because they can be easily retained, separated, and removed from the remedied environment. These types of nanomaterials can be used for the removal of metals and chlorinated organic solvents (Guerra et al. 2018). Iron NPs usually have a core-shell structure, where the core is composed of Fe^0 ("zerovalent") and the shell is formed by mixed valent oxides (Fe(II) and Fe(III)) (Li and Zhang 2006). The reactivity of these materials can be significantly affected when aggregation occurs, reducing their efficiency in the remediation of environmental contaminants. In addition, the toxicity of the materials involved when using metal and metal oxide NPs is another important factor that must be considered. To overcome some of the limitations associated with monometallic NPs, a second metal can be added to the formulation, increasing the solution stability of the material preventing its aggregation (Guerra et al. 2018).

Mesoporous silica-based adsorbents are a class of materials commonly employed in water remediation. Its beneficial features for remediation include high specific surface area, large pore size, facile surface modification, and chemical inertness. This type of highly porous adsorbent can have its surface functionalized with a wide variety of chemical components. The presence of hydroxyl groups on the silica surface is important for adsorption and surface phenomena and modification. A variety of different materials were synthesized and proved to be efficient for the adsorption of organic and inorganic pollutants, showing the versatility of mesoporous silica-based adsorbents (Guerra et al. 2018; Diagboya and Dikio 2018).

21.2.2 Carbon-Based Nanomaterials

Carbon-based nanomaterials have unique properties such as small size, high porosity, high reactivity, high thermal and chemical stability, and an active surface. They are receiving much attention in the field of environmental remediation because their large surface area creates more active sites for effective interaction of the material with different chemical species from water or wastewater (Madima et al. 2020; Madhura et al. 2019). Carbon-based nanomaterials have a structural composition of elemental carbon with mutable hybridization states, which gives them different structural configurations such as graphite, diamond, fullerenes, carbon nanotubes, graphene, etc. (Guerra et al. 2018).

Carbon nanotubes (CNTs) are an allotropic form of carbon composed of cylindrical shapes rolled up in a tube-like structure. They are divided into two types: multi-walled (MWCNTs) and single-walled carbon nanotubes (SWCNTs), depending on the number of carbon layers (Guerra et al. 2018; Madima et al. 2020). The presence of impurities that occurs during CNTs preparation as well as the oxygen content are factors that can affect the adsorption capacity of these materials. Changes in the surface properties of these nanomaterials can be prevented by functionalizing carbon nanotubes in the presence of acid and alkali solutions. The new functional group added to the material surface in this process can be very interesting in environmental remediation, enabling the use of CNTs in the removal of toxic metals and organic pollutants (Madima et al. 2020).

An allotrope of carbon that has gained significant attention as nanomaterials for environmental application is graphene. They have unique properties such as high specific surface area and high thermal conductivity and can be classified into graphene (G), graphene oxide (GO), and reduced graphene oxide (RGO) (Madima et al. 2020). Compared to carbon nanotubes, graphene-based materials may also need surface modification, however, they act as a promising adsorbent for environmental application in terms of production costs (Madhura et al. 2019).

Graphitic carbon nitrate (g-C_3N_4) is the most stable allotrope of carbon nitrides at ambient conditions and had been reported as a new sorbent for the removal of metals and organic compounds due to their attractive properties, including high photocatalytic activity, high thermal and chemical stability, good biocompatibility, and various available methods for surface modification (Sun et al. 2016).

21.2.3 Polymer-Based Nanomaterials

Polymers are commonly used as a host material to enhance the stability of nanoscale materials serving as a matrix or support to other types of materials. Despite having poor mechanical and thermal stability, numerous synthetic and natural polymers are used due to characteristics such as low weight, the incredible variety of chemical structures, and the possibility of their recyclability (Bushra 2018). They are used for the detection and removal of chemical compounds, organic pollutants, gases, and a wide array of biologics (Guerra et al. 2018).

Polymeric-nanocomposites (PNCs) are another class of adsorbent in environmental remediation and consist of a polymer or copolymer filled with inorganic compounds. The polymer is called matrix and the filler, when in the nanometer range, including CNTs, NPs, nanofiber, inorganic filler, and clay (Singh 2018). In this case, the nanocomposites have their properties improved to the high surface area and unique microstructures characteristics of nanofillers (Bushra 2018). In remediation, the polymer is used as a host material and the other constituents of the composite are responsible for the pollutant removal (Guerra et al. 2018).

Graphene oxides are highly compatible with polymers in the formation of PNC due to their unique properties. Because they have amphiphilic nature, they can bond with polar and nonpolar polymers to improve the mechanical properties of the composite. With respect to CNTs, their surface can be modified depending on the desired application, and it is already recognized that the structural features of MWCNTs can be improved when used as polymer composite (Bushra 2018).

21.2.4 Risks Associated with the Use of Nanoparticles and Solutions Toward Effective Management

The use of nanoparticles for environmental remediation is a technique that has been increasingly efficient with a large number of benefits. Although NPs can degrade pollutants, the same mechanisms can be toxic to biota, so their use in the environment is not free from risks. Once inside a matrix, nanomaterials can undergo different transformations, which are divided into chemical (reduction/oxidation, dissolution), physical (aggregation), and biotic (redox reactions in bacteria) (Marcon et al. 2021). Aggregation is one of the most prominent modifications and when NPs agglomerate, they form clusters losing their effectiveness as a nanoparticle. Because of their small size and higher mobility, NPs can easily disperse in the environment and cause ecotoxicity when spread over larger distances (Das 2018).

Since nanoparticles are highly persistent in the environment, potential human and ecotoxicological risks are associated with the dispersal, ecotoxicity, bioaccumulation, and reversibility of NPs (Ganie et al. 2021). In the case of nZVI nanoparticles, some sulphate-reducing bacteria are able to oxide them. When at a high concentration of nZVI, this oxidation leads to the formation of reactive oxygen species (ROS), which can cause oxidative stress, damaging the cell membrane and possibly leading to death (Diao and Yao 2009). Another report suggests that nZVI nanoparticles are toxic to plants when present in high concentrations because they reduce the transpiration rate and translocation to the shoots, which may result in stunted growth of some plants and depending on the exposure time, can also lead to death (Das 2018; Ma et al. 2013). In humans, a study showed the toxicity of SWCNTs assessed in keratinocytes cells. When keratinocytes were treated with SWCNP particles, the oxidative stress and inhibition of cell proliferation increased (Manna et al. 2005).

Due to the problems reported above, the disadvantages of employing nZVI nanoparticles can be overcome by using emulsified zero-valent iron. In this case, the material is prepared by encapsulating iron nanoparticles in a biodegradable oil membrane. This surface coating protects the zero-valent iron from other inorganic compounds or pollutants, preventing the reduction of iron capacity (Hara et al. 2006). The use of greener and more sustainable approaches for the synthesis of nanomaterials, such as the use of nanoparticles synthesized from plants or plants' part, reduces ecological toxicity by reducing the release of toxic by-products into the environment (Machado et al. 2013; Hoag et al. 2009). These approaches are alternatives that can be used effectively against the disadvantages and risks arising from the use of nanoparticles in environmental remediation.

21.3 Nano-phytoremediation

Nano-phytoremediation is a process that involves nanotechnology and phytoremediation for the degradation of pollutants in the environment (Verma et al. 2021). This technique uses plant species and nanoparticles for environmental remediation and has excellent potential. As mentioned before, nanomaterials are widely used in the remediation field and when combined with the phytoremediation technique, increases their efficiency (Srivastav et al. 2018).

The advantages of using plants to remove contaminants from the environment include cost-effectiveness, ecologically sound, long-term applicability, and the possibility of being directly applied at polluted sites, replacing other expensive treatment methods (Romeh and Ibrahim Saber 2020). Some factors can affect chemical uptake and distribution in living plants: (i) physical and chemical properties of the compounds; (ii) environmental characteristics such as pH, temperature, and organic matter; (iii) plant characteristics (Srivastav et al. 2018).

For effective nano-phytoremediation, plants and nanoparticles should possess some specific characteristics. The plants must have fast growth and well-developed root systems for greater remediation efficiency. In addition, they should be able to tolerate or accumulate contaminants. The technique is facilitated when the plants are easy to harvest, in addition to the need to be nonconsumable for humans and animals since they can be fatal. Finally, plants susceptible to genetic modification are generally preferred in this technique. Regarding the selection of nanoparticles, they should be nontoxic for plants and increase germination, seedling growth, plant height, and biomass. They must increase significantly phytoenzymes production in plants and enhance plant growth hormones. These nanoparticles should be capable to bind contaminants and increase bioavailability for plants. Remediation efficiency can be dramatically improved when all these factors are considered (Verma et al. 2021; Srivastav et al. 2018).

21.3.1 Nanoparticles and Microorganisms for Phytoremediation

As discussed in topic 3, the combination of plants (phytoremediation) and nanomaterials has attracted attention since some nanomaterials can improve the uptake of pollutants by plants and, consequently, increase the phytoremediation efficiency.

The nano-phytoremediation can employ inorganic nanoparticles (NPs) and also microorganisms (Table 21.1).

Reactive NPs of zero-valent iron (nZVI) are one of the most NPs employed for nano-phytoremediation with alfalfa (*Medicago sativa*). Recently, Wu et al. used nZVI for remediation of persistent organic pollutants (POPs) in the soil such as polychlorinated biphenyl (PCB). They reported that the phytoremediation from alfalfa increased from 66.7 and 38.5% to 93.1 and 52.3% when is added a concentration of nZVI of 1000 mg kg^{-1} for PCB28- and PCB180 respectively (Wu et al. 2021). It is also important to take into account that some syntheses of NPs employ toxic reagents and/or generate toxic residues which can be an issue for the environment. In order to overcome this, a green methodology can be employed by using plants to synthesize the NPs and also use these NPs to improve phytoremediation. A study by Romeh and co-workers employed two different NPs (AgNPs and

Table 21.1 Some nanoparticles and microorganisms used for nano-phytoremediation

Nanoparticles/microorganisms employed for nano-phytoremediation	References
Iron nanoparticles (FeNPs)	Romeh and Ibrahim Saber (2020)
Silver nanoparticles (AgNPs)	Romeh and Ibrahim Saber (2020)
TiO_2 nanoparticles	Singh and Lee (2016)
Rhizophagus irregularis and *Pseudomonas fluorescens*	Mokarram-Kashtiban et al. (2019)
Acaulospora mellea ZZ	Cheng et al. (2021)
Rhodococcus sp.	Hou et al. (2019)

FeNPs), synthesized by a green methodology, to enhance the phytoremediation of chlorfenapyr, an insecticide-miticide, in water and soil. They reported a reduction of about 90% in chlorfenapyr concentration in water (Romeh and Ibrahim Saber 2020). Zuo et al. also observed the improvement of phytoremediation of phenanthrene by *Erigeron annuus* when it was added SiO_2-NPs combined with the surfactant Triton X-100 (Zuo et al. 2020).

In general, the microorganisms combined with the phytoremediation are organisms found in the rhizosphere such as bacteria, fungi, oomycetes, nematodes, protozoa, and algae. As reported by Hou et al., the bacteria *Rhodococcus sp.* significantly increased Cd accumulation in *S. plumbizincicola,* and the phytoremediation efficiency was strongly correlated with the reshaped bacterial network topology (Hou et al. 2019).

In order to improve the phytoremediation process, it is also possible to combine both methods: the use of microorganisms and nanoparticles. Kashtiban and co-workers reported that the combination of *Rhizophagus irregularis* and *Pseudomonas fluorescens,* which are mycorrhizal fungus and rhizobacteria respectively, and nano-sized zero-valent iron (nZVI) were successfully employed to remediate soil with the toxic metals Pb, Cu, and Cd by increasing the bioconcentration factor (BCF) of the metals (Mokarram-Kashtiban et al. 2019). This same behavior was observed by Cheng et al. who employed *Acaulospora mellea ZZ*, an arbuscular mycorrhizal, and nZVI for phytoremediation of Cd, Pb, and Zn in soil by the plant sweet sorghum. The synergic effect of NPs and mycorrhizal promoted the immobilization of metals, especially Pb (Cheng et al. 2021).

21.4 Soil Nano-phytoremediation: Association of Nanotechnology and Remediation

The maintenance of soil with appropriate physicochemical characteristics and properties is essential for the support and quality of life. It is through the soil that nutrients necessary for autotrophic organisms that are essential to plant and animal nutrition are obtained and biogeochemical cycles are regulated.

However, land occupation and use have grown proportionally to technological advances and human scientific development. Although this development has enabled the growth of society, the exacerbated use of soil associated with inadequate disposal of pollutants has attracted the attention of researchers due to the accumulation of heavy metals and toxic compounds in the environment. These contaminants are not biodegradable and pose a threat to public health due to the possibility of accumulation in the human body by the biomagnification process (Yan et al. 2020). In this sense, many technologies have been studied to prevent these contaminants from being dissected by water, air, and land, and to remedy contaminated areas as a way of mitigating the possible damage to the affected region (Gerhardt et al. 2009).

In this sense, phytoremediation, a process in which plants are used for the removal of a wide range of contaminants, stands out as a low-cost strategy of operation, application, and adaptation to a multitude of elements (Gerhardt et al. 2009). The processes associated with the mechanisms and strategies of plants to eliminate soil pollution are well known and are based on phytovolatilization, phytoextraction, phytodegradation, phytostabilization, and phytostimulation (Fig. 21.2).

Phytoextraction is the phytoremediation process that consists of the bioaccumulation of a contaminant by a plant. Economically, this process has been reported by researchers as the most economical method when compared to conventional techniques since the phytoextraction plants have rapid growth, high performance,

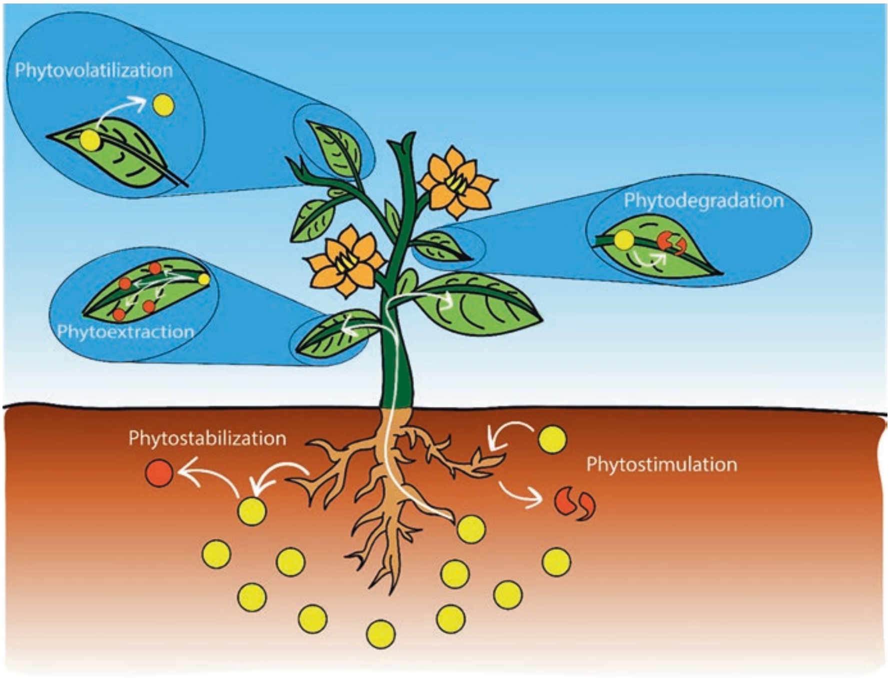


Fig. 21.2 Strategies to phytoremediation of soils by plants

extended roots system, and high biomass production (Zand et al. 2020). However, this application for the toxic elements' neutralization can take years depending on the climatic condition, physicochemical properties, and the phytotoxicity of the pollutant. For this reason, many strategies are employed to improve the phyto and environmental efficiency as agronomic management, chemical additives, and nanomaterials application (Song et al. 2019). The association between nanoparticles and environmental phytoremediation is identified as nano-phytoremediation. Nano-phytoremediation consists of a green and ecological technology that involves the application of nanomaterials with chemical properties that stand out when associated with plant metabolism. Recent studies show these materials through adsorption processes or redox reactions lead to the bioavailability of contaminants in plants stimulating healthy growth and removal of heavy metals in soil and water (Alka et al. 2021; Rai et al. 2020).

21.4.1 Nano-phytoremediation: Arsenic in the Soil and Water

Arsenic is a toxically metalloid that combines with other elements to form organic and inorganic compounds. Inorganic arsenic is a worldwide problem as it is the most prevalent form in soil and the most toxic when compared to organic forms found in living organisms (Shrivastava et al. 2015) (Fig. 21.3).

The remediation of contaminated soils with arsenic has been studied for decades and several technologies have developed (Alka et al. 2021). The phytoremediation of arsenic inorganic consists of the hyperaccumulation of the metalloid in the plant tissue (phytoextraction) or the phytostabilization through redox reactions in the roots. The fern *Pteris vittata* (brake fern) is the most popular plant for removing As.

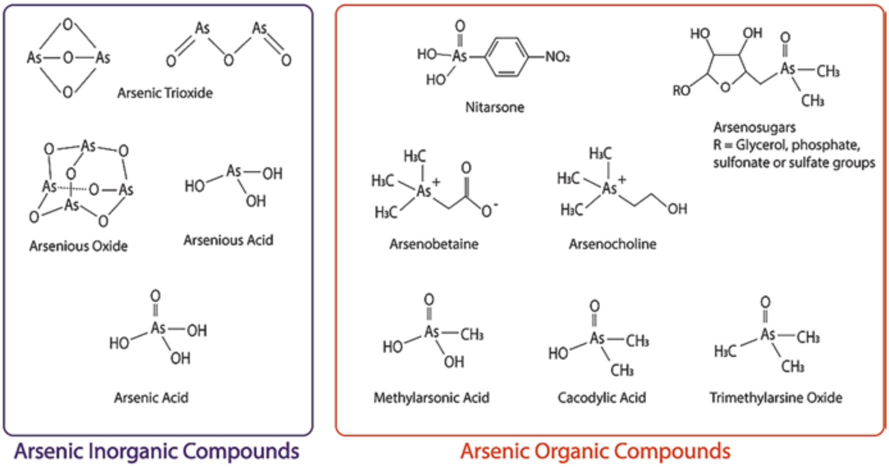


Fig. 21.3 Arsenic organic and inorganic compounds

This plant is extremely efficient in converting As(V) to As (III) and translocating to roots and fronds (Saffari et al. 2009; Ma et al. 2001). In the aquatic environment, *Pistia stratiotes*, often named water lettuce, is an alternative plant to remediate in the aquatics system. However, different from plants used in the soil, *Pistia stratiotes* have the potential to remediate low concentrations of arsenic (Paul et al. 2019).

Although these phytoremediation processes are auxiliary in the treatment of contaminated areas, the necessity to understand mechanisms that accelerate this procedure is fundamental to combat the increasing contamination of arsenic in environmental matrices. The *Isatis cappadocica Devis* associated with salicylic acid nanoparticles showed significant results in plant growth and a good response to stress caused by As. Preliminary studies show that the metalloid aggregates to the root surface and decreases the concentration of the element available for metabolization and accumulation in the shoot (Souri et al. 2017). The use of extracts from leaves of *Quercus virginiana* (Oaktree), *Punica granatum* (Pomegranate), and *Eucalyptus globulus* (Eucalyptus) suggest that the presence of iron oxide nanoparticles can be used as mechanisms for nano-phytoremediation of water due to the high affinity of NPs for Arsenic (V). In addition, among these species, Eucalyptus leaves have a high adsorption capacity of 40 mg of As/mg of leaves (Kamath et al. 2020).

21.4.2 Nano-phytoremediation of Organochlorine Compounds

Organochlorine compounds (OCCs) are organic molecules with high molecular weight, low solubility in water, highly lipophilic, containing halogens or condensed aromatic rings in its composition (Flores et al. 2004). These compounds attract the attention of public agencies because they are involved with the progressive increase of toxic elements and substances in the animal trophic status, a process known as biomagnification. The remediation of contaminated areas with OCC occurred simultaneously with the development of potential synthetic organic pesticides (Romeh and Ibrahim Saber 2020). The DDT (dichlorodiphenyltrichloroethane) is the precursor of the "Organochlorine Age", the period where agricultural and chemical development has yielded to the discovery and synthesis of chlorine-based compounds for agricultural purposes.

The nano-phytoremediation of OCC is mainly based on the improvement of phytoextraction and phytodegradation processes. Pesticides such as *Clorfenapir* are quickly and efficiently removed from water and soil by *Plantago major L.* in the presence of iron (ZVIs) and silver nanoparticles adsorbed in activated charcoal by mobilization of roots to leaves through metabolization and stabilization in leaves. Moreover, it is observed that this process of nano-phytoremediation is associated with agents that increase the solubility of OCC in the soil uptake the dispersion of the compound in order to increase the capture process by the roots (Flores et al. 2004).

Although for *P. major L.* the nZVIs act mainly as mediators of the adsorption/absorption process, this nanoparticle can also act in a pre-interaction step with the

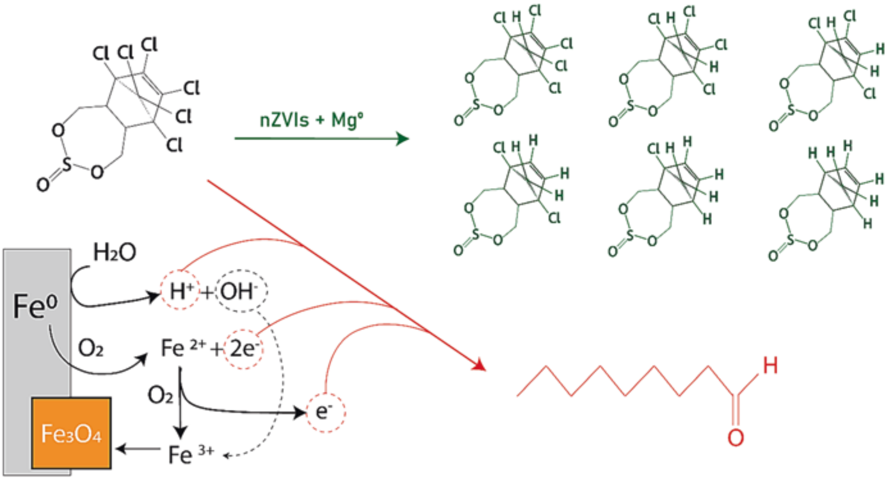


Fig. 21.4 A conceptual model for dehalogenation of Endosulfan by nZVIs with Mg^0 (sub-products in green) and nZVIs in anoxic or aerobic conditions (the process in red). (Adapted from Abbas et al. (2019), Schrick et al. (2002), Singh and Bose (2017))

plant. The high surface area of nZVIs and concentration of Fe^{2+} are the properties responsible for the dichlorination of Endosulfan by *Alpinia calcarata* (the Endosulfan hyperaccumulator) (Pillai and Kottekottil 2011). As shown in Fig. 21.4, the degradation process of Endosulfan by reductive reaction with iron is well known and described in the literature. However, Romeh and Ibrahim Saber (2020) observed that the combination of nZVIs with compounds that allowed the pesticide to be solubilized in the soil was essential for plants to absorb dehalogenation residues through the incorporation of these substances into the biomass of the phytoremediator.

21.4.3 Potentially Toxic Metals

Potentially toxic metals (PTMs) are metals often found in rocks and potentially toxic to the human body after mobilizing these elements to the biosphere through anthropogenic activities (Chojnacka and Mikulewicz 2014). Due to the similarity of the physical and chemical properties of these elements with the micronutrients essential to human development, PTM can be related to several diseases and short- and long-term problems in human health.

However, just as for humans the chemical similarity of these metals is a problem for the organism's absorption, a similar process is observed in plants. In this aspect, the nano-phytoremediation processes stand out in terms of reducing the toxicity of this contaminant to people as well as reducing the toxicity to the plant.

Chromium (Cr), for example, is a metal widely used in industry (mainly textile) and is considered an essential trace element for humans due to its insulin potentiating activity. However, Cr is a metal that presents various oxidation states, and Cr (VI) is extremely toxic and harmful to the human body. For plants, recent research have shown that Cr(VI) is directly associated with changes in physiological, biochemical, and molecular processes in order to alter growth procedures until the generation of reactive oxygen species. Tripathi et al. (2015) observed that the application of silicon nanoparticles (SiO_2) to soil contaminated with chromium can help combat the phytotoxicity of this metal (Tripathi et al. 2015). The authors concluded that an application of SiNPs was essential to reduce metal phytostabilization in the roots and to control oxidative stress since there was a decrease in the number of reactive oxygen species (ROS). In contrast, Brasili and collaborators (2020) observed that this metal can be removed from soil and water through a redox process with nZVIs associated with the germination of *Solanum lycopersicum* (tomato) (Brasili et al. 2020). They found that the seeds treated with the metal and the nanoparticle had better results in terms of growth, germination, and color development.

Cadmium (Cd) is considered to be the most toxic trace metal among PTMs. Despite being mostly associated with zinc minerals, anthropogenic activity has enabled its mobilization and migration to the surface and, consequently, its disposal in aquatic environments. As a very water-soluble metal, Cd easily travels through trophic levels and when absorbed by a plant promotes oxidative reactions that generate stress and cellular damage. However, Singh and Lee (2016) presented a mechanism for phytoextraction and bioaccumulation of this metal through the association of TiO_2 nanoparticles with *Glycine max* (Singh and Lee 2016). Gong et al. (2017) also evaluated the Cadmium remediation process using as a premise the equilibrium between the metal's phytotoxicity and the observable adaptations for the maintenance of the metabolic activities of *Boehmeria nivea L. Gaudich*. However, contrary to the study by Singh and Lee (2016), the researchers observed that just as the concentration of the contaminant in the soil was a determining factor for the generation of ROS, the nZVIs used aggravated the cellular damage to the phytoremediator plant when in high concentrations. At low concentrations, the nano-phytoremediation process is a promising technique for environmental decontamination of Cadmium (Gong et al. 2017) (Fig. 21.5).

Copper (Cu) is also characterized as an element that at the trace level has a biological function (in the electron transport chain) but which in excess has toxicity by generating free radicals. The Copper surplus in the soil, however, needs to be controlled before being taken up by the plants. Two main natural biological mechanisms are observed in plants exposed to excess copper to control oxidative stress: hyperaccumulation in shoots or metal stabilization in roots (Manceau et al. 2008). Manceau et al. (2008) analyzed the response of *Phragmites australis* and *Iris pseudoacorus* located in an environment contaminated for 10 years with sewage residues with high levels of Zn, Cu, and Cd. The study revealed that the association of the roots of these plants with endomycorrhizal fungi was able to synthesize ascorbic acid and promote the conversion of Cu^{2+} ions into copper nanoparticles. This biomining process of a contaminant corresponds to a nano-phytoremediation method mediated by the phytostimulation of the roots. Plant response mechanisms

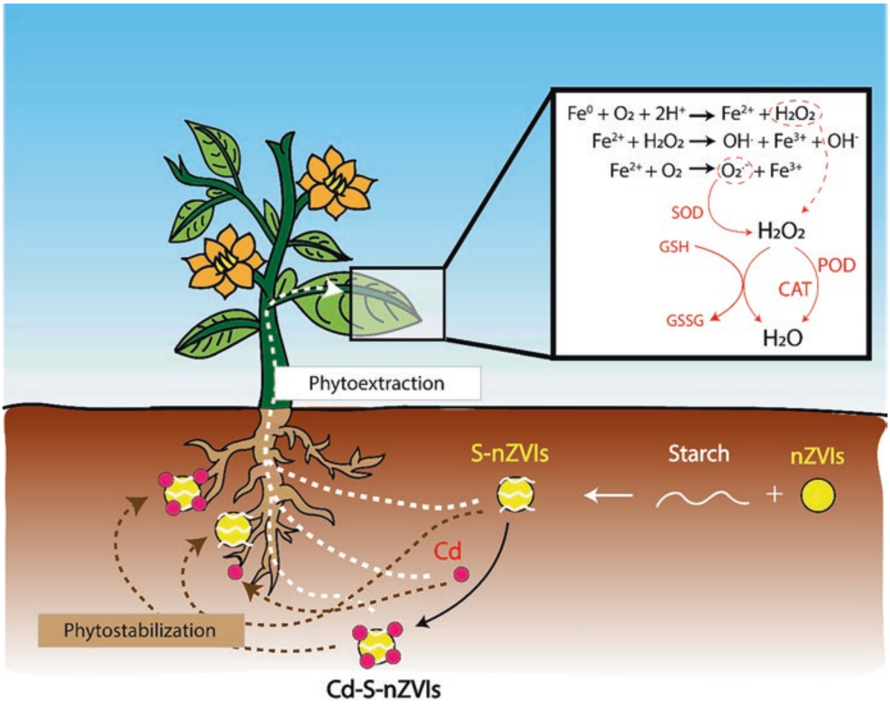


Fig. 21.5 Phytostabilization and phytoextraction of S-nZVIs adsorbed with Cd and oxidative stress caused by iron ions. In this figure: SOD superoxide dismutase; POD guaiacol peroxidase; CAT catalase; GSH reduced glutathione; GSSG oxidized glutathione. (Adapted from Gong et al. (2017))

were already described in the literature since biomolecular reactions to oxidative stress were already known for *Oryza sativa* (in the roots), *Cannabis sativa* (upper leaves), and *Allium sativum* (in the root tip) *(*Manceau et al. 2008*;* Lidon and Henriques 1994*;* Arru et al. 2004*;* Liu and Kottke 2004*)*.

21.5 Challenges and Future Perspectives of Nano-phytoremediation

Considering the advances in phyto and nano-phytoremediation it is clear the great potential of remediation of this method. However, there are some challenges to face in order to improve this method such as: (i) long-term experiments are required to see the effects of the nanomaterials in soils and the phytoremediation process, (ii) before the application of nanomaterials it is important to study their transformation in the environment (aggregation, dissolution, complexation, and mobility), (iii) it is necessary to evaluate the potentially toxic effects of nanomaterials employed for

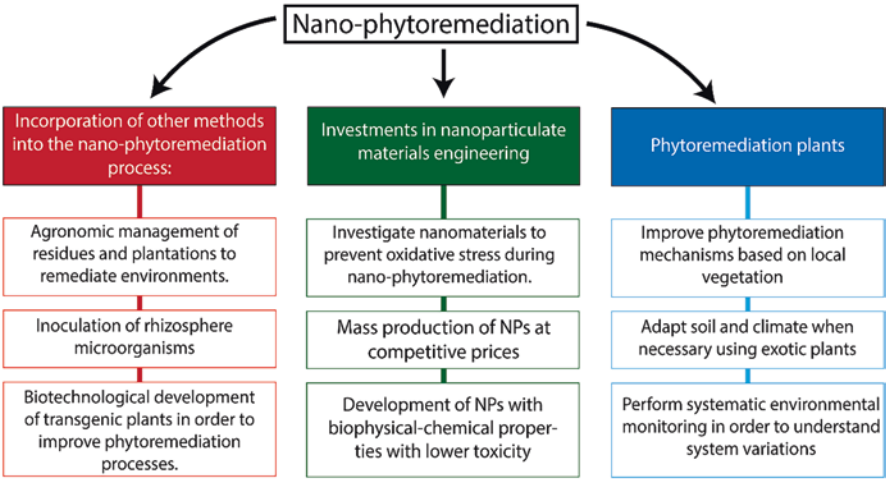


Fig. 21.6 Future challenges and perspectives in nano-phytoremediation method

nano-phytoremediation to the environment, and (iv) perform experiments in large scale/in real environment in order to ensure the efficiency of the methodology (Srivastav et al. 2018).

In face of these challenges to overcome, future studies about nano-phytoremediation are expected the use of green nanomaterials, the selection of suitable plant species with the best synergism for improve the remediation (preferably using local species of plant), and also use the biotechnology to improve the phytoremediation by using transgenic plants (Fig. 21.6).

References

Abbas T, Wadhawan T, Khan A et al (2019) Iron turning waste media for treating Endosulfan and heptachlor contaminated water. Sci Total Environ 685:124–133. https://doi.org/10.1016/J.SCITOTENV.2019.05.424

Alka S, Shahir S, Ibrahim N et al (2021) Arsenic removal technologies and future trends: a mini review. J Clean Prod 278:123805. https://doi.org/10.1016/j.jclepro.2020.123805

Arru L, Rognoni S, Baroncini M et al (2004) Copper localization in Cannabis sativa L. grown in a copper-rich solution. Euphytica 1401(140):33–38. https://doi.org/10.1007/S10681-004-4752-0

Boršev I, Boršev M, Jović D et al (2020) Chapter 19 - Nanotechnology and remediation of agrochemicals. In: Prasad Treatment and Remediation MNVBT-AD (ed). Butterworth-Heinemann, pp. 487–533

Brasili E, Bavasso I, Petruccelli V et al (2020) Remediation of hexavalent chromium contaminated water through zero-valent iron nanoparticles and effects on tomato plant growth performance. Sci Reports 101(10):1–11. https://doi.org/10.1038/s41598-020-58639-7

Bushra R (2018) Nanoadsorbents-based polymer nanocomposite for environmental remediation. New Polym Nanocompos Environ Remediat. https://doi.org/10.1016/B978-0-12-811033-1.00011-1

Cheng P, Zhang S, Wang Q et al (2021) Contribution of Nano-zero-valent iron and arbuscular mycorrhizal fungi to phytoremediation of heavy metal-contaminated soil. Nano 11:1264. https://doi.org/10.3390/NANO11051264

Chojnacka K, Mikulewicz M (2014) Bioaccumulation. Encycl Toxicol Third Ed 456–460. https://doi.org/10.1016/B978-0-12-386454-3.01039-3

Das P (2018) Phytoremediation and nanoremediation: emerging techniques for treatment of acid mine drainage water. Def Life Sci J. https://doi.org/10.14429/dlsj.3.11346

Diagboya PNE, Dikio ED (2018) Silica-based mesoporous materials; emerging designer adsorbents for aqueous pollutants removal and water treatment. Microporous Mesoporous Mater 266:252. https://doi.org/10.1016/j.micromeso.2018.03.008

Diao M, Yao M (2009) Use of zero-valent iron nanoparticles in inactivating microbes. Water Res 43:5243. https://doi.org/10.1016/j.watres.2009.08.051

El-Ramady H, Alshaal T, Abowaly M et al (2017) Nanoremediation for sustainable crop production, pp 335–363

Flores AV, Ribeiro JN, Neves AA, de Queiroz ELR (2004) Organoclorados: um problema de saúde pública. Ambient Soc 7:111–124. https://doi.org/10.1590/s1414-753x2004000200007

Ganie AS, Bano S, Khan N et al (2021) Nanoremediation technologies for sustainable remediation of contaminated environments: recent advances and challenges. Chemosphere 275:130065. https://doi.org/10.1016/j.chemosphere.2021.130065

Gerhardt KE, Huang XD, Glick BR, Greenberg BM (2009) Phytoremediation and rhizoremediation of organic soil contaminants: potential and challenges. Plant Sci 176:20–30. https://doi.org/10.1016/j.plantsci.2008.09.014

Gong X, Huang D, Liu Y et al (2017) Stabilized nanoscale zerovalent iron mediated cadmium accumulation and oxidative damage of Boehmeria nivea (L.) Gaudich cultivated in cadmium contaminated sediments. Environ Sci Technol 51:11308–11316. https://doi.org/10.1021/acs.est.7b03164

Guerra F, Attia M, Whitehead D, Alexis F (2018) Nanotechnology for environmental remediation: materials and applications. Molecules 23. https://doi.org/10.3390/molecules23071760

Hara SO, Krug T, Quinn J et al (2006) Field and laboratory evaluation of the treatment of DNAPL source zones using emulsified zero-valent iron. Remediat J 16:35–56. https://doi.org/10.1002/rem.20080

Hoag GE, Collins JB, Holcomb JL et al (2009) Degradation of bromothymol blue by 'greener' nano-scale zero-valent iron synthesized using tea polyphenols. J Mater Chem 19:8671. https://doi.org/10.1039/b909148c

Hou J, Liu W, Wu L et al (2019) Rhodococcus sp. NSX2 modulates the phytoremediation efficiency of a trace metal-contaminated soil by reshaping the rhizosphere microbiome. Appl Soil Ecol 133:62–69. https://doi.org/10.1016/J.APSOIL.2018.09.009

Jiang JQ (2007) Research progress in the use of ferrate(VI) for the environmental remediation. J Hazard Mater 146:617–623. https://doi.org/10.1016/J.JHAZMAT.2007.04.075

Kamath V, Chandra P, Jeppu GP (2020) Comparative study of using five different leaf extracts in the green synthesis of iron oxide nanoparticles for removal of arsenic from water. Int J Phytoremediation 22:1278–1294. https://doi.org/10.1080/15226514.2020.1765139

Karn B, Kuiken T, Otto M (2011) Nanotechnology and in situ remediation: a review of the benefits and potential risks. Cien Saude Colet 16:165. https://doi.org/10.1590/S1413-81232011000100020

Khairy M, El-Safty SA, Shenashen MA (2014) Environmental remediation and monitoring of cadmium. TrAC Trends Anal Chem 62:56–68. https://doi.org/10.1016/J.TRAC.2014.06.013

Khan MM, Adil SF, Al-Mayouf A (2015) Metal oxides as photocatalysts. J Saudi Chem Soc 19:462. https://doi.org/10.1016/j.jscs.2015.04.003

Kuppusamy S, Thavamani P, Venkateswarlu K et al (2017) Remediation approaches for polycyclic aromatic hydrocarbons (PAHs) contaminated soils: technological constraints, emerging trends and future directions. Chemosphere 168:944. https://doi.org/10.1016/j.chemosphere.2016.10.115

Li X, Zhang W (2006) Iron nanoparticles: the core−shell structure and unique properties for Ni(II) sequestration. Langmuir 22:4638. https://doi.org/10.1021/la060057k

Lidon F, Henriques F (1994) Subcellular localisation of copper and partial isolation of copper proteins in roots from rice plants exposed to excess copper. Funct Plant Biol 21:427–436. https://doi.org/10.1071/PP9940427

Liu D, Kottke I (2004) Subcellular localization of copper in the root cells of Allium sativum by electron energy loss spectroscopy (EELS). Bioresour Technol 94:153–158. https://doi.org/10.1016/J.BIORTECH.2003.12.003

Ma LQ, Komar KM, Tu C et al (2001) A fern that hyperaccumulates arsenic. Nature 409:579–579

Ma X, Gurung A, Deng Y (2013) Phytotoxicity and uptake of nanoscale zero-valent iron (nZVI) by two plant species. Sci Total Environ 443:844. https://doi.org/10.1016/j.scitotenv.2012.11.073

Machado S, Pinto SL, Grosso JP et al (2013) Green production of zero-valent iron nanoparticles using tree leaf extracts. Sci Total Environ. https://doi.org/10.1016/j.scitotenv.2012.12.033

Madhura L, Singh S, Kanchi S et al (2019) Nanotechnology-based water quality management for wastewater treatment. Environ Chem Lett 17:65. https://doi.org/10.1007/s10311-018-0778-8

Madima N, Mishra SB, Inamuddin I, Mishra AK (2020) Carbon-based nanomaterials for remediation of organic and inorganic pollutants from wastewater. A review Environ Chem Lett 18:1169. https://doi.org/10.1007/s10311-020-01001-0

Manceau A, Nagy KL, Marcus MA et al (2008) Formation of metallic copper nanoparticles at the soil-root interface. Environ Sci Technol 42:1766–1772. https://doi.org/10.1021/es072017o

Manna SK, Sarkar S, Barr J et al (2005) Single-walled carbon nanotube induces oxidative stress and activates nuclear transcription factor-κB in human keratinocytes. Nano Lett 5:1676. https://doi.org/10.1021/nl0507966

Marcon L, Oliveras J, Puntes VF (2021) In situ nanoremediation of soils and groundwaters from the nanoparticle's standpoint: a review. Sci Total Environ: 148324. https://doi.org/10.1016/j.scitotenv.2021.148324

McCullagh C, Skillen N, Adams M, Robertson PKJ (2011) Photocatalytic reactors for environmental remediation: a review. J Chem Technol Biotechnol 86:1002–1017. https://doi.org/10.1002/JCTB.2650

Mokarram-Kashtiban S, Hosseini SM, Tabari Kouchaksaraei M, Younesi H (2019) The impact of nanoparticles zero-valent iron (nZVI) and rhizosphere microorganisms on the phytoremediation ability of white willow and its response. Environ Sci Pollut Res 2611(26):10776–10789. https://doi.org/10.1007/S11356-019-04411-Y

Muthusaravanan S, Sivarajasekar N, Vivek JS et al (2018) Phytoremediation of heavy metals: mechanisms, methods and enhancements. Environ Chem Lett 164(16):1339–1359. https://doi.org/10.1007/S10311-018-0762-3

Paul M, Goswami C, Mukherjee M, Roychowdhury T (2019) Phyto-remedial detoxification of arsenic by Pistia stratiotes and assessment of its anti-oxidative enzymatic changes. Biorem J 23:175–184. https://doi.org/10.1080/10889868.2019.1640182

Pillai HPS, Kottekottil J (2011) Nano-Phytotechnological remediation of endosulfan using zero valent iron nanoparticles. J Environ Prot (Irvine, Calif) 7:734–744. https://doi.org/10.4236/jep.2016.75066

Rai PK, Kim KH, Lee SS, Lee JH (2020) Molecular mechanisms in phytoremediation of environmental contaminants and prospects of engineered transgenic plants/microbes. Sci Total Environ 705:135858. https://doi.org/10.1016/j.scitotenv.2019.135858

Romeh AA, Ibrahim Saber RA (2020) Green nano-phytoremediation and solubility improving agents for the remediation of chlorfenapyr contaminated soil and water. J Environ Manag 260:110104. https://doi.org/10.1016/J.JENVMAN.2020.110104

Saffari M, Fathi H, Emadi M et al (2009) Uptake, translocation, and transformation of arsenic by four fern species in arsenic-spiked soils. Commun Soil Sci Plant Anal 40:3420–3434. https://doi.org/10.1080/00103620903325992

Schrick B, Blough JL, Jones AD, Mallouk TE (2002) Hydrodechlorination of trichloroethylene to hydrocarbons using bimetallic nickel-iron nanoparticles. Chem Mater 14:5140–5147. https://doi.org/10.1021/cm020737i

Shafi A, Ahmad N, Sultana S et al (2019) Ag2S-sensitized NiO–ZnO heterostructures with enhanced visible light photocatalytic activity and acetone sensing property. ACS Omega 4:12905. https://doi.org/10.1021/acsomega.9b01261

Shah V, Daverey A (2020) Phytoremediation: a multidisciplinary approach to clean up heavy metal contaminated soil. Environ Technol Innov 18:100774. https://doi.org/10.1016/J.ETI.2020.100774

Shrivastava A, Ghosh D, Dash A, Bose S (2015) Arsenic contamination in soil and sediment in India: sources, effects, and remediation. Curr Pollut Reports 1:35–46. https://doi.org/10.1007/s40726-015-0004-2

Singh PP (2018) Environmental remediation by nanoadsorbents-based polymer nanocomposite. New Polym Nanocompos Environ Remediat. https://doi.org/10.1016/B978-0-12-811033-1.00010-X

Singh SP, Bose P (2017) Reductive dechlorination of endosulfan isomers and its metabolites by zero-valent metals: reaction mechanism and degradation products †. RSC Adv 7:27668–27677. https://doi.org/10.1039/c7ra02430d

Singh J, Lee BK (2016) Influence of nano-TiO2 particles on the bioaccumulation of cd in soybean plants (Glycine max): a possible mechanism for the removal of cd from the contaminated soil. J Environ Manag 170:88–96. https://doi.org/10.1016/J.JENVMAN.2016.01.015

Song B, Zeng G, Gong J et al (2017) Evaluation methods for assessing effectiveness of in situ remediation of soil and sediment contaminated with organic pollutants and heavy metals. Environ Int 105:43–55. https://doi.org/10.1016/J.ENVINT.2017.05.001

Song B, Xu P, Chen M et al (2019) Using nanomaterials to facilitate the phytoremediation of contaminated soil. Crit Rev Environ Sci Technol 49:791–824. https://doi.org/10.1080/10643389.2018.1558891

Souri Z, Karimi N, Sarmadi M, Rostami E (2017) Salicylic acid nanoparticles (SANPs) improve growth and phytoremediation efficiency of Isatis cappadocica Desv., under As stress. IET Nanobiotechnol 11:650–655. https://doi.org/10.1049/iet-nbt.2016.0202

Souza LRR, Pomarolli LC, da Veiga MAMS (2020) From classic methodologies to application of nanomaterials for soil remediation: an integrated view of methods for decontamination of toxic metal(oid)s. Environ Sci Pollut Res 27:10205–10227. https://doi.org/10.1007/s11356-020-08032-8

Srivastav A, Yadav KK, Yadav S et al (2018) Nano-phytoremediation of pollutants from contaminated soil environment: current scenario and future prospects. Phytoremediation. https://doi.org/10.1007/978-3-319-99651-6_16

Sun Y, Ha W, Chen J et al (2016) Advances and applications of graphitic carbon nitride as sorbent in analytical chemistry for sample pretreatment: a review. TrAC Trends Anal Chem 84:12. https://doi.org/10.1016/j.trac.2016.03.002

Tahir MB, Rafique M, Rafique MS et al (2020) Photocatalytic nanomaterials for degradation of organic pollutants and heavy metals. Nanotechnol Photocatal Environ Appl. https://doi.org/10.1016/B978-0-12-821192-2.00008-5

Tripathi DK, Singh VP, Prasad SM et al (2015) Silicon nanoparticles (SiNp) alleviate chromium (VI) phytotoxicity in Pisum sativum (L.) seedlings. Plant Physiol Biochem 96:189–198. https://doi.org/10.1016/J.PLAPHY.2015.07.026

Verma A, Roy A, Bharadvaja N (2021) Remediation of heavy metals using nanophytoremediation. Adv Oxid Process Effl Treat Plants. https://doi.org/10.1016/B978-0-12-821011-6.00013-X

Wu T, Liu Y, Yang K et al (2021) Synergistic remediation of PCB-contaminated soil with nanoparticulate zero-valent iron and alfalfa: targeted changes in the root metabolite-dependent microbial community. Environ Sci 8(4):986–999. https://doi.org/10.1039/d1en00077b

Yan A, Wang Y, Tan SN et al (2020) Phytoremediation: a promising approach for revegetation of heavy metal-polluted land. Front Plant Sci 11:1–15. https://doi.org/10.3389/fpls.2020.00359

Zand AD, Daryabeigi A, Mikaeili A (2020) The influence of association of plant growth-promoting rhizobacteria and zero-valent iron nanoparticles on removal of antimony from soil by Trifolium repens. Environ Sci Pollut Res 27:42815–42829

Zuo R, Liu H, Xi Y et al (2020) Nano-SiO2 combined with a surfactant enhanced phenanthrene phytoremediation by Erigeron annuus (L.) Pers. Environ Sci Pollut Res 2716(27):20538–20544. https://doi.org/10.1007/S11356-020-08552-3

Chapter 22
Nanobioremediation and Its Application for Sustainable Environment

Trinath Biswal

Abstract People in the twenty-first century are struggling for proper remediation and management of huge amounts of contamination which is generated daily from various sources, and cause environmental degradation and posing a challenge to the survival of the global biological community. Nanomaterials deliver amazing properties, are economically viable and eco-friendly and they can therefore be used effectively in the bioremediation of environmental contaminates. The technique of nano-bioremediation is a hybrid method, which can be used for the detoxification or remediation of pollutants through the use of nanotechnology. The nanoparticles (NPs) used in the method of bioremediation of pollutants can be synthesized biologically from various plant extracts, bacteria, algae, enzymes and fungi. The application of these synthesized biogenic NPs exhibits high performance in the remediation of contaminates from our ecosystem, offering a sustainable and highly promising approach for the cleaning up of the environment. The technique of nano-bioremediation is an excellent sustainable advanced technology for the remediation of pollutants from the ecosystem through the application of biologically produced NPs. There are several metallic NPs, such as Zn, Fe, Ag, Cu and Au, that can be used in the remediation of contaminants, but these are toxic to many essential soil microorganisms. The use of NPs synthesized biologically by using various plant extracts, yeasts, algae, bacteria and fungi is eco-friendly and sustainable, proving highly effective for the detoxification of some specific pollutants from the environment. Hence, the combination of remediation and biosynthesis by using nanotechnology results in sustainable development and, eventually, a sustained environment.

Keywords Biosynthesis · Nanobioremediation · Sustainability · Eco-friendly · Detoxification · environmental clean-up

---

T. Biswal (✉)
Department of Chemistry, VSS University of Technology, Burla, India

L. Newman et al. (eds.), *Phytoremediation*, https://doi.org/10.1007/978-3-031-17988-4_22

22.1 Introduction

The complete removal, or even the decrease, of organic and inorganic contaminates, from the environment of polluted sites through the use of nanomaterials (NMs) or nanoparticles (NPs) produced by algae, bacteria and fungi assisted by nanotechnology is termed nanobioremediation. In the present day, environmental contamination is considered a major issue throughout the world and a threat to the biotic community. The development of excessive industrial complexes over the past two centuries is the cause of the addition of a large amount of toxic contaminates or unused waste materials to the air, soil and water and the cause of health hazards among both human beings and animals (Sherry Davis et al. 2017; Yadav et al. 2021). Sustainability towards the environment is defined as responsible collaboration with the environment to prevent the degradation or depletion of natural resources and permit the maintenance of environmental quality on a long-term basis. However, the worldwide definition of sustainability is simply sustainable development which also leads to environmental degradation, and the programs of sustainability now comprise the restoration and protection of the natural resources of the environment. One of the vital strategies for the restoration of natural resources is bioremediation, which is carried out by using microbes. The term "remediate" is used to remove the contaminates, whereas the term "bio-remediate" means the removal of contaminates from the environment by using biological organisms. The technique of bioremediation is highly beneficial to the traditional process of remediation because it is highly capable and economical, the optimization of biological and chemical sludge (with no need for any supplementary nutrient), selectivity towards specific metals and the possibility of recovery of metals and restoration of biosorbent. However, this method of remediation is not practicable for the sites polluted with some specific toxic materials, especially aromatic and chlorinated compounds, which are hazardous to most of the microbial community. The NPs possess a high capacity for remediating such kinds of hazardous pollutants and produce a healthy substrate, which facilitates microbial activity and enhances the level of environmental clean-up. Although NPs are synthesized by a physicochemical process, the synthesis by biological route is more sustainable and beneficial (Pandey 2018; Gothandam et al. 2020). In the process of nanobioremediation, the NPs used may be either nonmetallic or metallic and of different dimensions. The metallic NPs are of various kinds, including single metal NPs, carbon-based NPs, modified NPs, bimetallic NPs, etc. The NPs of metals are applied in various fields, including drug delivery, the synthesis of nanocomposites, electronics, medical imaging, sensors, non-linear optics, antimicrobial agents, biolabelling and hyperthermia of tumours. The microorganisms such as algae, bacteria, protozoans, fungi, etc. are stimulated during the growth process by adjusting or modifying the environmental condition. If the level of the contaminates is extremely high, then there is a possibility that the microorganisms might be destroyed; hence, in order to solve this problem the biological process of nanotechnology associated with physiochemical approaches is commonly termed "nanobioremediation" (Samson et al. 2021; Patra Shahi et al. 2021).

22.2 Nanobioremediation

The rapid establishment of industrial complexes, deforestation, population growth and the development of technology have led to the addition of excessive amounts of contaminants into the environment. The vital contaminants such as toxic inorganic, organic materials, heavy metals, chlorinated compounds and other complex materials are hazardous not only to human society but also to the entire biological world and environment. Over the past two decades, NPs have been used effectively for the treatment materials, owing to their eco-friendly nature, high efficiency and cost-effectiveness. The Fe-NPs are regarded as the first NP used for the remediation of contaminates from the environment. The process of nanobioremediation is a promising method of using the combined form of biological and physicochemical technology. This process used NPs to degrade or break down the pollutants to the concentration up to the favourable level of biodegradation and results in the remediation of pollutants. The technology of nanobioremediation is highly effective in cleaning up the toxic pollutants from soil and water by using NPs, which are synthesized biologically from microorganisms or phytoextracts. The zerovalent Fe-NPs are highly effective in the treatment of acidic water containing a high concentration of heavy metals (HMs) because the surface of the NPs is able to adsorb the HMs at its surface. The extreme chemical, thermal stability, excellent affinity and adsorption properties of CNTs proved themselves as a beautiful candidate material for remediation of pollutants from the environment (Rajput et al. 2022; Pete et al. 2021). It is a perfect replacement for activated carbon for cleaning up inorganic and organic contaminates along with heavy metals such as Cr (VI), Pb, Zn, Hg, etc. The Zn NP is a photocatalyst, having semiconducting characteristics, and is capable of the full degradation of several toxic substances from dyes and pharmaceutical drugs. Again, the NPs of Au, Cu and Ag have different applications in a diversified field and are found to be mainly effective against the remediation of organic dyes from wastewater. The technique of nanobioremediation is a multi-technology method of remediation of contaminates because of its sustainability, efficiency, non-toxicity, time duration and availability of resources. The NPs of TiO_2, metallo-porphyrinogens, dendrimers, CNTs and swellable organically-modified silica (SOMS) are potentially effective in the remediation of contaminates in both in-situ and ex-situ methods. The NPs of TiO_2 offer high performance in the remediation of a wide variety of chemical fertilizers, pesticides, insecticides and herbicides by the method of photocatalysis from the resources of infected groundwater (Kumar and Gopinath 2016; Fang et al. 2011). NPs such as Fe, Ti, Cu synthesized biologically in combination with the NPs of metal catalysts such as Au, Pt, Ni, Pd increases the rate of redox reaction. The NPs of Pd possess the capability of catalyzing the method of reduction of $C_2H\ Cl_3$ to C_2H_4 without the production of any vinyl chloride as a by-product. The NPs of silica stimulate the remediation of Pb, the NPs of Zn remediate CS_2 from air and hydroxyapatite in nanocrystalline form is effective for removal of Cd and Pb. NMs such as fullerenes, zerovalent nano-Fe, ZnO, TiO_2 NPs and CNTs are highly effective in the remediation of the highly toxic pollutants such as DDT, carbamates and heavy metals such as As, Cd, Cr and Pd from the soil. The Fe-NPs synthesized biologically can be widely applied in the remediation of 2, 3, 7, 8-tetrachlorodibenzo-p dioxin, Lindane, PCBs, dyes, pesticides and hydrocarbons by using bacterial metabolism (Yadav and Ahmaruzzaman 2021).

The remediation of different kinds of pollutants, the use of nanomaterials (NMs), and their method of synthesis were represented in Table 22.1.

The nanobioremediation is highly popular for the following two reasons:

- The first one is the presence of NPs, which promotes the increase in the surface area, leading to the increase in the rate of reactivity.
- It is the cause of the requirement of less activation energy, for which the reaction can proceed easily and effectively.

The technique of surface plasmon resonance (SPR) is another technique, which is used for the detection of toxic heavy metals by using NPs. Finally, we can conclude that nanobioremediation is highly effective for the remediation of groundwater, solid wastes, soil, surface water, wastewater and especially effective for the removal of heavy metals and uranium (Patel et al. 2020).

Table 22.1 Kinds of NMs, their method of synthesis and pollutants remediated (Rizwan et al. 2014)

Kinds of NMs	Methods of synthesis	Pollutants remediated
Nanoparticles (NPs) of metals	Photochemical Electrochemical Thermochemical Biochemical	Pt, Ni, Rh, Cu, Pd, Au, Ir, Ag, Co, FeNi, CdTe, Cu_3Au, ZnS, CoNi, CdSe
Carbon NMs	Arc-discharge Chemical vapour deposition Laser ablation	MWNT, SWNT, fullerenes
Nanocomposite	Innovative techniques	Nanocomposite of polyethylene oxide and polyethyleneimine; conjugated polymer composites, CNT epoxy composites include hydrocarbon polymer composites, fluoropolymers, polyethylene glycol, CNTs with polycarbonates, polyester polyamides, and so forth
NPs of metal oxide	Hydrothermal Reverse micelles method Solvothermal Electrochemical deposition Sol-gel technique	ZnO, MgO, $BaSO_4$, Fe_2O_3, Fe_3O_4, TiO_2 $BaCO_3$
Bionanomaterials	Biological	Viruses, protein NPs and plasmids
Polymer NMs	Electrochemical method of polymerization	Nanowire of polypyrrole, poly(3,4-ethylenedioxythiophane) dendrimers (PAMAM), polyaniline

22.2.1 Challenges of NPs in Nanobioremedaition

The use of nanotechnologies for the remediation of pollutants is, at present, only confined to the laboratory scale and its industrialization for application in practical purposes is still a challenge. Although NPs show promising outcomes for the remediation of pollutants, there are some disadvantages related to their application in polluted sites, such as decreases in reactivity over time, and the impact on microorganisms and transportation.

Example The NPs of some metals gradually decreases their reactivity after the use of a particular period of remediation owing to their restriction of movement through obstructing the effectiveness of soil. Therefore, to overcome these difficulties suitable stabilizers such as lactate are added in order to enhance the ionic mobility of the Fe-NP within the soil.

Another vital problem of using NPs in the process of nanobioremediation is the limited information about the impact of NPs related to the growth of microbes. Some NPs show a toxic effect on the microbial community. Although several experimental studies were carried out to learn about the impact of NPs or nanotechnology on the microbial community in a controlled and regulatory manner, the results are still contradictory. Some of the experimental studies show inhibitory impact on microorganisms such as *Escherichia coli* and *Staphylococcus aureus* have been observed, whereas in a few cases the stimulatory effect of NPs is found because of electron donation to microorganisms such as methanogens and bacteria. The existence of soil microorganisms in the environment is highly essential and is considered a vital part of the natural cycle of nutrients in our ecosystem, playing a key role in the remediation of inorganic and organic pollutants and the immobilization of heavy metals from nature. The substantial decrease in the population of soil microorganisms is the cause of weakening the resistance power of soil towards the remediation of contaminants. Several different mechanism pathways have been suggested to explain the toxicity of NPs leading to the death of microorganisms, which includes the disruption of the cell membrane by generating reactive oxygen and the interruption of the absorption of nutrients by the cell membrane, resulting in the decrease in growth of microbes. In the case of the growth of the fungal colonies, no impact of NPs is observed. Again, some specific microorganisms are capable of secreting particular polysaccharides and enzymes to protect themselves from the toxicity of the NPs (Zhou et al. 2022; Ali et al. 2016). This problem of NP toxicity can be prevented by coating the NPs with some polymeric materials. The various use of NMs are given in Fig. 22.1.

22.2.2 The Principle of Nanobioremediation

The method of nanobioremediation possesses the capability of decreasing the average cost of remediating large-scale contaminates in a shorter space of time. The basic principle of nanobioremediation may be defined as the degradation of waste

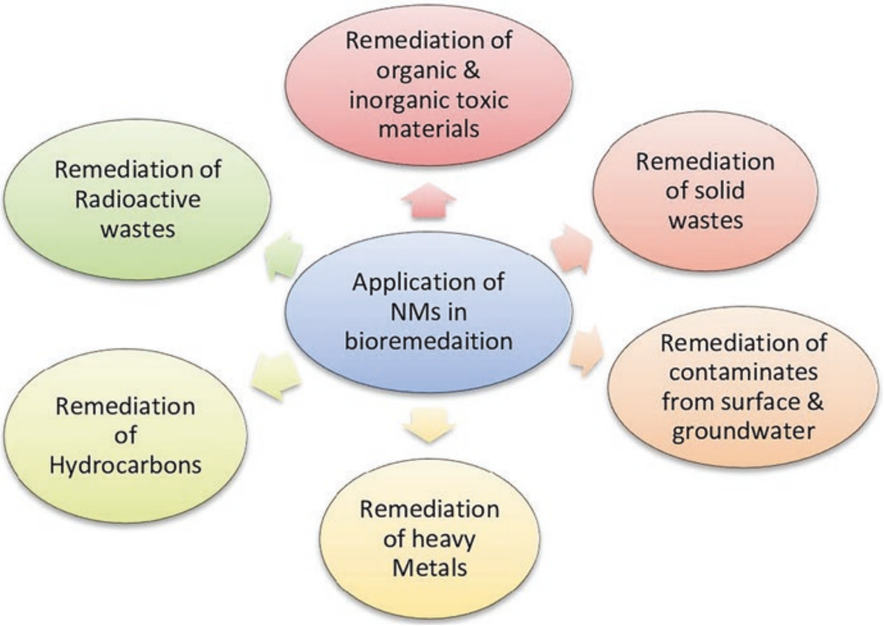


Fig. 22.1 Different application of NMs in the process of bioremediation

materials (contaminates) by using a catalyst in the nanoscale as a medium, which permits these to enter deep inside the toxic contaminants and remediate these wastes safely through different microorganisms without degrading the surrounding environment. These microbial communities exist worldwide and are competing with each other for their existence and growth. These microbes provide many benefits to the environment such as remediating heavy metals (HMs) into a non-toxic state through the mineralization of waste organic pollutants as end products (H_2O, CO_2) may be converted into different metabolic intermediate products, which can be utilized as metabolites for the growth of these microbes. The use of these toxic materials causes defence of their cell walls due to the formation of degradative enzymes, which make these suitable for fighting with different HMs and also consumed by the microbial community. For successful and effective nanobioremediation, now that modified microorganisms are being used, which may be able to control and regulate the activity of microbes, and also the mechanism of their growth activity in the polluted sites is easily recognized. The response of these microorganisms concerning changes in climatic conditions can be easily monitored. After the absorption of the pollutants by the microorganisms, special kinds of membranes are created around these microbes, which support them in protecting them from the access of foreign materials into the cells. The vital fact in which the technique of nanobioremediation defines is the dimension of the NPs, because the NPs are extremely small particles, being generally bacterial or fungal, which can easily be inserted within the contaminates with the microorganisms and are able to degrade the pollutant matter. The NPs show improved activity than microparticles because NPs penetrate easily into the sites of pollutants and facilitate the clean-up process than the usual bioremediation technology. The substances of nanoscale dimension used for the remediation of the contaminated sites include NMs, nanoclusters, nanostructured materials, etc. The added NPs are also used for the further immobilization of the cells of the microorganisms, which may be used for recovering some particular chemicals (Parthipan et al. 2021; Dzionek et al. 2016).

22.2.3 Challenges of Nanobioremediation

As mentioned earlier, the use of nanotechnologies for the remediation of contaminates from the environment is now restricted just to the laboratory scale and its industrialization and commercialization in the application of practical field is still a challenge for researchers. Although the use of NPs in the method of nanobioremediation provides amazing results for the removal of pollutants, there are still some limitations related to their application such as transportation, the influence of microorganisms and the loss of reactivity over time.

Example Some NPs of metals become inactive after their reactivity of some specific period during the remediation of pollutants from the contaminated sites owing to the limitation of passing fluids because of the blocking impact of soil. Hence, to solve these problems stabilizers such as lactate can be used to improve the rate of mobility of Fe-NPs in soil.

The toxicity of NPs with regard to microorganisms is a major challenge towards nanobioremediation, which results in the death of some kind of microorganisms due to damage to the cell membrane by generating reactive oxygen, a decrease in the absorption of nutrients through the cell membrane through retarding the rate of growth. The influence of the filter is generally carried out at the ultimate phase of deposition, which is the cause of clogging or blocking the pores of the soil and prevents the passage of any particles inside the soil. Therefore, the process of filtration is a vital limitation and challenge for the application of nZVI remediation because it restricts the NPs to reach the bottom layer. Again the NPs have more density than water, which is the cause of settling the NPs in a fluid medium and contributes, in part, to the clogging effect. Hence, to increase the mobility, reactivity and stability of the NPs various kinds of improved surface coatings materials have to be developed. The use of inert polymeric material for coating is an effective process of stabilizing NPs with the help of sodium carboxymethyl cellulose (CMC), lactate and guar gum as additive materials (Azubuike et al. 2016; Vázquez-Núñez et al. 2020).

22.2.4 Interaction of NPs with Microbes and Soil

The detailed explanation of the interactions of the NPs with the native microbial community and soil particles is a highly challenging job owing to a lower number og monitoring points and few periods of monitoring. The major parameters monitored and controlled at the time of application for the remediation of the contaminates are the oxidation-reduction potential exhibited by nano-zerovalent iron (nZVI) over time, electrical conductivity, the concentration of Fe, pH, dissolved oxygen in case of groundwater, etc. After the insertion of nZVI, the redox potential decreased to a substantial level at the subsurface, a finding which is confirmed by the production of H_2 gas. Although the addition of nZVI suspension made the system alkaline, no appreciable change in pH at the subsurface is observed because of buffering through the groundwater. The existence of micro-biota in the soil normally depends on the properties and level of contamination of the sites and creates some indigenous species, which possess the ability to to degrade or remediate the waste contaminant of the soil. The addition of nZVI stabilizes with the polymeric materials and functions as a promoter for growth by offering massive biodegradation or bioremediation of toxic organic materials and facilitates decontamination in the polluted sites. The formation of complex compounds with Fe^{3+} and Fe^{2+} after the addition of a suspension of nanoferro materials can cause chemical changes on the surfaces of NPs under a normal ambient environment. These compounds formed influence directly to the native flora and might interfere with the long-term immobilization of toxic inorganic or metallic contaminates such as uranium (IV) and chromium (VI) (Cao et al. 2019; Perea Vélez et al. 2021).

22.2.5 Advantages of Nanobioremediation

The major advantages or benefits of applying NPs in coupling with bioremediation are as follows:

- The increase in the rate of removal of contaminates because of the comparatively greater surface area of the NPs
- More reactivity towards the contaminants
- NPs can easily penetrate or diffuse inside the zone of contamination, which the microorganisms are unable to reach.
- Much enhanced reactivity to redox-amenable pollutants
- Very much quicker rate of degradation than normal microbial degradation
- The production or manufacturing cost is comparatively less
- The NPs added can immobilize microbial cells
- Suitable NPs and microbes must be chosen according to the environmental conditions for the degradation of toxic waste materials.
- It is a completely sustainable and natural process with minimal or almost no side effects

- It can be applied in both ex-situ and in-situ conditions of the contaminated sites for improving the environmental condition.
- The rate of reversal is very quick and satisfactory; the water and soil can also be again reutilized for other different purposes
- In this technique, the toxic organic materials are effectively degraded into simple non-toxic substances and cannot be moved to other areas.
- In nanobioremediation, a sensor can be used for environmental variability
- Among the various NPs the nZVI and its derivatives are found to be more important in nanoremediation
- Because of the improved efficiency, the low cost of treatment and sustainability and its use at a large scale the in-situ method of remediation is more preferable and feasible (Singh et al. 2020; Koul and Taak 2018).

22.2.6 The Science of Nanobioremediation

Presently, a huge number of NMs have been used successfully in the treatment of wastewater, air and soil. The removal of toxic contaminates by using nanobioremediation is effective because of some of the amazing properties of the NMs, which include a large surface area, an extremely high capacity of reactivity, the quick rate of dissolution and the higher ability of sorption. These unique properties play a vital role in cleaning up the contaminants from the environment. Several approaches based on nanotechnology were found to be successful or effective only on a laboratory scale, and apparently very few of them can be used in commercial settings. However, there are some sings that among these processes some, such as nanoadsorbents, nanotech-based membranes and nano-photocatalysts, have proved popular and also commercialized. The various properties possessed by different NMs are highly advantageous in using bioremediation to clean up the ecosystem (Abatenh et al. 2017).

Example The NMs applied for nanobioremediation have normally more volume of contact for interaction with the pollutants causing an increase in its reactivity (Jeevanandam et al. 2018).

Furthermore, NMs possess a quantum effect, which is the cause of decreasing the necessary activation energy and making feasible the chemical reactions associated with the bioremediation. Another fact exhibited by the NPs is surface plasmon resonance, which can be effectively utilized for the identification of the toxicity level of the affected regions. According to the dimension, a number of non-metallic and metallic NMs have been used for bioremediation of contaminates and the cleaning up of the environment. This is because the NPs possess the capability to infiltrate or diffuse into the zone of contamination, where the micro-particles are incapable of entering and the reactivity of the NPs towards redox-sensitive contaminates is considerably higher. Experimentally, it was found that the Fe^0 in the nanoscale form on coating with oxide possesses the capability to produce weak

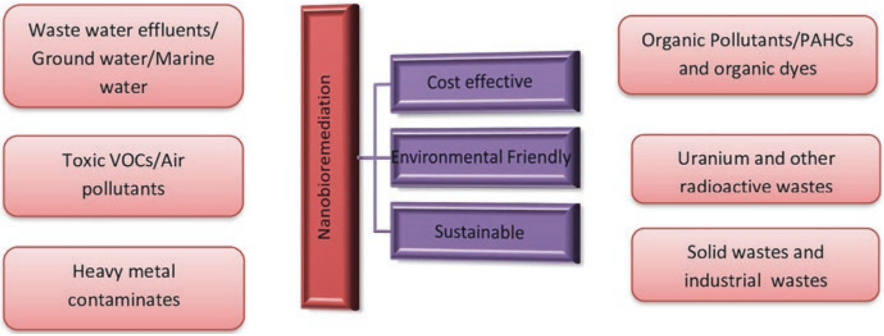


Fig. 22.2 Schematic diagram representing the different contaminate targets and the three most significant attributes of nanobioremediation

complexes on combination with CCl_4 and pollutants of a similar category, leading to the increase in its reactivity. Usually, CCl_4 undergoes reaction through electron transfer and is transformed into either CO_2, or CH_4, formate, but in the field assessment and batch experiments halogenated aliphatic hydrocarbons, trichloroethene and benzoquinone can be degraded into some simple by-product materials of comparatively much less toxicity (Rahman and Singh 2020). Figure 22.2 represents different contaminate targets and the three most significant attributes of nanobioremediation.

Moreover, the destruction of pentachlorophenol (PCP) is also carried out in the laboratory by using TiO_2 nanotubes via photoelectrocatalytic reaction and single-metal NPs can also be applied as biocatalysts for the reduction and removal of chlorine (Shen et al. 2009).

Again, an assessment of bioreductive was carried out, in which it was detected that Pd(0) NPs were successfully deposited inside the cytoplasm and cell wall of *Shewanella oneidensis*. The addition of some electron donors, including H_2, formate and acetate, is the cause of charging Pd(0) along with the formation of H* radicals. When a chlorinated toxic pollutant like PCP comes into contact with Pd(0)-coated, charged *S. oneidensis*, the H* radicals reacts on the Pd (0) and the cause of the successful removal of chlorine. The microbial cells possess the ability of biorecovering or degrading some particular chemicals on immobilization with the added NPs. The magnetic Fe_3O_4 NPs on modification by the addition of ammonium oleate were on coating with the cell surface the microorganism *Pseudomonas delafieldii* exhibits magnificent results. By the use of an external magnetic field, the cell walls were detached from the bulk solution and subsequently recycled for remediation or treatment. The NPs coated with the microbial cells can able to desulfurize the organic sulfur present in the fossil fuel in a system of bioreactors (Baragaño et al. 2020; Kumari and Singh 2016).

22.3 Various NPs Used in Nanobioremediation

The different NPs used in the process of nanobioremediation are as follows:

22.3.1 *Nano-Fe and Its Related Derivatives Applied in Bioremediation*

The nanosize of zero-valent iron (nZVI) can be suitably synthesized and effectively applied for the removal of As(III), which is normally recognized in groundwater, mobile and extremely dangerous for human health. Through the application of nZVI, the toxic contaminate As (IV) can be effectively eliminated from groundwater because arsenic is converted into a colloidal state and serves as a reactive barrier material. The NPs of nZVI supported by ferragels are able to immobilize and separate Cr (VI) and Pb (II) at a rapid rate from the aqueous solution by reducing Cr (VI) to Cr (III) and Pb to Pb (0), but Fe is oxidized to goethite (α-FeOOH). The NPs of (Fe/PAA) of nZVI supported by poly (acrylic acid) were identified to be extremely effective for the separation of chlorinated hydrocarbons from soil and groundwater. The nano-Fe serves as a reactive wall in the path of contaminated groundwater plumes for the bioremediation of the toxic halogenated organic materials. NPs of Fe and Ni in the ratio of 3:1 show very good performance in the separation of halogen from trichloroethylene. The toxic substance, such as PCP, can be removed from the aqueous solution through the application of zero-valent metals (ZVMs). This is due to the dechlorination or sorption at the surface associated with ZVM. Recently, it is shown that DDT can be decontaminated by eliminating Cl_2 and its associated compounds, which is extremely effective by the application of fine nanopowdered zero-valent Fe. This zero-valent Fe in nanopowder form in buffered aqueous solution without or with Triton X-114 (non-ionic surfactant) can be highly effective in the elimination of DDT, DDE [2,2-bi's(p-chlorophenyl)-1 and DDD [1,1-dichloro-2,2-bis(pchlorophenyl)ethane]. Specifically, we can say that Fe possesses the capability of elimination of DDT, DDE and DDD effectively (Bhalerao 2014; Betancur-Corredor et al. 2015). Table 22.2 represents the remediation of different pollutants significantly by using nano-iron technology.

22.3.2 *Use of Dendrimers in Bioremediation*

The term “dendrimers” is a Greek word, combining the two words “dendri”, which means the branch of a tree, and “meros”, which means part of a tree. Dendrimers are usually monodisperse and highly branch macromolecular compounds, which are recently recognized in the field of polymers. The compound dendrimer is a polymeric material, which is a giant molecule comprisingseveral small molecules

Table 22.2 Remediation of different pollutants through nano-iron technology (Rizwan et al. 2014)

Carbon tetrachloride (CCl_4)	Chrysoidine	Cis-dichloroethene
Trichlorobenzene $C_6H_3Cl_3$	Cadmium (Cd)	NDMA
Chloroform ($CHCl_3$)	Tropaeolin	Trans-dichloroethene
Chloromethane (CH_3Cl)	Acid red	Vinyl chloride
Dichloromethane (CH_2Cl_2)	Acid orange	1,1-Dichloroethan
Orange II	Trichloroethane ($C_2H_3Cl_3$)	Nitrate (NO^{3-})
Hexachlorobenzene	Mercury (Hg)	PCBs
Lindane	Tetrachloroethene($C_2H_2Cl_4$)	Perchlorate
Pentachlorobenzene ($C_2H\ Cl_5$)	Nickel (Ni)	Dioxins
DDT	Arsenic (As)	Dibromochloromethane
Dichlorobenzene	Bromoform($CHBr_3$)	TNT
Chlorobenzene (CH_5Cl)	Dibromochloromethane	Dichromate

(monomers) by covalent bonds. Dendrimers have some specific important applications and also some potential applications. Dendrimers are highly branched and monodispersed giant molecules having controlled or regular design and composition containing three components:

- A central core
- Radial symmetry or interior branch cells
- A peripheral group or design containing three components

Since dendrimers contain many voids on their surface, it is easier for them to interact with other materials. Hence, NPs composite associated with dendrimers can be applied for increasing the catalytic properties in many chemical reactions. This kind of modern composite material can be efficiently used for the treatment of water, wastewater and dyes because of their greater surface area, lower toxicity and high reactivity. The composite PAMAM/dendrimers are specifically used for the treatment of water, since they are a non-toxic and effective agent for water treatment. A new simple filtration unit is now developed for of organic contaminants by using TiO_2 porous ceramic filters, where the pores present in its surfaces were saturated with a dendrimer of alkylated poly(propylene imine), a β-cyclodextrin or poly(ethyleneimine) hyperbranched polymer producing a hybrid model of inorganic/organic filter modules which has a greater surface area and high mechanical strength (Najafi et al. 2021; Sudhakar et al. 2020).

22.3.3 Carbon Nanotubes (CNTs) and Nanocrystals Used in Bioremediation

CNTs are now treated as a new modified adsorbent used for the removal of different toxic heavy metals such as Cd, Cr(VI), Pb, Ni, Cu, Hg Zn, As and Co. Hence, CNTs are considered an interesting adsorbent material for the remediation of heavy metals and its ions from aqueous solutions. Now, CNT(s) and cyclodextrins (CD) are effectively used as suitable less cost materials for the treatment of water and wastewater (Mubarak et al. 2013).

Example FeO/multiwall CNTs on modification by cyclodextrin (FeO/MWCNTs/CD) were synthesized by adding 1,6-diisocyanatohexane as the cross-linking agent, which is found to be an interesting material for remediation of organic contaminates (Hu et al. 2010).

The efficiency of the removal of p-nitrophenol from water by using the NMs of these composite is around 70%. Again another study identified that the NMs of FeO/MWCNTs/CD possess the outstanding capability of regeneration and are a promoter of excellent low-cost material in the treatment of water and wastewater. Therefore, some specific exceptional properties of carbon-based NMs, including CNTs, nanocrystals facilitate advanced technologies to recognize and solve a wide range of environmental problems and can be applied as sorbents, technologies for renewable energy, membranes of high-flux, antimicrobial agents, environmental sensors, or as depth filters which help in the strategies for pollution prevention. The NMs, such as multi-walled carbon nanotubes (MWCNTs), single-walled carbon nanotubes (SWCNTs) and also hybrid carbon nanotubes (HCNTs), show excellent performance for the removal of toxic C_6H_5 (C_2H_5) from contaminated water. The SWCNTs show a better capability of sorption for ethylbenzene than MWCNTs and HCNTs and serve as an excellent material to maintain good water quality. Hence, SWCNTs can be applied to remediate the environment to avoid diseases caused by ethylbenzene. Now, CNTs and CDs, both in combination, can be used for the monitoring and treatment of water pollution. Recently, another NM composite (CD-co-hexamethylene/toluene-di-isocyanate polyurethanes modified by CNTs) has been developed, which can be effectively applied for the removal of organic pollutants from wastewater up to a very low level of concentration. The polymer nanocomposites associated with CNT, thiacalixarenes and calixarenes are observed to be an appropriate material for the removal of organic pollutants such as p-nitrophenol and some metal pollutants such as Cd^{2+} and Pb^{2+} from contaminated wastewater. The NM CNTs calcium alginate (CA) possesses the excellent property of adsorption of copper and possesses almost 69.9% copper removal efficiency, even at a pH as low as 2.1. The NMs of magnetic-MWCNT composite can be successfully used for the removal of cationic dye from contaminated water and MWCNTs can be used effectively for the removal of Ni^{2+} ions from industrial effluents (Zhang et al. 2019; Sivashankar et al. 2014; Bina et al. 2012).

22.3.4 Enzyme NPs Used in Bioremediation

Proteins and enzymes are found to be highly precise and effective, which serves as a biocatalyst for the bioremediation of many contaminates. Figure 22.3 shows different approaches of enzymatic bioremediation.

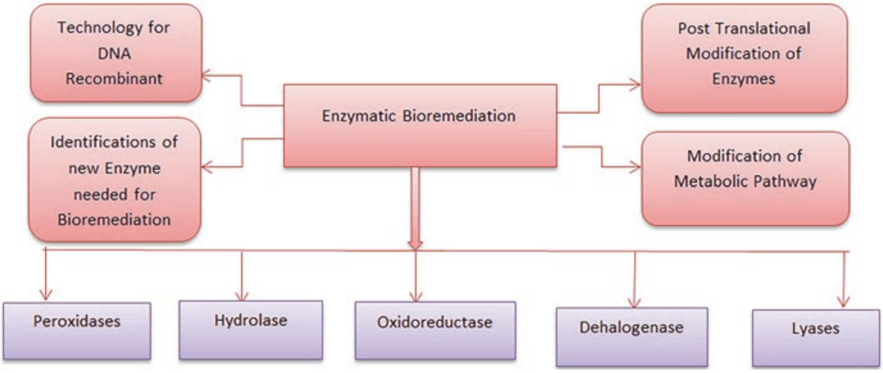


Fig. 22.3 Approaches of enzymatic bioremediation

The remediation of the pollutants through the use of various microbes is usually a slow process, which sometimes retards the possibility of bioremediation. Therefore, microbial enzymes obtained from their cells can be used more successfully for bioremediation than total microorganisms, in order to overcome this problem. Again, enzymes are biological macromolecules having complex structure and catalyzes various biochemical reactions associated with the path of degredation of contaminates. The use of enzymes is the cause of decreasing the energy of activation of the reactant molecules or species, and therefore sdincreases the reaction rate of sbioremediation. The bioremediation associated with the purified and partly purified enzyme never depend upon the growth and reproduction capability of the specified microorganism in the contaminated atmosphere, whereas it can depend upon the function of the enzyme as a catalyst concealed by the microbial community. In a soil which has a lower concentration of nutrients, bioremediation can be achieved successfully by the use of purified enzymes. The toxic materials generated during the microbial biotransformation are never formed by the use of enzymatic biotransformation, which maintains a clean, safe and sustainable environment. The enzymes are more mobile and specific towards the substrate in the environment as compared to the microbial community. However, the inadequate level of stability and comparatively less catalytic lifetimes of the used enzymes present a problem in their being used as a suitable profitable alternatives as catalysts. The activity of enzymes decreases because of oxidation, which is the cause of their shorter lifetime and the reduction in stability, thereby interpreting these as less efficient in catalytic activity. Again, there is another pathway of stabilizing and reusing the enzyme NPs for a longer period due to the addition of magnetic Fe NPs to it. If the Fe-NPs are strongly attached to enzymes, then enzymes can be easily eliminated from products or reactants through the application of a magnetic field (Sharma et al. 2018; Kumar and Bharadvaja 2019).

22.3.4.1 Single-Enzyme NPs Used in Bioremediation

Enzymes are usually structural proteins and are effective in specific reactions as biocatalysts for the remediation of pollutants from nature. However, their lower stability and their comparatively shorter life cycles restricts their applicability as potential catalysts when compared with synthetic catalytic material. Since enzymes easily undergo oxidation, they can rapidly lose their activity and becoming less effective. The attachment of NPs to enzymes forms a new substance, which is an effective pathway of enhancing their stability, success, reusability and longevity. The magnetic Fe-NPs are more suitable, because they can be separated easily after use through the application of a magnetic field. The two most potential catabolic enzymes used for this purpose are peroxides and trypsin; they form uniform core-shell magnetic nanoparticles (MNPs). The activity and lifetime of the enzymes used enhance histrionically from hours to weeks and the conjugation of enzyme and MNPs are highly stable, economical and show excellent performance. The MNPs can shield the enzymes leading to the prevention of oxidation during the time of bioremediation and increasing the lifetime of the added enzymes. Enzymes usually acted as magnificent biocatalysts, which are used in various potential applications, such as chemical conversions, bioremediation and biosensing; otherwise, if it is conjugated with NPs, then its performance increases exponentially. Recently, nanoporous silica on conjugation with enzymes shows a high surface-to-volume ratio and exhibits magnificent performance in the bioremediation of the contaminates present in nature (Kim et al. 2006; Rizwan and Ahmed 2019).

22.3.5 Engineered Polymer-Based NPs for Bioremediation of Contaminants

Those toxic organic contaminates having hydrophobic properties, mainly polycyclic aromatic hydrocarbons (PAHs) present in the soil, exhibit less solubility and mobility and strongly undergo sorption by the soil. Furthermore, the sequestration of sorption into the soil in the nonaqueous phase liquids (NAPLs) is the cause of decreasing bioavailability. The NP of amphiphilic polyurethane (APU) is developed for the remediation of PAHs present in the contaminated soil. The NPs are normally synthesized from poly(ethylene glycol) or polyurethane acrylate anionomer (UAA) or urethane acrylate (PMUA) with effective modification, undergo cross-linking and emulsion with water and cause the remediation of PAHs. The APU particles possess the capability of increasing transport and desorption in the similar way to surfactant micelles, but whereas this is similar to the components of surface-active micelles, the individual cross-linked forerunner chains in APU particles do not freely undergo sorption at the surface of the soil. The APU particles can able to attain desired properties, which are stable and their concentration is unchanged in the aqueous medium. The NPs of APU are designed in such a way that their interior regions possess a higher affinity towards phenanthrene (PHEN) and its hydrophilic surfaces stimulate the mobility of the particles in the soil. The attraction of the APU particles towards pollutants such as PHEN can be regulated by altering the dimension of the hydrophobic segment utilized in the synthesis of the chain. The rate of mobility of the colloidal particles of APU present in the soil can be regulated through the change in dimension of the sagging water-soluble chains, which are attached at the surface of the particle or charge density. The capability to regulate the properties of the particles provides great potential for synthesizing various kinds of NPs, which are able to optimize the ousvariety of pollutants and their kinds along with soil conditions. The addition of NPs based on polymeric materials enhances the solubility of the organic pollutant, PHEN, and also accelerates the rate of release of PHEN from the polluted aquifer substances. The NPs synthesized from poly (ethylene) glycol with modified urethane acrylate (PMUA) are the cause of accelerating the rate of bioavailability of PHEN. The NPs of PMUA also exhibit the rate of mineralization of PHEN crystal in an aqueous medium with sorption of PHEN on the aquifer substances and are able to dissolve hexadecane. The approachability of pollutants towards the PMUA particles via bacteria indicates the use of particles, which is highly effective in accelerating the rate of in-situ biodegradation for the bioremediation of contaminates via natural attenuation. The nature of the PMUA NPs is usually stable in the heterogeneous population of microbes; this leads to the reusability of these after the PHEN bonded with NPs, which are degraded through bacteria. Now, researchers made attention to the remediation of biogenic uraninite by using NPs because of the tiny particles and its biological occurrence (Dhillon et al. 2012; Tungittiplakorn et al. 2004; Mazarji et al. 2021).

22.3.6 Use of Biogenic Uraninite NPs for Remediation of Uranium

The reduction of U(VI) through the use of a microbial community has been represented to be catalyzed a number of microorganisms, among which most of these are sulphate or metal-reducing bacteria. The reduction of microbial U(VI) is preferably an unexpected method through which the microbial enzyme transfer occurs at a high concentration of electrons to U(VI). The initial step is the synthesis of biogenic uraninite and reduction of U(VI) to U(IV). The transfer of electrons is supposed to be mediated by cytochromes of c-type, which are localized either on the outer part of the membrane or in the periplasm. However, the mechanism through which cytochromes transfer requisite electrons to U(VI) is unidentified. Since U(V) is comparatively less stable as an aqueous complex, it is possible therefore to proceed with an enzymatic reduction from U(VI) to U(V) with simultaneous disproportionation to U(IV) and U(VI). Following the reduction of U(VI) to U(IV), in the second stage, the synthesis of biogenic uraninite involves the precipitation of mineral products. Now researchers are focussing on the synthesis and application of biogenic uraninite because of its significance in the strategies of bioremediation owing to its natural biological origin and its small dimensions. It was finally concluded that these significant NMs are highly effective in the bioremediation of subsurface U(VI) pollution (Banala et al. 2020; Vogt et al. 2011).

22.3.7 The Phytoremediation of Heavy Metals by Using NPs of **Noaea Mucronata**

The contamination of soil and water by toxic heavy metals has been a increasing global problem. for a few years. Researchers have been working continuously to remediate the contaminated sources of water and land. Experimentally, it was found that six important plant species, *Gundelia tournefortii, Noaea Mucronata, Centaurea virgata, Angustifolia, Reseda lutea, Eleagnum and Scariola Orientalis*, possess the capability of accumulating heavy metals such as Cu, Ni, Zn, Pb and its ions from water and soil. The plant species *Chenopodiaceae* is found to be the best accumulator of Pb and also a very good accumulator for the the heavy metals Zn, Ni, and Cu. In the case of Fe, the plant species *Reseda lutea* serves as the best accumulator. The NPs synthesized from *N. mucronata* possess the excellent capability of bioaccumulation. It was found that the concentration of HMs decrease drastically during the successful bioremediation of three days. Hence, the plant species *N. mucronata* is a highly efficient accumulator and the NPs of these particles exhibit high performance for bioremediation and detoxification in a critical situation (Mohsenzadeh and Chehregani Rad 2012; Chehregani et al. 2009).

22.3.8 Microbial Nano-biomolecules for the Remediation of Contaminants

The non-glucan exopolysaccharide is symbolized as EPS-605 self-assembled, which forms NPs of the spherical size of almost 176 nm radius. It consists of mannose, galactose and glucose, modified many times such as acylation, carboxylation, phosphorylation and sulfation, and possesses a higher negative charge. The NPs of EPS-605 exhibit a higher ability of biosorption for the heavy metal ions Pb^{2+}, Cd^{2+}, Cu^{2+}, and methylene blue as compared to nanosorbents and biosorbents. The capability of adsorption of EPS-605 is influenced by various environmental factors, such as temperature, pH and the initial concentration of the adsorbate, time of contact and the existence of circumstantial electrolytes. However, EPS-605 acts as an outstanding reductant for the formation of monodispersed silver and gold NPs (AgNPs and AuNPs). The nanoparticulate immobilized *laccase* possesses the capability to decolourize the toxic Congo red dye by the direct attachment of enzyme NPs on the glass bead surface in order to measure the activity of decolourization of the non-immobilized and immobilized *laccase* (Mandeep and Shukla 2020; Kalia and Singh 2020).

22.3.9 Engineered Polymeric NPs Used in the Remediation of Soil

The toxic organic pollutants polynuclear aromatic hydrocarbons (PAHs) are hydrophobic in nature and are a common contaminant present in the groundwater, which is strongly sorbed to soil, making their removal highly problematic. Another NP, amphiphilic polyurethane (APU), is highly effective in the bioremediation of PAHs from contaminated soil. The use of NPs of poly (ethylene glycol), polyurethane acrylate anionomer (UAA) and modified polyurethane acrylate (PMUA) is the cause of cross-linking and emulsification in water. The particles of APU possess the capability of increase in transport and desorption in the pathway similar to that of other surfactant micelles;however, it differs from the surface-active constituents of micelles. The different cross-linked predecessor chains in the APU particles freely sorb to the surface of the soil. The engineered APU particles have independent concentration, are stable in an aqueous medium and exhibit a greater affinity towards phenanthrene. Their surface exhibits hydrophilic properties, which stimulate the mobility of the particle in soil. The interaction of APU particles towards the pollutants can be regulated by the alternation of the hydrophobic segment that can be applied in the synthesis of chains. The mobility of the colloidal form of APU in the soil is regulated based on the size of the sagging water-soluble chains or charge density that can be found on the surface of the particle (Guerra et al. 2018; Thomé et al. 2015).

22.4 The Science Regarding Bioremediation by Using NM

There are several reasons for using various kinds of NMs in bioremediation to clean up the environment.

- The surface area of the NMs is much larger than that of any other materials; therefore, more quantities of the NM particles come into contact with the surrounding toxic materials, therefore tremendously increasing the reactivity.
- Since NMs exhibit a quantum effect, which is the cause of the requirement ofa lesser amount of activation energy to feasible the chemical reactions for bioremediation.
- There is another property, known as surface plasmon resonance, which is provided by NPs, and causes the identification of toxic contaminated materials.
- Because of the tiny size of different non-metallic and metallic NPs such as single metal NPs, carbon base NMs and bimetallic NPs, etc., they can be highly

effective for cleaning of the environment (Rahman et al. 2020). The science behind this is as follows.

1. NPs possess the capacity to penetrate or diffuse inside the zone of contamination, whereas microparticles or any other particles cannot be penetrated.
2. NPs show higher reactivity towards the redox reaction of the contaminants. It was found that the oxide-coated zero-valent Fe develops feeble complexes in the outer sphere of the contaminants such as tetrachloride (CT). The oxide coating accelerates the reactivity via electron transfer. CT undergoes cleavage and produces CH_4, formate and CO_2. Again the toxic compound benzoquinone is broken and converted into C_2HCl_3 and other hazardous chlorinated compounds are broken down into comparative molecules of less toxicity.
3. TiO_2 nanotubes possess the potential to degrade or break down pentachlorophenol (PCP) into non-toxic simple products via photoelectrocatalytic reaction. The single metal NPs shows good performance as biocatalysts in case of reductive dechlorination.
4. The NPs of Pd(0) are gathered inside the cytoplasm and cell wall of *Shewanella oneidensis*, which is charged by the radicals due to the incorporation of various substrate molecules such as hydrogen, formate and acetate and act as electron donors in the bioreductive analyze comprising Pd (II). At the time of deposition of charged Pd (0), *S. oneidensis* cells come into contact with the chlorinated compounds, where the radicals of Pd (0) react catalytically with PCP and cause of elimination of Cl_2 molecules from toxic chlorinated materials (Cecchin et al. 2017; Zhang and Hu 2018).
5. NPs also used effectively for the immobilization of microbial cells, which can undergo degradation or biorecovery of some specific chemical compounds. Like usual cell immobilization on an immovable surface or micron-sized media, the magnetic NPs (specifically Fe_3O_4) undergo functionalization with ammonium oleate with a coating over the *Pseudomonas delafieldii* surface. By the application of an external magnetic field to the microbial cells, the cells coated with magnetic NP are deposited at a particular location on the surface of the reactor wall, which is detached from the bulk solution and then recycled to make it suitable for the treatment of the substrate.
6. The addition of microbial cells in a bioreactor having a high level of biomass concentration leads to the removal of sulfur from the fossil fuel (dibenzothiophene) similar to non-NP-coated cells (Liu et al. 2009).

22.5 Conclusion

The science of nanotechnology is an advanced field, which can be used potentially in the environmental sector such as with the treatment of water and wastewater, green synthesis, sensor design and the remediation of pollutants. The toxic contaminates and organic substances can be effectively removed from the polluted area by using NMs of the appropriate kind. The NMs produced biologically are playing a key role in cleaning the polluted area or regions. The microbial cells, such as compartments of cytoplasmic vesicular and periplasmic space, control the size and shape of NMs, which is necessary for suitable application. The field of nanotechnology potentially influences the interaction between environment and energy. Since NMs are toxic towards the environment and undergo bioaccumulation, therefore we have to adopt the green synthesis process of destroying contaminants without any kind of toxic effect on the biota and environment. More emphasis is given to the formation of smart NMs for the effective remediation of the environment and maintaining sustainability. The application of NMs not only reduces the cost of detoxification of waste materials but also catalyzes the remediation reaction and increases the effectiveness of the microorganisms. Although, the approach of nanobioremediation plays a vital role in maintaining a sustainable environment, so far as a safety factor is concerned the use of NMs is the cause of health risk impacts considering the relation between use and synthesis. The NPs synthesized biologically are more suitable to inhabit the toxic effect on the microbes and maintain a sustainable environment.

References

Abatenh E, Gizaw B, Tsegaye Z (2017) Application of microorganisms in bioremediation-review. J Environ Microbiol 1(1):2–9

Ali A, Zafar H, Zia M, ul Haq I, 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

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(11):180–197. https://doi.org/10.1007/s11274-016-2137-x

Banala UK, Das NPI, Toleti SR (2020) Microbial interactions with uranium: towards an effective bioremediation approach. Environ Technol Innov 1–17:101254. https://doi.org/10.1016/j.eti.2020.101254

Baragaño D, Alonso J, Gallego JR, Lobo MC, Gil-Díaz M (2020) Magnetite nanoparticles for the remediation of soils co-contaminated with As and PAHs. Chem Eng J 399:1–10. https://doi.org/10.1016/j.cej.2020.125809

Betancur-Corredor B, Pino NJ, Cardona S, Peñuela GA (2015) Evaluation of biostimulation and Tween 80 addition for the bioremediation of long-term DDT-contaminated soil. J Environ Sci 28:101–109. https://doi.org/10.1016/j.jes.2014.06.044

Bhalerao TS (2014) A review: applications of iron nanomaterials in bioremediation and in detection of pesticide contamination. Int J Nanopart 7(1):73–89

Bina B, Amin M, Rashidi A, Pourzamani H (2012) Benzene and toluene removal by carbon nanotubes from aqueous solution. Arch Environ Prot 38(1):3–25. https://doi.org/10.2478/v10265-012-0001-0

Cao X, Alabresm A, Pin Chen Y, Decho AW, Lead J (2019) Improved metal remediation using a combined bacterial and nanoscience approach. Sci Total Environ 704:1–31. https://doi.org/10.1016/j.scitotenv.2019.1353

Cecchin I, Reddy KR, Thomé A, Tessaro EF, Schnaid F (2017) Nanobioremediation: integration of nanoparticles and bioremediation for sustainable remediation of chlorinated organic contaminants in soils. Int Biodeterior Biodegradation 119:419–428. https://doi.org/10.1016/j.ibiod.2016.09.02

Chehregani A, Noori M, Yazdi HL (2009) Phytoremediation of heavy-metal-polluted soils: screening for new accumulator plants in Angouran mine (Iran) and evaluation of removal ability. Ecotoxicol Environ Saf 72(5):1349–1353. https://doi.org/10.1016/j.ecoenv.2009.02.012

Dhillon GS, Kaur S, Verma M, Brar SK (2012) Chapter 3: Biopolymer-based nanomaterials. In: Analysis and risk of nanomaterials in environmental and food samples, vol 59, pp 91–129. https://doi.org/10.1016/b978-0-444-56328-6.00003-7

Dzionek A, Wojcieszyńska 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

Fang Y-L, Miller JT, Guo N, Heck KN, Alvarez PJJ, Wong MS (2011) Structural analysis of palladium-decorated gold nanoparticles as colloidal bimetallic catalysts. Catal Today 160(1):96–102

Gothandam KM, Ranjan S, Dasgupta N, Lichtfouse E (eds) (2020) Environmental biotechnology, Environmental chemistry for a sustainable world, vol 2, pp 1–221. https://doi.org/10.1007/978-3-030-38196-7

Guerra F, Attia M, Whitehead D, Alexis F (2018) Nanotechnology for environmental remediation: materials and applications. Molecules 23(7):1760–1783. https://doi.org/10.3390/molecules2307176

Hu J, Shao D, Chen C, Sheng G, Li J, Wang X, Nagatsu M (2010) Plasma-induced grafting of cyclodextrin onto multiwall carbon nanotube/iron oxides for adsorbent application. J Phys Chem B 114(20):6779–6785. https://doi.org/10.1021/jp911424k

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 9:1050–1074. https://doi.org/10.3762/bjnano.9.98

Kalia A, Singh S (2020) Myco-decontamination of azo dyes: nano-augmentation technologies. 3 Biotech 10(9):384–412. https://doi.org/10.1007/s13205-020-02378-z

Kim J, Jia H, Lee C, Chung S, Kwak JH, Shin Y, Grate JW (2006) Single enzyme nanoparticles in nanoporous silica: a hierarchical approach to enzyme stabilization and immobilization. Enzym Microb Technol 39(3):474–480. https://doi.org/10.1016/j.enzmictec.2005.11.0

Koul B, Taak P (2018) Nanobioremediation. In: Biotechnological strategies for effective remediation of polluted soils. Springer, Singapore, pp 197–220. https://doi.org/10.1007/978-981-13-2420-8_8

Kumar L, Bharadvaja N (2019) Chapter 6: Enzymatic bioremediation: a smart tool to fight environmental pollutants. In: Smart bioremediation technologies. Elsevier, pp 99–118. https://doi.org/10.1016/b978-0-12-818307-6.00006-8

Kumar SR, Gopinath P (2016) Chapter 2: Nano-bioremediation applications of nanotechnology for bioremediation. In: Remediation of heavy metals in the environment, pp 27–48. https://doi.org/10.1201/9781315374536-3

Kumari B, Singh DP (2016) A review on multifaceted application of nanoparticles in the field of bioremediation of petroleum hydrocarbons. Ecol Eng 97:98–105. https://doi.org/10.1016/j.ecoleng.2016.08.006

Liu J-C, Chen W-J, Li C-W, Mong K-KT, Tsai P-J, Tsai T-L, Chen Y-C (2009) Identification of Pseudomonas aeruginosa using functional magnetic nanoparticle-based affinity capture combined with MALDI MS analysis. Analyst 134(10):2087–2096. https://doi.org/10.1039/b908069d

Mandeep, Shukla P (2020) Microbial nanotechnology for bioremediation of industrial wastewater. Front Microbiol 11:1–18

Mazarji M, Minkina T, Sushkova S, Mandzhieva S, Bidhendi GN, Barakhov A, Bhatnagar A (2021) Effect of nanomaterials on remediation of polycyclic aromatic hydrocarbons-contaminated soils: a review. J Environ Manag 284:112023. https://doi.org/10.1016/j.jenvman.2021.112023

Mohsenzadeh F, Chehregani Rad A (2012) Bioremediation of heavy metal pollution by nanoparticles of *Noaea mucronata*. Int J Biosci Biochem Bioinform 2(2):1–5. https://doi.org/10.7763/IJBBB.2012.V2.77

Mubarak NM, Sahu JN, Abdullah EC, Jayakumar NS (2013) Removal of heavy metals from wastewater using carbon nanotubes. Sep Purif Rev 43(4):311–338. https://doi.org/10.1080/15422119.2013.821996

Najafi F, Salami-Kalajahi M, Roghani-Mamaqani H (2021) A review on synthesis and applications of dendrimers. J Iran Chem Soc 18:503–517. https://doi.org/10.1007/s13738-020-02053-3

Pandey G (2018) Prospects of nanobioremediation in environmental cleanup. Orient J Chem 34(6):2838–2850. https://doi.org/10.13005/ojc/340622

Parthipan P, Prakash C, Perumal D, Elumalai P, Rajasekar A, Cheng L (2021) Biogenic nanoparticles and strategies of nano-bioremediation to remediate PAHs for a sustainable future. In: Joshi SJ, Deshmukh A, Sarma H (eds) Biotechnology for sustainable environment. Springer, Singapore, pp 609–626. https://doi.org/10.1007/978-981-16-1955-7_13

Patel HK, Kalaria RK, Khimani MR (2020) Nanotechnology: a promising tool for bioremediation. In: Removal of toxic pollutants through microbiological and tertiary treatment, pp 515–547. https://doi.org/10.1016/b978-0-12-821014-7.00020-4

Patra Shahi M, Kumari P, Mahobiya D, Kumar Shahi S (2021) Nano-bioremediation of environmental contaminants: applications, challenges, and future prospects. In: Bioremediation for environmental sustainability, pp 83–98. https://doi.org/10.1016/b978-0-12-820318-7.00004-6

Perea Vélez YS, Carrillo-González R, González-Chávez M (2021) Interaction of metal nanoparticles–plants–microorganisms in agriculture and soil remediation. J Nanopart Res 23:206–232. https://doi.org/10.1007/s11051-021-05269-3

Pete AJ, Bharti B, Benton MG (2021) Nano-enhanced bioremediation for oil spills: a review. ACS EST Eng 1(6):928–946. https://doi.org/10.1021/acsestengg.0c00217

Rahman Z, Singh VP (2020) Bioremediation of toxic heavy metals (THMs) contaminated sites: concepts, applications and challenges. Environ Sci Pollut Res Int 27:27563–27581. https://doi.org/10.1007/s11356-020-08903-0

Rahman A, Kumar S, Nawaz T (2020) Biosynthesis of nanomaterials using algae. In: Microalgae cultivation for biofuels production. Elsevier, pp 265–279. https://doi.org/10.1016/b978-0-12-817536-1.00017-5

Rajput VD, Minkina T, Kumari A (2022) A review on nanobioremediation approaches for restoration of contaminated soil. Eurasian J Soil Sci 11:1–19. https://doi.org/10.18393/ejss.990605

Rizwan M, Ahmed MU (2019) Nanobioremediation: ecofriendly application of nanomaterials. In: Martínez L, Kharissova O, Kharisov B (eds) Handbook of ecomaterials. Springer, Cham, pp 99–118. https://doi.org/10.1007/978-3-319-68255-6_97

Rizwan M, Singh M, Mitra CK, Morve RK (2014) Ecofriendly application of nanomaterials: nanobioremediation. J Nanopart 2014:1–7. https://doi.org/10.1155/2014/431787

Samson MG, Yavuz SY, LaDonna W, William G, Jamal U, Hyeonggon K, Sitther V (2021) Zero-valent iron nanoparticles induce reactive oxygen species in the cyanobacterium, Fremyella diplosiphon. ACS Omega:1–9. https://doi.org/10.1021/acsomega.1c04482

Sharma B, Dangi AK, Shukla P (2018) Contemporary enzyme based technologies for bioremediation: a review. J Environ Manag 210:10–22. https://doi.org/10.1016/j.jenvman.2017.12.075

Shen X, Zhu L, Liu G, Tang H, Liu S, Li W (2009) Photocatalytic removal of pentachlorophenol by means of an enzyme-like molecular imprinted photocatalyst and inhibition of the generation of highly toxic intermediates. New J Chem 33(11):2278–2297. https://doi.org/10.1039/b9nj00255c

Sherry Davis A, Prakash P, Thamaraiselvi K (2017) Nanobioremediation technologies for sustainable environment. Environ Sci Eng:13–33. https://doi.org/10.1007/978-3-319-48439-6_

Singh R, Behera M, Kumar S (2020) Nano-bioremediation: an innovative remediation technology for treatment and management of contaminated sites. In: Bharagava R, Saxena G (eds) Bioremediation of industrial waste for environmental safety. Springer, Singapore, pp 165–182. https://doi.org/10.1007/978-981-13-3426-9_7

Sivashankar R, Sathya AB, Vasantharaj K, Sivasubramanian V (2014) Magnetic composite an environmental super adsorbent for dye sequestration – a review. Environ Nanotechnol Monit Manag 1–2:36–49. https://doi.org/10.1016/j.enmm.2014.06.001

Sudhakar MS, Aggarwal A, Sah MK (2020) Engineering biomaterials for the bioremediation: advances in nanotechnological approaches for heavy metals removal from natural resources. In: Emerging technologies in environmental bioremediation, pp 323–339. https://doi.org/10.1016/b978-0-12-819860-5.00014-6

Thomé A, Reddy KR, Reginatto C, Cecchin I (2015) Review of nanotechnology for soil and groundwater remediation: *Brazilian perspectives*. Water Air Soil Pollut 226(4):121–140. https://doi.org/10.1007/s11270-014-2243

Tungittiplakorn W, Lion LW, Cohen C, Kim J-Y (2004) Engineered polymeric nanoparticles for soil remediation. Environ Sci Technol 38(5):1605–1610. https://doi.org/10.1021/es0348997

Vázquez-Núñez E, Molina-Guerrero CE, Peña-Castro JM, Fernández-Luqueño F, de la Rosa-Álvarez MG (2020) Use of nanotechnology for the bioremediation of contaminants: a review. PRO 8(7):826–841. https://doi.org/10.3390/pr8070826

Vogt SJ, Stewart BD, Seymour JD, Peyton BM, Codd SL (2011) Detection of biological uranium reduction using magnetic resonance. Biotechnol Bioeng 109(4):877–883. https://doi.org/10.1002/bit.24369

Yadav GK, Ahmaruzzaman M (2021) Recent advances in the development of nanocomposites for effective removal of pesticides from aqueous stream. J Nanopart Res 23:213–232. https://doi.org/10.1007/s11051-021-05290-6

Yadav VK, Khan SH, Choudhary N, Tirth V, Kumar P, Ravi RK, Godha M (2021) Nanobioremediation: a sustainable approach towards the degradation of sodium dodecyl sulphate in the environment and simulated conditions. J Basic Microbiol:1–13. https://doi.org/10.1002/jobm.202100217

Zhang H, Hu X (2018) Biosynthesis of Pd and Au as nanoparticles by a marine bacterium Bacillus sp. GP and their enhanced catalytic performance using metal oxides for 4-nitrophenol reduction. Enzym Microb Technol 113:59–66. https://doi.org/10.1016/j.enzmictec.2018.03

Zhang W, Zhang D, Liang Y (2019) Nanotechnology in remediation of water contaminated by poly- and perfluoroalkyl substances: a review. Environ Pollut 247:266–276. https://doi.org/10.1016/j.envpol.2019.01.045

Zhou Y, Kumar M, Sarsaiya S, Sirohi R, Awasthi SK, Sindhu R, Awasthi MK (2022) Challenges and opportunities in bioremediation of micro-nano plastics: a review. Sci Total Environ 802:1–15

Chapter 23
Nanoparticles-Assisted Phytoremediation of Polluted Soils: Potential Application and Challenges

Muhammad Umair, Muhammad Zia-ur-Rehman, Muhammad Akram Qazi, Ali Rizwan, Muhammad Javid Qamar, and Sehar Razzaq

Abstract Soil pollution with various types of organic and inorganic substances is a well-known global issue. Various techniques have been implied to remediate these polluted soils. Among these techniques, phytoremediation is the best-known economical and eco-friendly way to deal with such soil problems. Despite its widespread use, phytoremediation has some limitations as it is a slow process and requires decades for remediation. The efficiency of this process can be enhanced by increasing the degradation and phytoavailability of pollutants. Several practices are there to assist the rate of phytoremediation. Among these practices, a novel technique is nano-phytoremediation which includes the application of nanoparticles (NPs) during phytoremediation. Nanoparticles can help in phytoremediation by direct removal of pollutants, promotion of plant growth, and/or increasing pollutant bioavailability. Different types of nanoparticles are there to facilitate the phyto-based remediation processes like nano zero-valent iron, fullerene, carbon nanotubes, etc. Soil conditions and properties also affect the efficiency of the nano-phytoremediation to a great extent. Several challenges are also there to apply this technique for phytoremediation due to its cost and other environmental issues. This chapter has addressed the role of nanoparticles in the phytoremediation of organic and inorganic pollutants of soil, production technologies of NPs, and their application constraints. It can be an effective strategy to clean up soils but requires further research and long-term studies for its potential acceptability.

M. Umair · M. Zia-ur-Rehman (✉) · A. Rizwan
Institute of Soil and Environmental Sciences, University of Agriculture, Faisalabad, Pakistan

M. A. Qazi
Soil Fertility Research Institute, Lahore, Punjab, Pakistan

M. J. Qamar
Soil and Water Testing Laboratory, Bahawalpur, Pakistan

S. Razzaq
State Key Laboratory of Eco-hydraulics in Northwest Arid Region of China, Xi'an University of Technology, Xi'an, China

L. Newman et al. (eds.), *Phytoremediation*, https://doi.org/10.1007/978-3-031-17988-4_23

Keywords Nano-phytoremediation · Nanoparticles · Soil pollution · Ecotoxicity · Nano-remediation · Soil remediation

23.1 Introduction

Soil is the most important component of the biosphere and plays a crucial role in the development of life on earth. Usually the terms "land" and "soil" are commonly used as synonyms, but land is a broader term in which soil is a component (Blum 2002). Soil not only acts as a medium for plant growth and food synthesis but also controls the primary processes of the earth, ensuring sustainable life (Schoonover and Crim 2015). These incorporate biogeochemical processes, water cycle, climatic conditions of earth, pollutant removal, biological gaseous exchange, ecosystem rehabilitation, and supporting biodiversity (Ayub et al. 2020). Concerning current perspective, soil pollution is an alarming environmental concern that is posing a severe threat to soil health and food quality (Rehman et al. 2021). Among these pollutants, there are inorganic heavy metals which have high persistency in the soil environment, and organic pollutants consisting of hazardous compounds (Ayub et al. 2021; Rehman et al. 2019). Among organic pollutants, polycyclic aromatic hydrocarbons (PAHs) and recalcitrant organic pesticides have appeared as influential factors affecting soil quality. Uncontrolled and irrational application of agrochemicals and wastewater irrigation is resulting in their build-up in soil and leading to food chain contamination (Ayub et al. 2021; Rehman et al. 2018).

Ever-increasing soil pollution with toxic substances requires remediation practices to ensure safe food production. Various techniques have been devised to combat pollutants in agricultural soils (Song et al. 2017a). Among these techniques, phytoremediation is the most suitable and environmentally acceptable technique. If we compare it with other techniques, phytoremediation is cost-effective, simple to operate, highly acceptable to the public, suitable to be adopted, and beneficial for soil health (Rizwan et al. 2018). Since the 1980s, phytoremediation has been an effectively as well as commonly used in-situ technique to restore soils affected by various organic and inorganic pollutants (Sharma and Pandey 2014; Dubchak and Bondar 2019). It has proved its potential worldwide through successful field trials; therefore, the global phytoremediation demand is vast (Gerhardt et al. 2017). However, phytoremediation is a long-term soil remediation strategy and various factors limit its application such as slow uptake and degradation of pollutants, plant growth, climatic conditions, land quality, and extent of contaminant phytotoxicity. To enhance the usefulness of phytoremediation, various approaches are being used such as field practices, addition of chemical treatments, inoculation with effective microbes, and use of genetic manipulation techniques (Gerhardt et al. 2017). However, the effectiveness of phytoremediation has become broader with the development of nanotechnology due to the emergence of new ideas to improve its efficiency (Gong et al. 2018). Nanoparticles (NPs) are materials having a size between 1 and 100 nm in at least one dimension (Sohail et al. 2019). For a few years, various nano-based products have been produced to fight against plant diseases and improve crop production, like nano-pesticides, nano-fertilizers, and nanosensors (Servin et al. 2015).

The application of nanotechnology is going on increasing in various sectors such as agriculture, food processing and packaging, medical treatments, genetic modifications, drug delivery in humans, and cancer medicaments among many others (Irshad et al. 2021; Ayub et al. 2019: Sohail et al. 2019). Aside from all others, it has been extensively used for the remediation of environmental matrixes like soil and water. They have certain unique characteristics like a high surface-to-volume ratio that generates quantum effects and certain specific physio-chemical characteristics due to which their application in environmental remediation has been increased (El-Ramady et al. 2020). Recently, various studies have reported the application of nanoparticles to improve the efficiency of phytoremediation. These incorporate wastewater treatment, groundwater treatment, and detoxification of soils affected by pollutants (Ibrahim et al. 2016). Significant work has been done successfully on its application in environmental pollution remediation in Europe and USA (Mueller and Nowack 2010). The application of nanomaterials to enhance the efficiency of phytoremediation ensures promising results. Nano-phytoremediation involves three basic components: plant, pollutant, and nanoparticles. Nanomaterials can improve phytoremediation directly as well as indirectly. They can speed up phytoremediation directly by altering the characteristics of pollutants as well as plants, and indirectly by improving the existing relationship between pollutant and plant. Nano-phytoremediation of soil pollutants using hyperaccumulator plants and nanoparticles can be a novel approach in the field of environmental remediation.

23.2 Nano-phytoremediation of Soil Pollutants

Many techniques have been developed to minimize pollutants in soils or to restrict their entry into the food chain (Ansari et al. 2019; Khan 2020). Among these, phytoremediation is the most suitable technique due to its low cost, ease of operation, minimum environmental harm, and high public acceptance (El-Ramady et al. 2020). Nanomaterial-assisted phytoremediation has been proved highly efficient in removing pollutants from soil. Nanoparticles have certain unique characteristics like high surface-to-volume ratio and specific physio-chemical characteristics which make them pertinent for environmental remediation (El-Ramady et al. 2020). Liang et al. (2017a) reported that phytoremediation of lead can be enhanced by applying nanomaterials. They reported that phytoextraction of lead increased by 16.74–31.76% within 45 days with hydroxyapatite nanoparticles application to rye grass *(Lolium perenne),* a hyper-accumulator of lead (Liang et al. 2017a). *Isatis cappadocica* is a hyper accumulator of arsenic; it can uptake arsenic in an appreciable amount, but the application of salicylic acid nanoparticles further enhanced the uptake of arsenic

(Souri et al. 2017). Nano-phytoremediation of organic pollutants like organochlorine, polycyclic aromatic hydrocarbons, petroleum, and explosives has also been found very effective. It can facilitate the degradation of such pollutants and can enhance their uptake by plants. Fullerene nanoparticles can enhance the phytoremediation of soils contaminated with trichloroethylene up to 82% (Kang 2014). Nano-phytoremediation can help in the remediation of a vast variety of pollutants in soil matrices containing both inorganic and organic substances as discussed below:

23.2.1 Inorganic Soil Pollutants

Agricultural and atmospheric deterioration with heavy metals and other inorganic pollutants like soluble salts is a serious issue concerning food security and human health. Environmental threats associated with inorganic pollutants vary significantly owing to complicated interactions at extracellular and intracellular levels (Saha et al. 2017). Salts of the alkali group influence the physio-chemical properties of the soil and disturb the soil-plant and water relationships. Toxic metallic ions interact with soil minerals more actively than other soluble salts depending on their speciation and elemental nature. Even at their minute concentration and lower mobility in the soil, they disturb the metabolic processes and influence the physiology of the plants. Heavy metals are defined as a group of metalloids having density and an atomic number greater than 5 g cm^{-3} and 20, respectively (Ali and Khan 2018). Some of these trace elements (Zn, Cu, Ni, Mo, Mn, Fe) are essential for the structural and biochemical processes in the plants including proper growth, tissue development, electron transport, redox reactions, and many other metabolic processes (Andresen et al. 2018). While nonessential heavy metals including lead, mercury, cadmium, chromium, arsenic, etc., are found toxic for plants growth with no known biological function along with food chain contamination even at minute concentrations (Rehman et al. 2019; Chibuike and Obiora 2014). Su et al. (2014) have reported worldwide average contamination of heavy metals including Cr, Cu, Pb, Zn, Ni, and Cd as 66.08, 49.60, 1733.94, 289.78, 29.14, and 1.52 mg kg^{-1} in urban soils, respectively. If we compare the persistency of heavy metals with organic pollutants, heavy metals do not undergo chemical or microbial decomposition and keep on accumulating to higher concentrations in soil matrices and cause ecotoxicity (Adriano et al. 2004). Several studies have shown nano-phytoremediation as an efficient way to combat with problem of heavy metal contamination. Ramie seedlings applied with a low dose of iron nanoparticles have a magnificent effect on the phytoremediation of cadmium-contaminated soils (Gong et al. 2017). On the other hand, the application of iron NPs significantly reduced the Cr uptake in the edible portion of rape and Chinese cabbage (Mokarram-Kashtiban et al. 2019). Nanoparticles have been effective in heavy metals immobilization in roots of the plants. Nano-hydroxyapatite with size 1 to 100 nm was applied to ryegrass which reduced the Pb accumulation in shoots and increased its deposition in root tissues. The formation of pyromorphite by Pb and nano-hydroxyapatite was the main mechanism of Pb immobilization in ryegrass in slightly alkaline soils (Xiaocan et al. 2019). If we compare herbaceous plants with woody plants with respect to food chain contamination, woody plants are more effective regarding sink pollutants than herbaceous plants due to their longer life, extensive root system, and better competition ability (Mokarram-Kashtiban et al. 2019). Due to their longer life, they can store heavy metals for longer periods without affecting the food chain and ecosystem hence problem of disposal of plants containing heavy metals is minimized (Mokarram-Kashtiban et al. 2019). Nano-phytoremediation of inorganic soil pollutants using different plant species and sources of NPs can be a novel approach in the field of environmental remediation.

23.2.2 Organic Soil Pollutants

Organic soil pollution includes a large variety of hazardous synthetic organic compounds being dumped into agricultural soils. These are of various kinds like organic phenols, pesticides, chlorinated phenols, azo dyes, poly aromatic hydrocarbons, persistent organic pollutants (POPs), polychlorinated biphenyls (PCBs), dichloro diphenyl trichloro ethane, and transformation products (DDTs), polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDDs/PC DFs), dioxin-like PCBs (dl-PCBs), endocrine disrupting chemicals, short-chain chlorinated paraffin, etc. (Bogdal et al. 2013; Hao et al. 2021). These organic products are prepared and used in huge amounts because of their vast application in a large number of sectors (Zhang et al. 2017). Among these, persistent organic pollutants (POPs) are most hazardous due to their resistance to degradation in the environment (high persistency) and accumulation in human and animal tissues. They affect food chains and are associated with chronic ecotoxic effects (Bogdal et al. 2013). Much of POPs have been banned worldwide but a few are being produced and used nowadays especially in less developed countries (Hao et al. 2021). Commonly ex situ approaches are being used for their remediation which isdestructive, very costly, and inefficient. Among physical techniques, controlled incineration is used which is slow and inefficient (Ebrahimbabaie and Pichtel 2021). These organic pollutants can also be decomposed by microorganisms and plants (Dolinová et al. 2017). Phytoremediation is the most suitable in situ method of soil remediation because of its being green and low cost (Rostami and Azhdarpoor 2019). Many studies have concluded that organic pollutants accumulate in the soil in much higher concentration and result in low plant growth, making phytoremediation less efficient (Košnář et al. 2018). Nanomaterials can directly decompose organic pollutants, facilitate their phytoavailability, or can improve overall plant health and growth (Song et al. 2019). Among numerous nanomaterials, nanoscale zero-valent iron (nZVI) is used to facilitate the phytoremediation of organic pollutants hence its potential is established because of its high reactivity and controllable phytotoxicity (Ebrahimbabaie and Pichtel 2021). nZVI has been used to remove endosulfan an insecticide from soil and results indicated that it can increase the efficiency of phytoremediation from 65% to 86%, from 21% to 76%, and from 81% to 100% for *Cymbopogon citratus*, *Ocimum sanctum L. and Alpinia calcarata Roscoe,* respectively (Pillai and Kottekottil 2016). Fullerene nanoparticles increased uptake of trichloroethylene (TCE) by 26% and 82% when applied at a rate of 2 mg L^{-1} and 15 mg L^{-1}, respectively (Ma and Wang 2010). SiO_2 nanoparticles combined with Triton X-100 not only improved stress tolerance in plants but also improved uptake of polycyclic aromatic hydrocarbons hence improved efficiency of phytoremediation (Zuo et al. 2020).

23.3 Characteristics of Remediation Plants

Plants use different mechanisms to uptake and translocate pollutants from soil to roots and further in the upper portion of plants. In general, metal accumulation by plants depends upon many factors which include variation in plant species, the growth stage of the plant, physiological adaptations, and heavy metal ion characteristics (Nouri et al. 2009). Heavy metals remediation requires hyperaccumulator plants which can concentrate and metabolize elements and compounds in their tissues (Nouri et al. 2009). Hyper-accumulator is defined differently by different scientists. Brooks et al. (1977) defined hyper-accumulators as those plants which can store heavy metals from soil to aerial parts more than the threshold level with respect to their dry weight. The threshold level is different for different heavy metals, for example, in the case of Zn, the threshold level is 10,000 ppm (Brooks et al. 1977). Tangahu et al. (2011) defined hyper-accumulators as plants that have shoot-to-root heavy metal ratios greater than 1. Yang et al. (2015) described hyper-accumulating limits for different heavy metals as Cu >1000 mg kg^{-1}, Zn >10,000 mg kg^{-1}, Cd >100 mg kg^{-1} dry weight to differentiate hyper-accumulator plants from non-hyper-accumulator plants. These unique characteristics are a function of plant root systems, together with translocation, bioaccumulation, and degradation of pollutants being utilized for phytoremediation and effective removal of pollutants from soil (Tangahu et al. 2011). There are about 700 plant species known as hyper-accumulators of heavy metals belonging to 101 plant families (Robinson et al. 1997). Among all angiosperms, 2% have capabilities to be used in phytoremediation, and among these hyperaccumulators, Brassica species have been found to be most effective (Robinson et al. 1997).

It is a prerequisite for a hyper-accumulator plant to have rapid growth with large biomass, to have a great deal of survival, to develop stability with soil and the ability to remove contaminants from various kinds of soils, to grow more than once in a year, and to contain substances that restrict eating them by herbivores to avoid pollutant entry into the food chain (Gisbert et al. 2003; Laghlimi et al. 2015; Nordlander et al. 2008). All hyper-accumulators use the same strategies to uptake, translocate and metabolize pollutant heavy metals present in the soil. Therefore, it is concluded that phytoremediation is strongly related to efficient nutrient uptake systems which are dependent on above-mentioned characteristics of plants (Tangahu et al. 2011).

On the other hand, some plants also have specificity for uptake of certain pollutants which have been adapted by soil-plant characteristics, conditions, metal ion nature, climate, and various other factors in different ways (Gisbert et al. 2003). Ingle et al. (2008) described working on *Alyssum lesbiacum* and concluded that Ni uptake into vacuoles from root tissues is enhanced by the presence of Mg-ATP which is responsible for the energization of vacuolar H^+ATPase. Similarly, *Astragalus bisulcatus* and *Brassica oleracea* use specialized transporter proteins like selenocysteine methyl transferase to accumulate Se in plants (Sarma 2011). *Stanleya sp*. and *astragalus bisulcatus* can store 0.1–1.5% (1000–150,000 ppm) of Se even when a very low concentration of Se is present in the surroundings (Sarma 2011). Hg binds with amino acids which are rich in nitrogen and sulfur ligands and get entry into cells and accumulate in them. Cd and Zn get to accumulate in the cell wall of roots, vacuole of the epidermis, and bundle sheath of leaves. Some plant roots experience strong symplastic and apoplastic pathways for the adsorption; of Cd, as a result, Cd can be effectively extracted from the soil through their roots. Cd influx and efflux in cell routes depend upon tonoplast transporters and expression of the cell membrane (Sarma 2011). Water moving through evapotranspiration act as a pump to translocate nutrients and other pollutants from soil to roots and further into upper portion of the plant; therefore, plants with a high evapotranspiration rate have a high potential for phytoremediation (Tangahu et al. 2011). All these characteristics are concerned with phytoextraction, phytostabilization, rhizofiltration, and phytovolatilization (Tangahu et al. 2011).

23.4 Processes Involved in NPs-Assisted Phytoremediation

Plants, contaminants, and nanoparticles are the three main components of the nanomaterial-assisted phytoremediation system. Nanoparticles can assist in phytoremediation by direct immobilization/degradation of pollutants and promotion of plant growth or by indirectly affecting the interaction of pollutants and plants. The following section examines how nanomaterials enhance the process of phytoremediation from three perspectives: direct pollutant removal, plant growth promotion, and increased availability of contaminants to plants.

23.4.1 Direct Removal of Pollutants

Nanoparticles are also capable of removing pollutants from the soil system directly during phytoremediation which reduces the proportion of stress on remediator plants. For direct removal of pollutants, nanoparticles can immobilize them through redox or adsorption reactions (Rizwan et al. 2021). For example, carbon nanotubes (CNTs) can immobilize the pollutants in soil by adsorbing them on their surfaces which is a phenomenon similar to phytostabilization. CNTs have well-reported adsorption behavior for various pollutants, particularly for hydrophobic organic compounds (Song et al. 2017b; Kang et al. 2018). They were found to immobilize organic pollutants in soil by hydrophobic interaction, p-p bonding, and electrostatic attraction, but the relations between heavy metals and nanoparticles involve physical adsorption, electrostatic attraction, surface precipitation, and complexation (Song et al. 2018). Various interactions do exist which make pollutants and nanoparticles relatively stable in the adsorption reactions. In this regard, NZVI is the most promising for removing pollutants. Usually, nZVI serves as an electron donor for stabilization or reductive degradation of contaminants. nZVI has been used in many studies for reductive dechlorination of chlorine-containing organic pollutants (such as organochlorine pesticides and polychlorinated biphenyls) and reductive alteration of toxic metals with high valence (such as U(VI) and Cr(VI)) (Di Palma et al. 2015; El-Temsah et al. 2016; Huang et al. 2016). nZVI also serves as an adsorbent for inorganic ions and make coprecipitates with them, apart from their reduction (Li et al. 2018). Several other nanoparticles that are being widely used for removing toxic pollutants (organic and inorganic) from the soil matrices include phosphate-based nanoparticles, iron oxide nanoparticles, natural mineral nanoparticles, iron-containing bimetallic nanoparticles, and carbon nanotubes, etc. (Long et al. 2011; Trujillo-Reyes et al. 2014; Wan et al. 2018; Rizwan et al. 2021). Table 23.1 reviews some recent studies reported on the application of nanoparticles for remediation of the polluted soils. It is hypothetically feasible for all these reported nanoparticles to aid the process of phytoremediation.

The efficiency of phytoremediation is greatly dependent on the background concentration of the pollutants. Plants are very effective in remediating soil with low concentrations of pollutants (Khalid et al. 2019). A high concentration of pollutant, well above the tolerance limit of the plant will affect the growth and remediation ability of the plant by reducing its biomass and accumulation potential (Rehman et al. 2017). Hence, plants can only accumulate or metabolize pollutants within a tolerable limit. A high concentration of the targeted pollutant or other concomitant pollutants may result in the failure of the phytoremediation. Nanoparticles are capable of directly removing a portion of pollutants during the phytoremediation process, which ultimately reduces the phytotoxic effects caused due to stress imparted by the high concentration of contaminants. Chai et al. (2013) examined the application of CNTs on the accumulation of Cd in smooth cordgrass. Results revealed that CNTs promoted plant growth even under high concentrations of Cd (200 mg kg^{-1}) showing their role in protecting the plant from toxicity and growth inhibition.

Detailed studies of ionic concentration of calcium (Ca^{2+}) and potassium (K^+) have revealed that CNTs can alleviate the phytotoxicity of metals by improving the Ca^{2+} and K^+ uptake for osmotic regulations. Liang et al. (2017a) reported that the application of nano-carbon black and nano-hydroxyapatite promoted the Pb phytoextraction by ryegrass and the applied nanomaterials lessened the toxicity of Pb by stabilizing and adsorbing it. Furthermore, the phytoremediation efficacy is limited within a short time and can take many years (even decades) to remove the pollutants completely by using just plants. The use of NPs for direct removal of some fraction

Table 23.1 A summary of studies on the applications of NPs for phytoremediation of soil pollutants

Nanoparticles	Plant species	Pollutants	NPs' Functions	Removal % of pollutants	References
Metal-based NPs					
nZVI	Panicum (*Panicum maximum* Jacq.)	Trinitrotoluene	Nano zero-valent iron particles remove trinitrotoluene directly	After 120 days, nano zero-valent iron particles increased the elimination efficiency of trinitrotoluene from 85.7% to 100%	Jiamjitrpanich et al. (2012)
nZVI	Chittaratha and lemon grass	Endosulfan	Nano zero-valent particles remove endosulfan directly	For A. calcarata, O. sanctum, and C. citratus, clearance rates of endosulfan from the soil increased from 81.2% to 100%, from 20.76% to 76.28%, and from 65.08% to 86.16%, respectively, using nZVI	Pillai and Kottekottil (2016)
nZVI	Ryegrass (*Lolium perenne* L.)	Pb	Enhanced Plant growth at low concentrations of nZVI	With 100 mg/kg of nZVI, the maximum accumulation of Pb in the root and shoot was 1175.4 mg kg^{-1} pot^{-1}	Huang et al. (2018)
nZVI	Sunflower (*Helianthus annus* L.) and ryegrass (*Lolium perenne* L.)	As, Cd, Pb and Zn	nZVI particles stabilize pollutant directly	In comparison to the control sample, the amounts of As, Cd, Pb, and Zn in roots and shoots fell by 50–60% after employing nZVI for Phyto stabilization	Vítková et al. (2018)
nZVI	Ramie (*Boehmeria nivea* L.)	Cd	Plant growth enhancement at a very less concentrations of nZVI	Cd concentrations in the roots, stems, and leaves increased by 31–73%, 29–52%, and 16–50%, respectively, after treatment with nZVI	Gong et al. (2017)
ZnO nanoparticles	White popinac [*Leucaena leu-cocephala* (Lam.) de Wit)	Cd and Pb	Increasing plant growth by reducing phytotoxicity	Cd and Pb accumulation in the plant enhanced from 1253.1 to 1863.5 mg/kg and 1026.8 to 1343.4 mg/kg, respectively, with the addition of ZnO nanoparticles	Venkatachalam et al. (2017)

(continued)

Table 23.1 (continued)

Nanoparticles	Plant species	Pollutants	NPs' Functions	Removal % of pollutants	References
Ag nanoparticles	Maize (*Zea mays* L.)	Cd, Pb and Ni	Increasing the size of the root system and the length of the roots	Cd, Pb, and Ni accumulation in the shoot rose with silver nanoparticles from 0.65 to 0.73 mg/kg, 129.1 to 232.7 mg/kg, and 0 to 12.4 mg/kg, respectively	Khan and Bano (2016)
Si nanoparticles	Pea (*Pisum sativum L.*)	Cr	Increasing plant growth tolerance to Cr (VI) stress by reducing phytotoxicity	The accumulation of Cr in the root and shoot were reduced from 1472.6 to 516.6 mg kg^{-1} and 62.5 to 35.2 mg kg^{-1}, respectively by silicon nanoparticles	Tripathi et al. (2015)
TiO_2 nanoparticles	Soybean [*Glycine max* (L.) *Merr.*]	Cd	Increasing plant germination, growth, and net photosynthetic rates	With increasing TiO_2 nanoparticle concentrations from 100 to 300 mg kg^{-1}, Cd absorption increased from 128.5 to 507.6 mg kg^{-1} per plant	Singh and Lee (2016)
Carbon-based nanoparticles					
Carbon nanotubes	Maize (*Zea mays* L.)	Three types of phenanthrene (1) Phenanthrene, (2) 3-CH3-phenanthrene, and (3) 9-NO_2-phenanthrene	CNT inhibited phenanthrene bioaccumulation in maize seedlings, in roots and shoots, and nanotubes were found in plant roots	Using CNT mean phenanthrene concentration in plant roots, dropped by 36.8, 27.8, and 43.7% for MW50, 28.0, 23.6, and 46.3% for MW8, and 24.2, 39.2, and 30.8% for SW, respectively	Wang et al. (2016b)
Multiwalled carbon nanotube	Cucumber (*Cucumis sativus* L.)	Pyrene	Pyrene root absorption was reduced by the nanotubes, but pyrene translocation from root to shoot was improved	The uptake of pyrene by roots was lessened by 54.32, 84.27, 95.45, and 99.21% for M8, by 40.15, 70.40, 94.11, and 99.23% for M30, and by 26.35, 55.71, 93.91, and 98.95% for M50, respectively, at nanotube exposures of different concentrations (1, 10, 100, and 1000 mg L^{-1})	Shen et al. (2018)

Multiwalled carbon nanotubes	Maize (*Zea mays* L.)	2 types of phyrene (1) pyrene and (2) 1- methylpyrene	Pyrene and 1-methylpyrene concentrations in roots and shoots were reduced, and their translocation in plants was inhibited with the help of multiwalled carbon nanotubes	Total hexachlorocyclohexanes reductions range from 13.7% to 89.2% by 0.058% MWCNTs and total dichlorodiphenyltrichloroethane reductions range from 25.0% to 90.6% by 0.058% of MWCNTs	Zhang et al. (2017)
Multiwall carbon nanotubes	Collard greens (*Brassica oleracea* L.)	Carbamazepine	CNTs inhibited carbamazepine accumulation and increased its translocation	pCNTs, cCNTs, and AC decreased root carbamazepine concentration in soil-grown plants by 29%, 53%, and 89%, respectively	Deng et al. (2017)
Multiwalled carbon nanotubes and C_{60} fullerenes	Zucchini, soybean, corn, and tomato	Chlordane, DDT, and metabolites of DDT	Nanotubes reduced the accumulation of these pollutants in all plants, whereas fullerenes increased chlordane accumulation in tomato and soybean plants	MWCNT co-exposure reduced chlordane and DDTs accumulation by 21–80%, but C_{60} increased uptake of DDTs by 50–34.9%	De La Torre-Roche et al. (2013)
C_{60} fullerenes	Zucchini, soybean, and tomato	p,p’-DDE	Bioaccumulation factor of dichlorodiphenyltrichloroethane was appreciably enhanced in the presence of C_{60} fullerenes	The fullerenes boosted p,p’- DDE uptake by 30 to 65%. Additionally raised the p,p′-DDE content of zucchini shoots by 29%; contaminant levels in soybean shoots were reduced by 48%, while tomato shoot content remained unchanged	Torre-Roche et al. (2012)
Fullerene nanoparticles	Eastern cottonwood (*Populus deltoides* Bartr.)	Trichloroethylene	Increasing trichloroethylene’s Phyto availability as a carrier	By 2 and 15 mg L^{-1} of fullerene nanoparticles, trichloroethylene uptake boosted by 26 and 82%, respectively	Ma and Wang (2010)

(continued)

Table 23.1 (continued)

Nanoparticles	Plant species	Pollutants	NPs' Functions	Removal % of pollutants	References
Engineered nanoparticles					
Nano-hydroxyapatite and nanocarbon black	Ryegrass (*Lolium perenne* L.)	Pb	The nanoparticles directly stabilize Pb, reducing phytotoxicity and increasing plant development	With nano-hydroxyapatite and nano-carbon black, removal rates of Pb from the soil were enhanced by 31.76 and 45.53%, respectively, after 12 months	Liang et al. (2017a)
Nano-hydroxyapatite	Ryegrass (*Lolium perenne* L.)	Pb	Pb stabilization using nano-hydroxyapatite and increased phosphorus concentration in soil to promote plant growth	Pb levels in the root and shoot reduced by 21.1% and 20.3%, respectively, when nano-hydroxyapatite was used	Ding et al. (2017)
Salicylic acid nanoparticles	(*Isatis cappadocica* Desv.)	As	Increasing the rate of nutrient absorption and utilization for plant growth	The maximal accumulation concentrations of As in the shoot and root using salicylic acid nanoparticles were 705 and 1188 mg/kg, respectively	Souri et al. (2017)
Nano-silica	Rye (*Secale montanum* Guss.)	Cd and Pb	Pb Phyto availability is being increased, and plant growth is being encouraged	Nano-silica was used to obtain maximum accumulation quantities of Pb by 533.6 mg kg^{-1} and Cd by 208.6 mg/kg in the roots	Moameri and Abbasi Khalaki (2019)
Nano-hydroxyapatite	Ryegrass (*Lolium perenne* L.)	Pb	Pb stabilization via nano-hydroxyapatite and plant growth enhancement	Under a Pb stress of 800 mg kg^{-1}, the plant's removal efficiency of Pb rose from 11.67% to 21.97% after 6 weeks with nano-hydroxyapatite	Jin et al. (2016)

of pollutants can lessen the burden on plants for removing pollutants and reduce the time required for remediation.

23.4.2 Increase in Bioavailability of Pollutants

The efficiency of phytoremediation, especially phytoextraction, is highly dependent on the bioavailability of pollutants in soil solution. Plants tend to absorb only those fractions of pollutants that are in available forms. The bioavailability of both organic and inorganic pollutants is strongly dependent on their chemical characteristics and dynamics in soil. For example, Wang et al. (2009) reported the bioavailability of Cd in different forms, it was found that the fraction of Cd adsorbed on gibbsite was the most available form to reed plants as compared to other mineral oxides (goethite, manganese oxide, alumina, and magnetite) in soil. Usually, the maximum bioavailability of metals in soil solution is their exchangeable form, followed by combined forms with organic matter, oxides, and minerals, and minimum in crystalline fraction (Sheoran et al. 2016; Liang et al. 2017b). Further, plant physiological characteristics and soil physicochemical properties also control the bioavailability of soil contaminants (Sheoran et al. 2016; Ren et al. 2018). Decreased bioavailability of these pollutants often reduces the phytoremediation efficiency. For example, Pb normally exists in the soil in insoluble forms due to precipitation, complexation, and adsorption which make its phytoextraction a bit difficult (Zaier et al. 2014). Hence, several practices are being suggested to enhance the bioavailability of pollutants such as the application of chemical amendments (chelating agents), agronomic practices (fertilization), use of genetic engineering, and inoculation of rhizospheric microorganisms (Glick 2010; Habiba et al. 2015; Franchi et al. 2017; Jacobs et al. 2018; Rehman et al. 2018, 2019). Increased bioavailability of toxic pollutants has been proved helpful in enhancing the phytoremediation efficacy. It has been concluded that nanoparticles have two diverse influences on the bioavailability of pollutants in the soil solution. On the one hand, nanoparticles tend to serve as a transporter of pollutants from soil to plants as they move into the root cells, thus increasing their phytoavailability (Su et al. 2013). On the other hand, adsorption of soil pollutants on the nanoparticles surfaces outside plants may decrease the labile pollutants, thus decreasing their phytoavailability (Ayub et al. 2019). Based on these aspects, two main conditions are needed for enhancing the bioavailability of soil pollutants using nanoparticles: First, the nanoparticles make combination with the pollutants (primarily by adsorption); second, the nanoparticle is phytoavailable. For example, fullerene NPs are widely used for this purpose as they have the capacity to enhance the pollutants' phytoavailability in soil solution. Ma and Wang (2010) applied fullerene (C-60) nanoparticles in combination with eastern cottonwood for removing trichloroethylene from soil using phytoremediation. The results revealed that fullerenes NPs increased the uptake of trichloroethylene by plants. It was concluded from this study that uptake was increased due to the co-transportation of trichloroethylene with fullerene NPs. The fraction of trichloroethylene adsorbed on fullerene NPs entered the plant with the uptake of nanoparticles. Similarly, Torre-Roche et al. (2012) described the increase in accumulation of dichlorodiphenyldichloroethylene (p,p'-DDE) in soybean, tomato, and zucchini by the application of fullerene (C-60). The applied fullerene enhanced the plant uptake of pollutants ranging from 30% to 65%, and it was most pronounced in the root tissues. Furthermore, it has been described that some other nanoparticles like quantum dots, Fe_3O_4 NPs, Si NPs, CNTs, and TiO_2 NPs could be directly taken up by plants (Wang et al. 2016a). These NPs have expanded the application of nano-phytoremediation for removing pollutants from soil matrices with enhanced efficiency and short duration.

23.4.3 Improvement in Plant Growth

Plant growth and biomass are two major factors that are considered while choosing a plant species for phytoremediation because the plant species with low biomass and stunned growth show poor tolerance against pollutants. Several strategies can be used to improve the process of phytoremediation, such as plant growth promoting bacteria (PGPB), transgenic plants, and some other plant growth regulators (Ma et al. 2016; Aderholt et al. 2017; Nahar et al. 2017; Yadu et al. 2018). The interaction of plants and nanoparticles like Ag NPs, CNTs, ZnO NPs, quantum dots, and nZVI NPs has shown that these materials enhance plant growth and biomass. They improve plant biomass and growth through different mechanisms. For example, Chakravarty et al. (2015) proposed that graphene quantum dots could be used as a nano-fertilizer and pesticide to boost the growth rates of *Coriandrum sativum* and *Allium sativum*, and Khodakovskaya et al. (2013) suggested that CNTs could activate the plant reproductive system, resulting in increased growth rate. Hence, they can improve the efficacy of phytoremediation systems by encouraging plant growth. Nanomaterials that remove pollutants directly also reduce phytotoxicity, which is good for plant growth. Nanomaterials may also affect plants by increasing their tolerance to contaminants. Praveen et al. (2018) used zinc oxide (ZnO) nanoparticles as physiological regulators of the plants to reduce the phytotoxicity of Cd and Pb towards white popinac in phytoremediation. The results of the experiments suggested that ZnO nanoparticles boosted plant tolerance through modulating enzyme genetic expression. Tripathi et al. (2015) reported a study that used silicon nanoparticles to alleviate Cr(VI) phytotoxicity in pea. The nanoparticles increased plant resistance to Cr(VI) stress, as evidenced by a lower level of reactive oxygen species, increased antioxidant activity, and improved photosynthetic performance. Apart from reducing pollution phytotoxicity, nanomaterials have the potential to boost plant development in phytoremediation systems by improving water and nutrient absorption, increasing photosynthetic rate, controlling soil microbial population, and alleviating abiotic stress (e.g., high salinity and drought). Ding et al. (2017) used nano-hydroxyapatite in ryegrass to remove lead which resulted in increased plant growth and improved phytoremediation effectiveness. In the arsenic phytoextraction study, Souri et al. (2017) used salicylic acid nanoparticles to boost the absorption and utilization rate of nutrients, which increased the plant biomass (fresh weight) of *Isatis cappadocica*. TiO_2 nanoparticles were also found beneficial in encouraging soybean growth by increasing the photosynthesis rate in a Cd phytoextraction study (Singh and Lee 2016). According to their findings, TiO_2 nanoparticles may reach the chloroplasts due to their small size and speed up light adaption and electron transfer. Further, Timmusk et al. (2018) reported that TiO_2 nanoparticles increased the performance of PGPR during phytoremediation and they performed better under abiotic stress conditions (drought, pathogen, and salt), resulting in an increase in plant biomass. These cases provide useful insight into the use of nanomaterials to enhance plant growth in phytoremediation systems.

23.5 Types of NPs Pertinent for Nano-phytoremediation

In developing nanotechnology, the attention of environmental researchers is increasingly focused on nanoparticles-assisted environmental remediation and pollution reduction. Nanotechnology is bringing new ideas and inspiration for the phytoextraction of pollutants from contaminated soils (Gong et al. 2018). The advantages of utilizing nanoparticles in plant systems have been described in several research. According to Ghormade et al. (2011), who investigated the use of nanomaterials in the nutrition and protection of plants, nanomaterials are used to deliver pesticides and fertilizers, detect plant diseases and contaminants, and protect soil structure. Metal-based nanoparticles and carbon-based nanoparticles are two of the most studied nanomaterials (Gong et al. 2009; Chen et al. 2017). However, many field applications were also successfully performed for engineered nanomaterials for soil and groundwater remediation (Mueller and Nowack 2010). Some studies have recently reported nanomaterial applications in contaminated soil for phytoremediation. Nanomaterials are promising to be incorporated into conventional plant remediation systems.

23.5.1 Metal-Based NPs

Plant roots can uptake metal-based NPs, which can then be translocated to different tissues of the plants along with adsorbed contaminants. The properties of metal-based NPs as well as plants and their interactions, all have an impact on NPs translocation. There are several metal-based NPs reported for remediation of contaminated soils including nZVI, TiO_2, ZnO, MgO, Fe_2O_3, etc. Huang et al. (2018) reported improved growth of ryegrass with the application of nZVI in Pb-contaminated soil. Further, it enhanced the Pb accumulation in rye up to 1175.4 mg pot^{-1} at the application rate of 100 mg kg^{-1} nZVI. However, a high application rate of nZVI (2000 mg kg^{-1}) generated extreme oxidative stress in the roots and shoots of the plant, which reduced lead accumulation. Likewise, the phytoremediation of Cd in soil has also been shown to be enhanced by certain nanomaterials. According to Singh and Lee (2016), TiO_2 nanoparticles have a favorable effect on Cd accumulation in the root and shoot of soybean. Cadmium accretion in the shoots increased by 1.9, 2.1, and 2.6 times with the assistance of TiO_2 nanoparticles, whereas cadmium accretion in the roots increased by 2.4, 2.5, and 3.4 times, with 50, 100 and 200 mg kg^{-1} TiO_2, respectively. Similarly, Gong et al. (2017) reported enhancement in Cd phytoextraction by *Boehmeria nivea* (L.) by using nano-zerovalent iron. Starch-stabilized nano zero-valent iron was applied before planting ramie at the rate of 100, 500, and 1000 mg kg^{-1} in the polluted soil. Results showed that the addition of nano zero-valent iron particles increased Cd accretion in the roots by 16–50%, in the stems by 29–52%, and 31–73% in the leaves. According to a recent study by Vítková et al. (2018), using nano zero-valent iron particles had a good effect on As stabilization in the rhizosphere of sunflowers. In another study, Jiamjitrpanich et al. (2012) used *Panicum maximum* to remove trinitrotoluene from polluted soil. They applied nano zero-valent iron particles in the soil in the range of 100–1000 mg kg^{-1} and measured the effective concentration of trinitrotoluene in the soil after a period of 120-day remediation. The findings showed that using nano zero-valent iron particles significantly lead to the removal of trinitrotoluene from the soil. Pillai and Kottekottil (2016) applied nZVI particles to help with endosulfan-contaminated soil phytoremediation. Different plant species such as *Ocimum sanctum*, *Alpinia calcarata*, and *Cymbopogon citratus* were studied both in the presence and absence of nano zero-valent iron particles. Endosulfan elimination rates increased with nano zero-valent iron particles and the elimination ratios of endosulfan in soil were enhanced by 81.2–100% for *A. calcarata*, 20.76–76.28% for *O. sanctum*, and from 65.08% to 86.16% by *C. citratus* with the use of nZVI particles.

Praveen et al. (2018) applied zinc oxide nanoparticles to reduce the toxicity of cadmium and lead for white popinac in phytoextraction as a physiological regulator of the plant. The results of the experiments suggested that zinc oxide nanoparticles boosted the tolerance of plants through the genetic representation of modulating enzymes. Tripathi et al. (2015) used nanoparticles of silicon to lessen chromium toxicity in pea. The nanoparticles improved plant resistance to chromium stress, as evidenced by a lower amount of reactive oxygen species, increased antioxidant activity, and improved photosynthetic performance. Manganese and iron oxides appear naturally as corrosion products in almost all types of soil, either as layers on soil particles or as concretions and nodules with a weakly crystalline structure (Post 1999). Manganese oxides are less prevalent in soils than iron oxides, but they appear to be more effective in immobilizing certain metals (O'Reilly and Hochella Jr 2003). This is owing to their huge specific surface area and low pH at zero charges, which results in a negative surface charge in normal soil circumstances (Essington 2015). In most cases, their unique structure, which is made up of sheets, permits water molecules or different cations to be accommodated in interlayer areas of sheets (Post 1999). Manganese oxides have high oxidative characteristics, and as a result, they participate in a variety of oxidation and reduction reactions and cation exchange reactions. However, manganese oxides can easily convert chromium to more harmful and bioavailable chromium, so they are not suitable for soils polluted with Cr (Fandeur et al. 2009). This oxidizing characteristic can be advantageous in the remediation of arsenic pollution; manganese oxides are effective in the oxidation of the As (III) to As (V) (Villalobos et al. 2014).

Apart from reducing pollution phytotoxicity, metal-based nanoparticles may help plants grow faster in phytoremediation systems by facilitating water and nutrient absorption, increasing photosynthetic rate, regulating the soil microbial population, and amending abiotic stress such as drought and high salinity.

23.5.2 Carbon-Based NPs

Carbon-based NPs, in combination with phytoremediator plants, have been shown to have good adsorption capability against a variety of contaminants in the soil, particularly some organic contaminants (Song et al. 2017b). Carbon nanotubes (CNTs) and fullerenes are two types of carbon-based nanoparticles. Single-walled carbon nanotubes and multi-walled carbon nanotubes are two mostly used for the remediation of soil pollutants. The interactions among CNTs and organic pollutants include complexation, electrostatic attraction, physical adsorption, and surface precipitation, whereas the exchanges among CNTs and heavy metals consist of complexation, electrostatic attraction, hydrophobic interaction, and p-p bonding (Song et al. 2018). Several interactions may collaborate in the process of adsorption, resulting in a very stable mixture of carbon nanotubes and contaminants. The influence of CNTs on cadmium accumulation in soft cordgrass was studied by Chai et al. (2013). CNTs at a concentration of 50 mg kg^{-1} were found suitable for alleviating Cd stress in plants at a contamination level of 50 mg kg^{-1}. The authors reported that carbon nanotubes might attenuate Cd phytotoxicity by boosting potassium and calcium uptake for osmotic modifications. Similarly, Ma and Wang (2010) reported that fullerene NPs could improve the phytoextraction of trichloroethylene by means of eastern cottonwood. Application of fullerene nanoparticles at a rate of 2 and 15 mg L^{-1}, trichloroethylene absorption increased by 26% and 82%, respectively. No toxicity symptoms were observed in amended plants showing the applicability of fullerene for remediation purposes. Fullerenes are carbon allotropes with a hollow cage structure containing 60 or more carbon atoms. They serve as efficient adsorbents for a number of contaminants and the remediation of soil pollutants.

23.5.3 Engineered NPs

Aside from metal and carbon-based NPs, there are several designed NPs that can also be used in soil phytoremediation. Zhang et al. (2010) used nano magnetite (nFe_3O_4) to immobilize As in soils, reporting that nFe_3O_4 had a greater stabilization efficacy than iron sulfide or nZVI. A mixed-valence magnetic iron oxide known as magnetite contains ferrous and ferric ions and can be generated in soil by weathering ferrihydrite with the assistance of bacteria (Sposito 2008). The use of nFe_2O_3 for boosting plant growth in contaminated soil has also been documented by Martínez-Fernández et al. (2015). The decrease in size of maghemite to nano size alter its atomic structure and particle surface which affect the efficacy of adsorption of metal ions (Auffan et al. 2008). Lead is mostly adsorbed by ferric oxide with surface complexes, whereas cadmium is expected to adsorb with a combination of inner as well as outer sphere complexes (Komárek et al. 2015). The sorption process is further influenced by the occurrence of some other processes in the soil system, for example, citrate complexes and organic acids (Vítková et al. 2015), as well as other nutrients (Martínez-Fernández et al. 2014). Liang et al. (2017a) reported the effect of nano hydroxy apatite (n-HAP) on ryegrass for lead phytoremediation and examined the Pb remediation efficiency after 1, 1.5, 2, 3, and 12 months. Pb removal (44.39%) was found most efficient after 3 months of n-HAP application. Similarly, salicylic acid nanoparticles found to improve the arsenic phytoextraction by *Isatis cappadocica* (Souri et al. 2017). The nanoparticles of salicylic acid were integrated in the phytoextraction of arsenic because salicylic acid has a crucial role in plant growth and arsenic tolerance. The seedlings of plant were treated with 250 mM nanoparticles of salicylic acid for 10 days before arsenic phytoextraction in their trials. Plant growth and phytoremediation efficiency both improved significantly with the help of salicylic acid nanoparticles. The arsenic level increased in root and shoot up to 705 mg kg^{-1} and 1188 mg kg^{-1}, respectively. A summary of nanoparticles for phytoremediation of soil pollutants is given in Table 23.1.

23.6 Factors That Affect Efficiency of Nano-phytoremediation

23.6.1 Soil Factors

Nanoparticles-assisted phytoremediation of pollutants is greatly dependent on soil chemical, biological, and physical properties. These properties have a significant influence on the fate of pollutants present in soil matrices. Subramanian et al. (2015) described that the concentration and nature of pollutants also influence the remediation process along with soil properties. Among these properties, soil pH is the most influential factor which determines the phytoavailability of the pollutants in soil solution. There is a linear trend between soil pH and pollutants uptake by plants along with nanoparticles (Tudoreanu and Phillips 2004). Soil temperature is also one of the key elements that control the efficacy of nano-phytoremediation by regulating plant growth processes. It regulates the physical, chemical, and biological activities in the soil. Soil temperature, biological activities such as seed germination, seedling emergence, plant root growth, and nutrient availability are all affected by the quantity of radiation absorbed by the soil (Haskell et al. 2012). The rate of organic matter breakdown and mineralization of various organic components in the soil is affected by soil temperature (Onwuka and Mang 2018). The soil temperature also affects the retention, transmission, and accessibility of soil water to plants which reduces root growth by decreasing the concentration of tissue nutrients, photosynthesis, and the uptake of nutrients. Srivastav et al. (2019) revealed that the soil's ability to absorb contaminants was the most essential property among the many soil variables that affect nano-phytoremediation. High content of organic matter in the soil leads to high adsorption capacity of contaminants in soil. The metal available in the soil is of primary concern instead of total metal concentration, as the available concentration is assumed to indicate the amount of plant uptake (Rehman et al. 2019). Therefore, both the existing and the total heavy metal concentration in the soil should be assessed in each investigation. For efficient nanophytoremediation of pollutants, there is also a need for some agronomic management practices like proper growth season, tillage practices, fertilization, and selection of plant species as they all affect the soil properties and ultimately the remediation process (Vangronsveld et al. 2009).

23.6.2 Plant Factors

There are number of growth and development traits of plants which affect their ability of pollutants remediation. These traits include highly branched root systems, stress tolerance capacity, ability to accumulate contaminants, fast development, root exudates, and high biomass (Ahmadpour et al. 2012). The physiological structure of the plant and the kind of root system play a significant role in the uptake of potentially hazardous substances. For example, Jarrah et al. (2019) reported high efficiency of sunflower for phytoextraction of Ni which might be due to its deeper root system. Similarly, Zehra et al. (2020) reported that significant amounts of Pb were accumulated in sunflower shoots with a greater translocation factor. The selection of appropriate plant species that are genetically capable of growing in polluted soil and absorbing toxic materials in their shoots and roots without indicating metabolic dysfunction is a crucial step in the phytoremediation process (Jaskulak et al. 2019). The ability of plant species to withstand potentially harmful materials toxicity and accumulation is determined by the plant's rooting depth and the amount of material translocated from root to shoot (Khodaverdiloo et al. 2020). Increased phytoremediation efficiency is achieved by using plants with high biomass (Moshiri et al. 2019; Shafigh et al. 2017). Maize (*Zea mays L.*) (Shafigh et al. 2016; Mojiri 2011), sorghum (*Sorghum bicolor L.*) (Soudek et al. 2014), tobacco (*Nicotiana tabacum*) (Rehman et al. 2019), and sunflower (*Helianthus annuus L.*) (Jarrah et al. 2019) are mostly recommended for phytoremediation due to their cash value. Plants' ability to absorb nanoparticles is also influenced by the penetration mechanism of nanoparticles (Pérez-de-Luque 2017). Apoplastic transport (which occurs outside the plasma membrane and xylem capillaries) and symplastic transport (which occurs between the cytoplasm and sieve pores) are the two routes for nanomaterials to travel inside plant tissues (Pérez-de-Luque 2017) which are influenced by environmental conditions. For phytoremediation, specifically phytoextraction, a contaminant-specific hyperaccumulator is recommended.

23.7 Production Technologies of NPs

Usually, most of NPs are produced as liquid phase NPs and have the following constituents: a liquid medium (in which chemical processes takes place), a precursor (salt which is the origin of NPs), a reducing agent (produce metallic specie from ionic form) and a stabilizing agent (help in surface cover to keep them apart and suspended in medium) (Kaneko et al. 2007). The success of NPs production techniques depends upon the cost of operation, cost to upgrade to large-scale production, and health hazard associated with the operation (Joye and Julian 2013). Usually, most of the techniques used for NPs synthesis cannot be used commercially due to the huge cost and low purity of raw materials, complex operation, and inappropriate size of particles (Wegner and Pratsinis 2005). Nanoparticle's synthesis techniques are generally divided into chemical, biological, and physical based on their mode of origin. The most practical technique is chemical synthesis in which the size and shape of NPs are controlled by kinetic processes (Khanna et al. 2019). On the other hand, they have been divided into bottom-up and top-down techniques based on their mode of modification which is discussed below. A comprehensive overview of synthesis techniques is given in Table 23.2.

23.7.1 Bottom-Up Technique

This technique produces NPs by combining materials at the atomic or molecular level rather than breaking the larger particles into smaller ones. Bottom-up techniques are more efficient than top-down techniques because the energy used for the production of NPs at the atomic level is less than that used for breaking large-sized particles to nano-sized ones (Panagiotou and Fisher 2013). NPs prepared by this technique are more stable than the top-down technique because the bonding strength between ions is more compared with other techniques (Shimomura and Sawadaishi 2001). Among various methods of bottom-up techniques, anti-solvent precipitation and spontaneous emulsification are most commonly used (Joye and Julian 2013). Overall bottom-up includes supercritical fluid solution, spinning, sol-gel process, chemical vapor deposition, molecular condensation, chemical reduction, and green synthesis (Khanna et al. 2019).

NPs prepared by anti-solvent precipitation possess uniform particle properties like morphology, size, and physical state (Joye and Julian 2013). To control the surface shape, various kinds of surfactants have been used including polyvinylpyrrolidone (PVP), sodium dodecyl sulfate (SDS), mercaptoethanol (ME),

Table 23.2 Production technologies of NPs

Material	Synthesis technique	Morphology	NPs Size	References
Bottom-up technology				
ZnO NPs	Sol-jel	Porous, random staking direction	3 nm	Mahato et al. (2009)
$ZnSO_4$	Anti-solvent precipitation	Crystalline	30–35 nm.	Jahangiri et al. (2019)
ZnO NPs	Sol-jel	Rod shaped	80.98 nm	Hasnidawani et al. (2016)
Hydroxyapatite NPs	Sol-jel	Crystalline powder	45–90 nm	Anjaneyulu et al. (2017)
TiO_2 anatase NPs	Sol-jel	Crystalline	29.7–39.7 nm	Mogilevsky et al. (2014)
Au nanospheres	Laser irradiation	Spherical	Diameter 75 nm Edge length 72 nm	Liu et al. (2015)
CuO NPs	Sol-jel	Porous crystalline	20–40 nm	Dörner et al. (2019)
Ag-NPs	Co-precipitation	Crystalline	5.5 nm	Dasaradhudu and Srinivasan (2020)
Amorphous silica NPs	Sol-jel	Amorphous	25–50 nm	Owoeye et al. (2021)
TiO_2 NPs	Hydrothermal Green synthesis	Crystalline	6–13 nm	Hariharan et al. (2018)
Au NPs	Hydrothermal synthesis	Crystalline	20 nm	Liu et al. (2014)
Fe-Co alloy NPs	Pulsed-laser inert gas condensation	Body-centered cubic structure	2–3 nm	Patelli et al. (2021)
Ge–Cu NPs	Inert gas condensation	Uniform porous structure having multiple contacts with neighboring NPs	10 nm	Zhao et al. (2013)
Ag NPs	Electromagnetic levitation gas condensation	Spherical shape	30–60 nm	Malekzadeh and Halali (2011)
Green synthesis				
Ag-NPs	Bacteria (*Bacillus endophyticus*), intracellular	Spherical	5–35 nm	Gan et al. (2018)
Au-NPs	Bacteria (*Shewanella loihica*), intra + extra cellular	Spherical	2–15 nm	Ng et al. (2013)

(continued)

Table 23.2 (continued)

Material	Synthesis technique	Morphology	NPs Size	References
Au-NPs	Fungus (*Alternaria alternate*), extracellular	Spherical, triangular and hexagonal	12–29 nm	Sarkar et al. (2011)
Ag-NPs	Fungus (*T. viride*), extracellular	Spherical	5–40 nm	Fayaz et al. (2010)
Pt NPs	Algae (*Padina gymnospora*)	Octahedral	5–50 nm	Ramkumar et al. (2017)
Pt NPs	Bacteria (*Saccharomy cesboulardii*)	Spherical	80–150 nm	Borse et al. (2015)
Top-down technology				
a-SiC	Hexamethyldisilane decomposition	Amorphous	9 nm	Zhou et al. (2021)
Coconut shell nanoparticles (CS-NPs)	Milling	Crystalline	4.52–281.4 nm	Bello et al. (2015)
Magnetite NPs	Top-down destructive approach	Spherical	20–50 nm	Priyadarshana et al. (2015)
Co_3O_4 NP_s	Laser fragmentation	Spherical	5.8 nm	Zhou et al. (2016)
Cu/TiO_2 NPs	Magnetron sputtering	Spherical	5.6–8.4 nm	Zhao et al. (2015)
Au NPs	Sputtering	Crystalline	3–4 nm	Matsuyama et al. (2020)
Pd NPs	Ionic liquid crystal microemulsion	Spherical	20 nm	Mangaiyarkarasi et al. (2020)
Bovine serum albumin nanoparticles (BSA NP_s)	Liquid microemulsions	Spherical	100 nm	Demirkurt et al. (2019)
ZnO NPs	Laser ablation	Sponge-like	32.27 nm	Khudiar et al. (2021)
Fe_3O_4 nanocomposite	Ultrasound	Globular shaped	90 nm	Veisi et al. (2021)
CuO NPs	Ultrasound	Spherical	6–7.8 nm	Gu et al. (2018)
Ag NPs	Spark discharge deposition	Spherical	45 nm	El-Aal et al. (2018)
Au/Ag NPs	Spark discharge generation	Spherical	10 nm	Kohut et al. (2020)
CuO/ZnO NPs	Template synthesis	Spherical	15–25 nm	Maruthupandy et al. (2017)
SiO_2 NPs	Template synthesis	Spherical	18–22 nm	Nguyen et al. (2021)

cetyl trimethyl ammonium bromide (CTAB), sodium hexametaphosphate (SHMP), thioglycerol (TG), etc. (Khanna et al. 2019). This technique does not require high-cost equipment, multiplex operation, or high cost to upgrade to commercial scale (Joye and Julian 2013). In a nutshell, the bottom-up technique is simple, efficient, and cost-effective. It produces superior quality NPs. Mahato et al. (2009) described the preparation of ZnO NPs by a sol-gel process with an average size of 55 nm. Jahangiri et al. (2019) described the preparation of $ZnSO_4$ NPs using anti-solvent with and without surfactant (SDS). It mostly includes chemical and biological synthesis techniques.

The biogenic (biological or green) synthesis of NPs is a process that uses biogenic sources (plants, fungi, algae, and natural plant extracts) that can reduce metals and stabilize the NPs formed (Heinemann et al. 2021). This technique usually involves biogenic materials which are regarded as waste like plant leaves, twigs, fruit peels, etc. Plant extracts usually contain antioxidants such as polyphenols, amino acids, and reducing sugars which can reduce the valence of metals (Haverkamp and Marshall 2008). The NPs prepared through green synthesis are found to be cost-effective, easily degradable in nature, and eco-friendly (Jayachandran et al. 2021). This technique has been successfully used for a number of metal oxide NPs preparations like CuO, ZnO, NiO, SnO_2, and Fe_2O_3 (Jain et al. 2021). Among them, the significance of Fe_2O_3 is well established due to their application in numerous fields like medicine, environmental application (especially wastewater treatment), and agriculture (Aksu Demirezen et al. 2019). Recently green methods are used to produce NPs at a lab-scale only but in near future, it has been predicted to be used for large-scale production without the utilization of expensive machinery and equipment (Bandeira et al. 2020). NPs synthesis through green technology is completed in three stages: (a) activation phase: reduction and nucleation of reduced metallic ion, (b) growth phase: stabilization of NPs, and (c) termination phase: formation of specific morphology (Love et al. 2015).

Jayachandran et al. (2021) reported the preparation of ZnO NPs by using *Cayratia Pedata* leaf extract. SEM, EDX, XRD, and FT-IR spectroscopy were used to characterize (structure, purity, composition, and bonding) NPs. The average size of NPs obtained through the wet chemical method was found to be 52.24 nm. Prepared NPs were used for enzyme immobilization and gave relative activity of 60%. This is 88.2% of activity when compared with native ZnO immobilization. Aksu Demirezen et al. (2019) described the preparation of ZnO NPs using fruit extract of *Ficus carica* (common fig) with a size between 5 and 13 nm and a spherical shape. These NPs are most suitable for medical utilization. For characterization, numerous techniques are used to describe the size, shape, surface area, and morphology of the surface. Techniques include dynamic light scattering, X-ray photoelectron spectroscopy, Fourier transform infrared and X-ray diffraction, etc. (Shah et al. 2015; Menon et al. 2017). The NPs formed by this method were uniform in size, making it the most suitable and environmentally friendly method.

23.7.2 Top-Down Technique

In top-down technique, the NPs are prepared by reducing the size of bulk materials. This technique commonly uses the methods of crushing and homogenizing to reduce the sizes of large particles in solid or liquid form (Merisko-Liversidge et al. 2003). Usually, size reduction is done by three disruptive forces: impact, shear, and compression (Joye and Julian 2013). It usually uses micro-fabrication techniques i.e., mechanical milling, chemical etching, sputtering, laser ablation, and electro-expulsion to cut large materials and shape them into desired size and structure (Nath and Banerjee 2013; Khan et al. 2019).

Bello et al. (2015) described the method of coconut shell (CS) NPs preparation by top-down technique. The milling method was used to reduce the sizes of raw CS powder after specific durations with ceramic balls and a well-known planetary mill. The results fulfill the Scherer equation, i.e., as milling time increases, the size of the crystal decreases. As time passes, the intensity of the brownish color reduces due to the reduction in the size of NPs. SEM results also synchronized with X-ray pattern, representing that NPs size reduces with time. Priyadarshana et al. (2015) reported the production of spherical magnetite NPs production from Fe_2O_3 ore by destructive top-down technique in the presence of organic oleic acid. Top down mostly include physical methods of preparation which are usually less efficient.

23.8 Toxicities and Challenges Associated with NPs Application in Soil

The toxicological effects of NPs on the soil environment, plants, and living cells have also been reported in several studies. The effects of NPs on plants have been well investigated. However, only a few studies in soil-plant systems have been conducted (Wang et al. 2016a; Watson et al. 2015), and the findings of these studies may differ from those published in plants grown on agar, nutrient solutions, or artificial soil media. To assess the fate of NPs in the environment, as well as their behaviors in soils and plants throughout crop growth and crop rotations, studies must be undertaken over the whole life cycle in environmentally realistic conditions (Rizwan et al. 2017; Servin and White 2016). Awet et al. (2018) described that the activity of enzymes involved in the C, N, and P cycles was reduced by the application of polystyrene NPs (0.1–1 mg kg^{-1}). Furthermore, Zhu et al. (2018) reported a decrease in the activity of key biomes that control the nitrogen cycle. Metallic NPs can cause oxidative stress in plants by promoting the production of reactive oxygen species at higher concentrations (Rizwan et al. 2017). Therefore, biomarkers for assessing the impact of NPs contaminated soils on plants include measures of reactive oxygen species levels and important metabolic pathways involved in the cellular defense mechanism against oxidative stress. Furthermore, some studies assessed the toxicity of pure NPs to plants without considering the expected changes that

Table 23.3 NPs mediated toxicities in the environment

Nanoparticles	Toxicity concentration in plants	Effect on plant growth	Toxicity concentration in animals	Effect on living organisms	References
Metallic nanoparticles					
ZnO nanoparticles	10 mg L^{-1}	ZnO nanoparticles have increased the infusion of onion roots (*Allium cepa*) and affecting elongation of root and inhibition of genetic materials as well as disturbing of metabolism in maize plant	100 μg mL^{-1}	Changes in cell shape, DNA damage, and mitochondrial activity in human hepatocytes and embryonic kidney cells have all been linked to ZnO nanoparticles	Lee et al. (2013), Guan et al. (2012)
Cu_2O nanoparticles	10 μg mL^{-1}	Cu_2O nanoparticles could obstruct water pathways through adsorption, making radical penetration into onion roots more likely	200 mg kg^{-1} day^{-1}	Cu_2O nanoparticles toxic to aquatic species, suppresses immune system, cell, and DNA destruction	Geremias et al. (2010), Lei et al. (2008)
Al_2O_3 nanoparticles	2 mg L^{-1}	Uncoated and phenanthrene-coated alumina nanoparticles phytotoxicity revealed that it hindered root elongation in cucumber, corn, carrot, cabbage, and soybean at 2 mgL^{-1} concentrations	25–40 μg mL^{-1}	Impair central nervous system, increase oxidative stress, and affect tight-knot blood-brain barrier protein expression liver toxicity, disrupt cellular viability, affect the mitochondrial function	Yamamoto et al. (2001), Chen et al. (2008)
Fe_3O_4 nanoparticles	0.5 g L^{-1}	Excess Fe_3O_4 nanoparticles treatment resulted in some oxidative stress, which inhibited photosynthesis and resulted in slower metabolic rates	10 mg mL^{-1}	After inhalation, magnetic iron oxide NPs were shown to collect in the liver, spleen, lungs, and brain, demonstrating their potential to traverse the BBB	Green and Etherington (1977), Liu et al. (2013)

(continued)

Table 23.3 (continued)

Nanoparticles	Toxicity concentration in plants	Effect on plant growth	Toxicity concentration in animals	Effect on living organisms	References
TiO_2 nanoparticles	2000–4000 mg L^{-1}	When TiO_2 nanoparticles met organisms or ultraviolet light, they produced reactive oxygen species, which increased inorganic nutrient absorption, expedited organic material breakdown, and caused quenching by oxygen free radicals created during the photosynthetic process	150 mg kg^{-1} BW	TiO_2 nanoparticles have harmful effects on liver, spleen, immunological function, kidney, glucose, myocardium, and lipid homeostasis in investigational animals, in addition to genotoxicity	Yang et al. (2006), Liu et al. (2009)
Ag nanoparticles	4500 µg mL^{-1}, 6000 µg mL^{-1}, and 3000 µg mL^{-1}	Negative impacts on seed germinations, root, and shoot growth on species of rice (*Oryza sativa*), mung bean (*Vigna radiata*), and Chinese cabbage (*Brassica campestris*), respectively	20 nm	A dose-dependent cytotoxicity, as well as the development of cellular DNA adducts after introducing polyvinylpyrrolidone-coated silver NPs to a human lung cancer cell line	Mao et al. (2004), Foldbjerg et al. (2011)
Au nanoparticles	225 mg L^{-1}	Disrupt the root tip cells of the onion (Allium cepa), resulting in the creation of chromatin bridges, cell disintegration, and stickiness, all of which harm the cell division process	120 nM	In human lung and liver cancer cell lines, there has been a variance in toxicity with respect to different cell lines	Feretti et al. (2007), Patra et al. (2007)
Non-metallic nanoparticles					
Carbon nanotubes	More than 500 nm	Due to aggregation, carbon nanotubes exhibit phytotoxic effects on plant cells and cause cell death in a dose-dependent manner. Electrolyte leaking and enlargement of the cell plant are signs of cell death	0.002 to 0.2 µg mL^{-1}	Researchers have investigated several forms of carbon nanotubes on lung cancer cells to evaluate cell capability with MTT assay	Torre-Roche et al. (2012), Magrez et al. (2006)

Single walled carbon nanotube	50 μg mL^{-1}	SWCNTs increased the production of reactive oxygen species (ROS), causing alterations in protoplast shape, turning green leaves yellow, and promoting necrosis and apoptosis in protoplast cells	1.0 mg	In experimental animals, caused changes in biochemical markers such as LDH, aspartate transaminases, alanine transaminases, glutathione, and malondialdehyde, as well as organ indices	Yuan et al. (2011), Yang et al. (2008)
Multiwalled carbon nanotubes	1.0 mg	Rice cell suspension cell walls prevent MWCNTs from entering the cytoplasm, generating black clumps that tightly wrap around and connect with the cells	100 μg ml^{-1}	After being injected into the peritoneal cavity of mice, MWCNTs produced carcinogenic effects like to asbestos	Chekin et al. (2012), Poland et al. (2008)
Fullerene nanoparticles	1 ng mL^{-1}	The fullerene nanoparticles' tiny size and hydrophobicity features induce fullerene permeability through the cell wall pores in the plant cell solution, resulting in low absorption	1 ng mL^{-1}	After 80 days of incubation with Chinese hamster ovary cells, human epidermoid-like carcinoma cells, and human embryonic kidney cells (HEK293), fullerenes cause DNA strand fracture, chromosomal destruction, and micronucleus production	Kole et al. (2013), Niwa and Iwai (2006)

these NPs will experience during their time in the soil. A summary of NPs toxicities in the environment is given in Table 23.3.

After being applied to the soil, NPs tend to interact with a variety of environmental components, and they frequently go through aggregation, dissolution, sedimentation, and change. ZnO NPs can be converted to rather stable Zn ion inner-sphere complexes (Reddy et al. 2016; Scheckel et al. 2010). However, with time, ZnO NPs undergo transformations and changes in soil, which influence their bioavailability (Amde et al. 2017). Ag NPs are being used in a range of consumer products, resulting in their release into the aquatic environment where they act as a source of dissolved Ag, harming aquatic species like bacteria, algae, fish, and daphnia (Navarro et al. 2008). The respiratory system is an important target of NPs toxicity because it is the entrance for inhaled particles as well as receiving the entire cardiac output (Ferreira et al. 2013). NPs are widely used in biotechnology, however, the potential of harmful health effects from sustained exposure at various concentration levels in humans and the environment has yet to be determined, despite nanobiotechnology's rapid advancement and early acceptance. NPs, on the other hand, are expected to have a greater impact on the environment in the future. The amount of organic matter or other natural particles (colloids) present in soil has a large impact on the fate of NPs in soil. Although many abiotic factors that influence ecotoxicities, such as pH, salinity, and the presence of organic matter, have yet need to be thoroughly investigated in ecotoxicological studies.

23.9 Future Perspectives

The use of nanoparticles to aid phytoremediation is a new concept that has emerged with the advancement of nanotechnology and bioremediation processes. In terms of actual applications, it faces numerous difficulties. The most concerning issue is the environmental risk of nanomaterials in the soil ecosystem. Many nanomaterials in the soil are poisonous to animals, plants, and microbial ecosystems (Maurer-Jones et al. 2013). In phytoremediation, the phytotoxicity of nanomaterials is of particular concern. Additional research regarding the environmental risk of nanomaterials is required to completely comprehend their toxicity. On the other hand, the use of nanomaterials in phytoremediation must be regulated to maximize their benefits while minimizing their risks. Although many positive outcomes have been gained, utilizing nanomaterials in phytoremediation is currently in the discovery and attempt phase. More application cases are needed and studies on the long-term performance of nanomaterials are necessary for their potential use in fields. The nZVI is largely explored and the use of nZVI to aid phytoremediation of contaminated soil has several advantages over other nanomaterials. The commercial uses of nZVI for soil remediation have already been established on a large scale (Mueller and Nowack 2010). Phytoremediation can be performed based on benefits harvested from a lot of previous experiences. Terzi et al. (2016) and Gil-Diaz and Lobo (2018) suggest that nZVI's strong reactivity and regulated phytotoxicity may make it a good approach for phytoremediation. However, Crane and Scott (2012) indicated that nZVI could suffer from particle aggregation, oxidative corrosion, and interference from soil components in their applications. Furthermore, particular reactions of nanomaterials in phytoremediation systems to diverse plant species, contaminants, soil types, and meteorological conditions should be explored further for broad applicability. Other methods, such as agronomic management, chemical additive treatment, rhizospheric microorganism inoculation, and genetic engineering, could be incorporated into phytoremediation assisted with nanomaterials to regulate nanomaterial performance and improved remediation efficiency. Nanotechnology is considered a helpful substitute for present practices due to the numerous benefits it provides, one should also take care of the potential hazards it poses to soil regarding its dose. Nano-phytoremediation has the potential to reduce the overall costs and time required for large-scale cleanup of contaminated locations. They are also good for on-site cleanup, which eliminates the need for transportation, treatment, and soil disposal afterward. To avoid any potential negative environmental effects, full-scale ecosystem studies with proper long-term evaluation are required before the use of nanoparticles on a large scale.

References

Aderholt M, Vogelien DL, Koether M, Greipsson S (2017) Phytoextraction of contaminated urban soils by *Panicum virgatum* L. enhanced with application of a plant growth regulator (BAP) and citric acid. Chemosphere 175:85–96

Adriano DC, Wenzel WW, Vangronsveld J, Bolan NS (2004) Role of assisted natural remediation in environmental cleanup. Geoderma 122:121–142

Ahmadpour P, Ahmadpour F, Mahmud TMM, Abdu A, Soleimani M, Tayefeh FH (2012) Phytoremediation of heavy metals: a green technology. African J Biotechnol 11:14036–14043

Aksu Demirezen D, Yıldız YŞ, Yılmaz Ş, Demirezen Yılmaz D (2019) Green synthesis and characterization of iron oxide nanoparticles using *Ficus carica* (common fig) dried fruit extract. J Biosci Bioeng 127:241–245

Ali H, Khan E (2018) What are heavy metals? Long-standing controversy over the scientific use of the term ‘heavy metals’–proposal of a comprehensive definition. Toxicol Environ Chem 100:6–19

Amde M, Liu J, Tan Z-Q, Bekana D (2017) Transformation and bioavailability of metal oxide nanoparticles in aquatic and terrestrial environments. A review. Environ Pollut 230:250–267

Andresen E, Peiter E, Küpper H (2018) Trace metal metabolism in plants. J Exp Bot 69:909–954

Anjaneyulu U, Priyadarshini B, Arul Xavier Stango S, Chellappa M, Geetha M, Vijayalakshmi U (2017) Preparation and characterisation of sol–gel-derived hydroxyapatite nanoparticles and its coatings on medical grade Ti-6Al-4V alloy for biomedical applications. Mater Technol 32:800–814

Ansari AA, Gill SS, Gill R, Lanza GR, Newman L (2019) Phytoremediation: management of environmental contaminants. Phytoremediation Manag Environ Contam 6:1–476

Auffan M, Rose J, Proux O, Borschneck D, Masion A, Chaurand P, Hazemann J-L, Chaneac C, Jolivet J-P, Wiesner MR (2008) Enhanced adsorption of arsenic onto maghemites nanoparticles: As (III) as a probe of the surface structure and heterogeneity. Langmuir 24:3215–3222

Awet TT, Kohl Y, Meier F, Straskraba S, Grün A-L, Ruf T, Jost C, Drexel R, Tunc E, Emmerling C (2018) Effects of polystyrene nanoparticles on the microbiota and functional diversity of enzymes in soil. Environ Sci Eur 30:1–10

Ayub MA, Sohail MI, Umair M, Rehman MZ, Usman M, Sabir M, Rizwan M, Ali S, Ahmad Z (2019) Cerium oxide nanoparticles: advances in synthesis, prospects and application in agro-ecosystem. In: Comprehensive analytical chemistry, vol 87. Elsevier, pp 209–250

Ayub MA, Usman M, Faiz T, Umair M, ul Haq MA, Rizwan M, Ali S, Zia ur Rehman M (2020) Restoration of degraded soil for sustainable agriculture. In: Soil health restoration and management. Springer, Singapore

Ayub MA, Usman M, Umair M, Rizwan M, Rasul A, Zia ur Rehman M (2021) Remediation of organic pollutants by brassica species. In: Handbook of bioremediation

Bandeira M, Giovanela M, Roesch-Ely M, Devine DM, da Silva CJ (2020) Green synthesis of zinc oxide nanoparticles: a review of the synthesis methodology and mechanism of formation. Sustain Chem Pharm 15:100223

Bello SA, Agunsoye JO, Hassan SB (2015) Synthesis of coconut shell nanoparticles via a top down approach: assessment of milling duration on the particle sizes and morphologies of coconut shell nanoparticles. Mater Lett 159:514–519

Blum WEH (2002) Environmental protection through sustainable soil management, a holistic approach. Sustain L Manag Prot Soil Phys Approach–Adv Geoecol 35:1–8

Bogdal C, Scheringer M, Abad E, Abalos M, Van Bavel B, Hagberg J, Fiedler H (2013) Worldwide distribution of persistent organic pollutants in air, including results of air monitoring by passive air sampling in five continents. TrAC Trends Anal Chem 46:150–161

Borse V, Kaler A, Banerjee UC (2015) Microbial synthesis of platinum nanoparticles and evaluation of their anticancer activity. Int J Emerg Trends Electr Electron 11:2320–9569

Brooks RR, Lee J, Reeves RD, Jaffre T (1977) Detection of nickeliferous rocks by analysis of herbarium specimens of indicator plants. J Geochemical Explor 7:49–57

Chai M, Shi F, Li R, Liu L, Liu Y, Liu F (2013) Interactive effects of cadmium and carbon nanotubes on the growth and metal accumulation in a halophyte *Spartina alterniflora* (Poaceae). Plant Growth Regul 71:171–179

Chakravarty D, Erande MB, Late DJ (2015) Graphene quantum dots as enhanced plant growth regulators: effects on coriander and garlic plants. J Sci Food Agric 95:2772–2778

Chekin F, Bagheri S, Arof AK, Abd Hamid SB (2012) Preparation and characterization of Ni (II)/polyacrylonitrile and carbon nanotube composite modified electrode and application for carbohydrates electrocatalytic oxidation. J Solid State Electrochem 16:3245–3251

Chen M, Zeng G, Xu P, Zhang Y, Jiang D, Zhou S (2017) Understanding enzymatic degradation of single-walled carbon nanotubes triggered by functionalization using molecular dynamics simulation. Environ Sci Nano 4:720–727

Chibuike GU, Obiora SC (2014) Heavy metal polluted soils: effect on plants and bioremediation methods. Appl Environ Soil Sci 2014:1–12

Crane RA, Scott TB (2012) Nanoscale zero-valent iron: future prospects for an emerging water treatment technology. J Hazard Mater 211–212:112–125

Dasaradhudu Y, Srinivasan MA (2020) Synthesis and characterization of silver nano particles using co-precipitation method. Mater Today Proc 33:720–723

De La Torre-Roche R, Hawthorne J, Deng Y, Xing B, Cai W, Newman LA, Wang Q, Ma X, Hamdi H, White JC (2013) Multiwalled carbon nanotubes and C60 fullerenes differentially impact the accumulation of weathered pesticides in four agricultural plants. Environ Sci Technol 47:12539–12547

Demirkurt B, Cakan-Akdogan G, Akdogan Y (2019) Preparation of albumin nanoparticles in water-in-ionic liquid microemulsions. J Mol Liq 295:111713

Deng Y, Eitzer B, White JC, Xing B (2017) Impact of multiwall carbon nanotubes on the accumulation and distribution of carbamazepine in collard greens (*Brassica oleracea*). Environ Sci Nano 4:149–159

Di Palma L, Gueye M, Petrucci E (2015) Hexavalent chromium reduction in contaminated soil: a comparison between ferrous sulphate and nanoscale zero-valent iron. J Hazard Mater 281:70–76

Ding L, Li J, Liu W, Zuo Q, Liang SX (2017) Influence of nano-hydroxyapatite on the metal bioavailability, plant metal accumulation and root exudates of ryegrass for phytoremediation in lead-polluted soil. Int J Environ Res Public Health 14:532

Dolinová I, Štrojsová M, Černík M, Němeček J, Macháčková J, Ševců A (2017) Microbial degradation of chloroethenes: a review. Environ Sci Pollut Res 24:13262–13283

Dörner L, Cancellieri C, Rheingans B, Walter M, Kägi R, Schmutz P, Kovalenko MV, Jeurgens LPH (2019) Cost-effective sol-gel synthesis of porous CuO nanoparticle aggregates with tunable specific surface area. Sci Rep 9:1–13

Dubchak S, Bondar O (2019) Bioremediation and phytoremediation: best approach for rehabilitation of soils for future use. In: Remediation measures for radioactively contaminated areas. Springer, pp 201–221

Ebrahimbabaie P, Pichtel J (2021) Biotechnology and nanotechnology for remediation of chlorinated volatile organic compounds: current perspectives. Environ Sci Pollut Res 28:7710–7741

El-Aal MA, Seto T, Kumita M, Abdelaziz AA, Otani Y (2018) Synthesis of silver nanoparticles film by spark discharge deposition for surface-enhanced Raman scattering. Opt Mater (Amst) 83:263–271

El-Ramady H, El-Henawy A, Amer M, Omara AE-D, Elsakhawy T, Salama A-M, Ezzat A, Elsherif A, Elmahrouk M, Shalaby T (2020) Agro-pollutants and their nano-remediation from soil and water: a mini-review. Environ Biodivers Soil Secur 0:0–0

El-Temsah YS, Sevcu A, Bobcikova K, Cernik M, Joner EJ (2016) DDT degradation efficiency and ecotoxicological effects of two types of nano-sized zero-valent iron (nZVI) in water and soil. Chemosphere 144:2221–2228

Essington ME (2015) Soil and water chemistry: an integrative approach. CRC Press, Boca Raton, 666 pp. https://doi.org/10.1201/b18385

Fandeur D, Juillot F, Morin G, Olivi L, Cognigni A, Webb SM, Ambrosi J-P, Fritsch E, Guyot F, Brown Gordon EJ (2009) XANES evidence for oxidation of Cr (III) to Cr (VI) by Mn-oxides in a lateritic regolith developed on serpentinized ultramafic rocks of New Caledonia. Environ Sci Technol 43:7384–7390

Fayaz M, Tiwary CS, Kalaichelvan PT, Venkatesan R (2010) Blue orange light emission from biogenic synthesized silver nanoparticles using *Trichoderma viride*. Colloids Surf B Biointerfaces 75:175–178

Feretti D, Zerbini I, Zani C, Ceretti E, Moretti M, Monarca S (2007) Allium cepa chromosome aberration and micronucleus tests applied to study genotoxicity of extracts from pesticide-treated vegetables and grapes. Food Addit Contam 24:561–5720

Ferreira AJ, Cemlyn-Jones J, Cordeiro CR (2013) Nanoparticles, nanotechnology and pulmonary nanotoxicology. Rev Port Pneumol (English Ed) 19:28–37

Foldbjerg R, Dang DA, Autrup H (2011) Cytotoxicity and genotoxicity of silver nanoparticles in the human lung cancer cell line, A549. Arch Toxicol 85:743–750

Franchi E, Rolli E, Marasco R, Agazzi G, Borin S, Cosmina P, Pedron F, Rosellini I, Barbafieri M, Petruzzelli G (2017) Phytoremediation of a multi contaminated soil: mercury and arsenic phytoextraction assisted by mobilizing agent and plant growth promoting bacteria. J Soils Sediments 17:1224–1236

Gan L, Zhang S, Zhang Y, He S, Tian Y (2018) Biosynthesis, characterization and antimicrobial activity of silver nanoparticles by a halotolerant Bacillus endophyticus SCU-L. Prep Biochem Biotechnol 48:582–588

Geremias R, Fattorini D, Fávere VTD, Pedrosa RC (2010) Bioaccumulation and toxic effects of copper in common onion Allium cepa L. Chem Ecol 26:19–26

Gerhardt KE, Gerwing PD, Greenberg BM (2017) Opinion: taking phytoremediation from proven technology to accepted practice. Plant Sci 256:170–185

Ghormade V, Deshpande MV, Paknikar KM (2011) Perspectives for nano-biotechnology enabled protection and nutrition of plants. Biotechnol Adv 29:792–803

Gil-Diaz M, Lobo MC (2018) Phytotoxicity of nanoscale zerovalent iron (nZVI) in remediation strategies. In: Faisal M, Saquib Q, Alatar AA, Al-Khedhairy AA (eds) Phytotoxicity of nanoparticles. Springer International Publishing, Cham, pp 301–333

Gisbert C, Ros R, De Haro A, Walker DJ, Bernal MP, Serrano R, Navarro-Aviñó J (2003) A plant genetically modified that accumulates Pb is especially promising for phytoremediation. Biochem Biophys Res Commun 303:440–445

Glick BR (2010) Using soil bacteria to facilitate phytoremediation. Biotechnol Adv 28:367–374

Gong J-L, Wang B, Zeng G-M, Yang C-P, Niu C-G, Niu Q-Y, Zhou W-J, Liang Y (2009) Removal of cationic dyes from aqueous solution using magnetic multi-wall carbon nanotube nanocomposite as adsorbent. J Hazard Mater 164:1517–1522

Gong X, Huang D, Liu Y, Zeng G, Wang R, Wan J, Zhang C, Cheng M, Qin X, Xue W (2017) Stabilized nanoscale zerovalent iron mediated cadmium accumulation and oxidative damage of *Boehmeria nivea* (L.) Gaudich cultivated in cadmium contaminated sediments. Environ Sci Technol 51:11308–11316

Gong X, Huang D, Liu Y, Peng Z, Zeng G, Xu P, Cheng M, Wang R, Wan J (2018) Remediation of contaminated soils by biotechnology with nanomaterials: bio-behavior, applications, and perspectives. Crit Rev Biotechnol 38:455–468

Green MS, Etherington JR (1977) Oxidation of ferrous iron by rice (*Oryza sativa* L.) roots: a mechanism for waterlogging tolerance? J Exp Bot 28:678–690

Gu H, Chen X, Chen F, Zhou X, Parsaee Z (2018) Ultrasound-assisted biosynthesis of CuO-NPs using brown alga *Cystoseira trinodis*: characterization, photocatalytic AOP, DPPH scavenging and antibacterial investigations. Ultrason Sonochem 41:109–119

Guan R, Kang T, Lu F, Zhang Z, Shen H, Liu M (2012) Cytotoxicity, oxidative stress, and genotoxicity in human hepatocyte and embryonic kidney cells exposed to ZnO nanoparticles. Nanoscale Res Lett 7:602

Habiba U, Ali S, Farid M, Shakoor MB, Rizwan M, Ibrahim M, Abbasi GH, Hayat T, Ali B (2015) EDTA enhanced plant growth, antioxidant defense system, and phytoextraction of copper by Brassica napus L. Environ Sci Pollut Res 22:1534–1544

Hao Z, Xu H, Feng Z, Zhang C, Zhou X, Wang Z, Zheng J, Zou X (2021) Spatial distribution, deposition flux, and environmental impact of typical persistent organic pollutants in surficial sediments in the Eastern China Marginal Seas (ECMSs). J Hazard Mater 407:124343

Hariharan D, Jegatha Christy A, Mayandi J, Nehru LC (2018) Visible light active photocatalyst: hydrothermal green synthesized TiO2 NPs for degradation of picric acid. Mater Lett 222:45–49

Haskell DE, Flaspohler DJ, Webster CR, Meyer MW (2012) Variation in soil temperature, moisture, and plant growth with the addition of downed woody material on lakeshore restoration sites. Restor Ecol 20:113–121

Hasnidawani JN, Azlina HN, Norita H, Bonnia NN, Ratim S, Ali ES (2016) Synthesis of ZnO nanostructures using sol-gel method. Procedia Chem 19:211–216

Haverkamp RG, Marshall AT (2008) The mechanism of metal nanoparticle formation in plants: limits on accumulation. J Nanopart Res 11:1453–1463

Heinemann MG, Rosa CH, Rosa GR, Dias D (2021) Trends in environmental analytical chemistry biogenic synthesis of gold and silver nanoparticles used in environmental applications: a review. 30

Huang D, Xue W, Zeng G, Wan J, Chen G, Huang C, Zhang C, Cheng M, Xu P (2016) Immobilization of Cd in river sediments by sodium alginate modified nanoscale zero-valent iron: impact on enzyme activities and microbial community diversity. Water Res 106:15–25

Huang D, Qin X, Peng Z, Liu Y, Gong X, Zeng G, Huang C, Cheng M, Xue W, Wang X, Hu Z (2018) Nanoscale zero-valent iron assisted phytoremediation of Pb in sediment: impacts on metal accumulation and antioxidative system of *Lolium perenne*. Ecotoxicol Environ Saf 153:229–237

Ibrahim RK, Hayyan M, AlSaadi MA, Hayyan A, Ibrahim S (2016) Environmental application of nanotechnology: air, soil, and water. Environ Sci Pollut Res 23:13754–13788

Ingle RA, Fricker MD, Smith JAC (2008) Evidence for nickel/proton antiport activity at the tonoplast of the hyperaccumulator plant Alyssum lesbiacum. Plant Biol 10:746–753

Irshad MA, Nawaz R, Rehman MZ, Adrees M, Rizwan M, Ali S, Ahmad S, Tasleem S (2021) Synthesis, characterization and advanced sustainable applications of titanium dioxide nanoparticles: a review. Ecotoxicol Environ Saf 212:111978

Jacobs A, De Brabandere L, Drouet T, Sterckeman T, Noret N (2018) Phytoextraction of Cd and Zn with *Noccaea caerulescens* for urban soil remediation: influence of nitrogen fertilization and planting density. Ecol Eng 116:178–187

Jahangiri AR, Sedighi M, Salimi F (2019) Synthesis of zinc-sulfate nano particles and detection of their induction time, nucleation rate and interfacial tension. Iran J Chem Chem Eng 38:45–52

Jain A, Wadhawan S, Mehta SK (2021) Environmental nanotechnology, monitoring & management biogenic synthesis of non-toxic iron oxide NPs via Syzygium aromaticum for the removal of methylene blue. Environ Nanotechnol Monit Manag 16:100464

Jarrah M, Ghasemi-Fasaei R, Ronaghi A, Zarei M, Mayel S (2019) Enhanced Ni phytoextraction by effectiveness of chemical and biological amendments in sunflower plant grown in Ni-polluted soils. Chem Ecol 35:732–745

Jaskulak M, Grobelak A, Grosser A, Vandenbulcke F (2019) Gene expression, DNA damage and other stress markers in Sinapis alba L. exposed to heavy metals with special reference to sewage sludge application on contaminated sites. Ecotoxicol Environ Saf 181:508–517

Jayachandran A, Aswathy TR, Nair AS (2021) Green synthesis and characterization of zinc oxide nanoparticles using Cayratia pedata leaf extract. Biochem Biophys Rep 26:100995

Jiamjitrpanich W, Parkpian P, Polprasert C, Kosanlavit R (2012) Enhanced phytoremediation efficiency of TNT-contaminated soil by nanoscale zero valent iron. In: 2nd international conference on environment and industrial innovation IPCBEE, pp 82–86

Jin Y, Liu W, Li X, Shen S, Liang S, Liu C, Shan L (2016) Nano-hydroxyapatite immobilized lead and enhanced plant growth of ryegrass in a contaminated soil. Ecol Eng 95:25–29

Joye IJ, Julian D (2013) Production of nanoparticles by anti- solvent precipitation for use in food systems. Trends Food Sci Technol 34:109–123

Kaneko K, Inoke K, Freitag B, Hungria AB, Midgley PA, Hansen TW, Zhang J, Ohara S, Adschiri T (2007) Structural and morphological characterization of cerium oxide nanocrystals prepared by hydrothermal synthesis. Nano Lett 7:421–425

Kang JW (2014) Removing environmental organic pollutants with bioremediation and phytoremediation. Biotechnol Lett 36:1129–1139

Kang J, Duan X, Wang C, Sun H, Tan X, Tade MO, Wang S (2018) Nitrogen-doped bamboo-like carbon nanotubes with Ni encapsulation for persulfate activation to remove emerging contaminants with excellent catalytic stability. Chem Eng J 332:398–408

Khalid H, Rehman MZ, Naeem A, Khalid MU, Rizwan M, Ali S, Umair M, Sohail MI (2019) *Solanum nigrum* L.: a novel hyperaccumulator for the phyto-management of cadmium contaminated soils. In: Cadmium toxicity and tolerance in plants: from physiology to remediation. Academic, pp 451–477

Khan AG (2020) Promises and potential of in situ nano-phytoremediation strategy to mycorrhizoremediate heavy metal contaminated soils using non-food bioenergy crops (Vetiver zizinoides & Cannabis sativa). Int J Phytoremediation 22:900–915

Khan N, Bano A (2016) Role of plant growth promoting rhizobacteria and Ag-nano particle in the bioremediation of heavy metals and maize growth under municipal wastewater irrigation. Int J Phytoremediation 18:211–221

Khan I, Saeed K, Khan I (2019) Nanoparticles: properties, applications and toxicities. Arab J Chem 12:908–931

Khanna P, Kaur A, Goyal D (2019) Algae-based metallic nanoparticles: synthesis, characterization and applications. J Microbiol Methods 163:105656

Khodakovskaya MV, Kim BS, Kim JN, Alimohammadi M, Dervishi E, Mustafa T, Cernigla CE (2013) Carbon nanotubes as plant growth regulators: effects on tomato growth, reproductive system, and soil microbial community. Small 9:115–123

Khodaverdiloo H, Han FX, Hamzenejad Taghlidabad R, Karimi A, Moradi N, Kazery JA (2020) Potentially toxic element contamination of arid and semi-arid soils and its phytoremediation. Arid L Res Manag 34:361–391

Khudiar SS, Nayef UM, Mutlak FAH (2021) Preparation and characterization of ZnO nanoparticles via laser ablation for sensing NO_2 gas. Optik (Stuttg) 246:167762

Kohut A, Kéri A, Horváth V, Kopniczky J, Ajtai T, Hopp B, Galbács G, Geretovszky Z (2020) Facile and versatile substrate fabrication for surface enhanced Raman spectroscopy using spark discharge generation of Au/Ag nanoparticles. Appl Surf Sci 531:147268

Kole C, Kole P, Randunu KM, Choudhary P, Podila R, Ke PC, Rao AM, Marcus RK (2013) Nanobiotechnology can boost crop production and quality: first evidence from increased plant biomass, fruit yield and phytomedicine content in bitter melon (Momordica charantia). BMC Biotechnol 13:1–10

Komárek M, Koretsky CM, Stephen KJ, Alessi DS, Chrastný V (2015) Competitive adsorption of Cd (II), Cr (VI), and Pb (II) onto nanomaghemite: a spectroscopic and modeling approach. Environ Sci Technol 49:12851–12859

Košnář Z, Mercl F, Tlustoš P (2018) Ability of natural attenuation and phytoremediation using maize (Zea mays L.) to decrease soil contents of polycyclic aromatic hydrocarbons (PAHs) derived from biomass fly ash in comparison with PAHs–spiked soil. Ecotoxicol Environ Saf 153:16–22

Laghlimi M, Baghdad B, El Hadi H, Bouabdli A (2015) Phytoremediation mechanisms of heavy metal contaminated soils: a review. Open J Ecol 05:375–388

Lei R, Wu C, Yang B, Ma H, Shi C, Wang Q, Wang Q, Yuan Y, Liao M (2008) Integrated metabolomic analysis of the nano-sized copper particle-induced hepatotoxicity and nephrotoxicity in rats: a rapid in vivo screening method for nanotoxicity. Toxicol Appl Pharmacol 232:292–301

Li Z, Wang L, Meng J, Liu X, Xu J, Wang F, Brookes P (2018) Zeolite-supported nanoscale zero-valent iron: new findings on simultaneous adsorption of Cd(II), Pb(II), and As(III) in aqueous solution and soil. J Hazard Mater 344:1–11

Liang SX, Jin Y, Liu W, Li X, Shen S g, Ding L (2017a) Feasibility of Pb phytoextraction using nano-materials assisted ryegrass: results of a one-year field-scale experiment. J Environ Manag 190:170–175

Liang J, Yang Z, Tang L, Zeng G, Yu M, Li X, Wu H, Qian Y, Li X, Luo Y (2017b) Changes in heavy metal mobility and availability from contaminated wetland soil remediated with combined biochar-compost. Chemosphere 181:281–288

Liu H, Ma L, Zhao J, Liu J, Yan J, Ruan J, Hong F (2009) Biochemical toxicity of nano-anatase TiO_2 particles in mice. Biol Trace Elem Res 129:170–180

Liu G, Gao J, Ai H, Chen X (2013) Applications and potential toxicity of magnetic iron oxide nanoparticles. Small 9:1533–1545

Liu H, Su X, Duan C, Dong X, Zhou S, Zhu Z (2014) Microwave-assisted hydrothermal synthesis of Au NPs-Graphene composites for H_2O_2 detection. J Electroanal Chem 731:36–42

Liu D, Li C, Zhou F, Zhang T, Zhang H, Li X, Duan G, Cai W, Li Y (2015) Rapid synthesis of monodisperse Au nanospheres through a laser irradiation-induced shape conversion, self-assembly and their electromagnetic coupling SERS enhancement. Sci Rep 5:7686

Long F, Gong JL, Zeng GM, Chen L, Wang XY, Deng JH, Niu QY, Zhang HY, Zhang XR (2011) Removal of phosphate from aqueous solution by magnetic Fe-Zr binary oxide. Chem Eng J 171:448–455

Love AJ, Makarov VV, Sinitsyna OV, Shaw J, Yaminsky IV, Kalinina NO, Taliansky ME (2015) A genetically modified tobacco mosaic virus that can produce gold nanoparticles from a metal salt precursor. Front Plant Sci 6:984

Ma X, Wang C (2010) Fullerene nanoparticles affect the fate and uptake of trichloroethylene in phytoremediation systems. Environ Eng Sci 27:989–992

Ma Y, Rajkumar M, Zhang C, Freitas H (2016) Inoculation of *Brassica oxyrrhina* with plant growth promoting bacteria for the improvement of heavy metal phytoremediation under drought conditions. J Hazard Mater 320:36–44

Magrez A, Kasas S, Salicio V, Pasquier N, Seo JW, Celio M, Catsicas S, Schwaller B, Forró L (2006) Cellular toxicity of carbon-based nanomaterials. Nano Lett 6:1121–1125

Mahato TH, Prasad GK, Singh B, Acharya J, Srivastava AR, Vijayaraghavan R (2009) Nanocrystalline zinc oxide for the decontamination of sarin. J Hazard Mater 165:928–932

Malekzadeh M, Halali M (2011) Production of silver nanoparticles by electromagnetic levitation gas condensation. Chem Eng J 168:441–445

Mangaiyarkarasi R, Priyanga M, Santhiya N, Umadevi S (2020) In situ preparation of palladium nanoparticles in ionic liquid crystal microemulsion and their application in Heck reaction. J Mol Liq 310:113241

Mao C, Yi K, Yang L, Zheng B, Wu Y, Liu F, Wu P (2004) Identification of aluminium-regulated genes by cDNA-AFLP in rice (Oryza sativa L.): aluminium-regulated genes for the metabolism of cell wall components. J Exp Bot 55:137–143

Martínez-Fernández D, Bingöl D, Komárek M (2014) Trace elements and nutrients adsorption onto nano-maghemite in a contaminated-soil solution: a geochemical/statistical approach. J Hazard Mater 276:271–277

Martínez-Fernández D, Vítková M, Bernal MP, Komárek M (2015) Effects of nano-maghemite on trace element accumulation and drought response of *Helianthus annuus* L. in a contaminated mine soil. Water Air Soil Pollut 226:1–9

Maruthupandy M, Zuo Y, Chen JS, Song JM, Niu HL, Mao CJ, Zhang SY, Shen YH (2017) Synthesis of metal oxide nanoparticles (CuO and ZnO NPs) via biological template and their optical sensor applications. Appl Surf Sci 397:167–174

Matsuyama K, Tsubaki T, Kato T, Okuyama T, Muto H (2020) Preparation of catalytically active Au nanoparticles by sputter deposition and their encapsulation in metal-organic framework of Cu3(BTC)2. Mater Lett 261:127124

Maurer-Jones MA, Gunsolus IL, Murphy CJ, Haynes CL (2013) Toxicity of engineered nanoparticles in the environment. Anal Chem 85:3036–3049

Menon S, Shanmugam R, Kumar V (2017) A review on biogenic synthesis of gold nanoparticles, characterization, and its applications. Resour Technol 3:516–527

Merisko-Liversidge E, Liversidge GG, Cooper ER (2003) Nanosizing: a formulation approach for poorly-water-soluble compounds. Eur J Pharm Sci 18:113–120

Moameri M, Abbasi Khalaki M (2019) Capability of Secale montanum trusted for phytoremediation of lead and cadmium in soils amended with nano-silica and municipal solid waste compost. Environ Sci Pollut Res 26:24315–24322

Mogilevsky G, Hartman O, Emmons ED, Balboa A, DeCoste JB, Schindler BJ, Iordanov I, Karwacki CJ (2014) Bottom-up synthesis of anatase nanoparticles with graphene domains. ACS Appl Mater Interfaces 6:10638–10648

Mojiri A (2011) The potential of corn (Zea mays) for phytoremediation of soil contaminated with cadmium and lead. J Biol Environ Sci 5:17–22

Mokarram-Kashtiban S, Hosseini SM, Tabari Kouchaksaraei M, Younesi H (2019) The impact of nanoparticles zero-valent iron (nZVI) and rhizosphere microorganisms on the phytoremediation ability of white willow and its response. Environ Sci Pollut Res 26:10776–10789

Moshiri F, Ebrahimi H, Ardakani MR, Rejali F, Mousavi SM (2019) Biogeochemical distribution of Pb and Zn forms in two calcareous soils affected by mycorrhizal symbiosis and alfalfa rhizosphere. Ecotoxicol Environ Saf 179:241–248

Mueller NC, Nowack B (2010) Nanoparticles for remediation: solving big problems with little particles. Elements 6:395–400

Nahar N, Rahman A, Nawani NN, Ghosh S, Mandal A (2017) Phytoremediation of arsenic from the contaminated soil using transgenic tobacco plants expressing ACR2 gene of Arabidopsis thaliana. J Plant Physiol 218:121–126

Nath D, Banerjee P (2013) Green nanotechnology – a new hope for medical biology. Environ Toxicol Pharmacol 36:997–1014

Navarro E, Baun A, Behra R, Hartmann NB, Filser J, Miao A-J, Quigg A, Santschi PH, Sigg L (2008) Environmental behavior and ecotoxicity of engineered nanoparticles to algae, plants, and fungi. Ecotoxicology 17:372–386

Ng CK, Sivakumar K, Liu X, Madhaiyan M, Ji L, Yang L, Tang C, Song H, Kjelleberg S, Cao B (2013) Influence of outer membranec-type cytochromes on particle size and activity of extracellular nanoparticles produced by Shewanella oneidensis. Biotechnol Bioeng 110:1831–1837

Nguyen TKM, Ki MR, Son RG, Kim KH, Hong J, Pack SP (2021) Synthesis of sub-50 nm bio-inspired silica particles using a C-terminal-modified ferritin template with a silica-forming peptide. J Ind Eng Chem 101:262–269

Niwa Y, Iwai N (2006) Genotoxicity in cell lines induced by chronic exposure to water-soluble fullerenes using micronucleus test. Environ Health Prev Med 11:292–297

Nordlander B, Krantz M, Hohmann S (2008) Hog1-mediated metabolic adjustments following hyperosmotic shock in the yeast. Current 20

Nouri J, Khorasani N, Lorestani B, Karami M, Hassani AH, Yousefi N (2009) Accumulation of heavy metals in soil and uptake by plant species with phytoremediation potential. Environ Earth Sci 59:315–323

O'Reilly SE, Hochella MF Jr (2003) Lead sorption efficiencies of natural and synthetic Mn and Fe-oxides. Geochim Cosmochim Acta 67:4471–4487

Onwuka B, Mang B (2018) Effects of soil temperature on some soil properties and plant growth. Adv Plants Agric Res 8:34

Owoeye SS, Abegunde SM, Oji B (2021) Effects of process variable on synthesis and characterization of amorphous silica nanoparticles using sodium silicate solutions as precursor by sol–gel method. Nano-Struct Nano-Objects 25:100625

Panagiotou T, Fisher RJ (2013) Producing micron- and nano-size formulations for functional foods applications. Funct Foods Health Dis 3:274

Patelli N, Cugini F, Wang D, Sanna S, Solzi M, Hahn H, Pasquini L (2021) Structure and magnetic properties of Fe-Co alloy nanoparticles synthesized by pulsed-laser inert gas condensation. J Alloys Compd 890:161863

Patra HK, Banerjee S, Chaudhuri U, Lahiri P, Dasgupta AK (2007) Cell selective response to gold nanoparticles. Nanomed Nanotechnol Biol Med 3:111–119

Pérez-de-Luque A (2017) Interaction of nanomaterials with plants: what do we need for real applications in agriculture? Front Environ Sci 5:12

Pillai HPS, Kottekottil J (2016) Nano-phytotechnological remediation of endosulfan using zero valent iron nanoparticles. J Environ Prot (Irvine, Calif) 07:734–744

Poland CA, Duffin R, Kinloch I, Maynard A, Wallace WAH, Seaton A, Stone V, Brown S, MacNee W, Donaldson K (2008) Carbon nanotubes introduced into the abdominal cavity of mice show asbestos-like pathogenicity in a pilot study. Nat Nanotechnol 3:423–428

Post JE (1999) Manganese oxide minerals: crystal structures and economic and environmental significance. Proc Natl Acad Sci 96:3447–3454

Praveen A, Khan E, Ngiimei S, Perwez M, Sardar M, Gupta M (2018) Iron oxide nanoparticles as nano-adsorbents: a possible way to reduce arsenic phytotoxicity in Indian mustard plant (*Brassica juncea* L.). J Plant Growth Regul 37:612–624

Priyadarshana G, Kottegoda N, Senaratne A, de Alwis A, Karunaratne V (2015) Synthesis of magnetite nanoparticles by top-down approach from a high purity ore. J Nanomater 2015:1–8

Ramkumar VS, Pugazhendhi A, Prakash S, Ahila NK, Vinoj G, Selvam S, Kumar G, Kannapiran E, Rajendran RB (2017) Synthesis of platinum nanoparticles using seaweed Padina gymnospora and their catalytic activity as PVP/PtNPs nanocomposite towards biological applications. Biomed Pharmacother 92:479–490

Reddy PVL, Hernandez-Viezcas JA, Peralta-Videa JR, Gardea-Torresdey JL (2016) Lessons learned: are engineered nanomaterials toxic to terrestrial plants? Sci Total Environ 568:470–479

Rehman MZ, Rizwan M, Ali S, Ok YS, Ishaque W, Saifullah NMF, Akmal F, Waqar M (2017) Remediation of heavy metal contaminated soils by using *Solanum nigrum*: a review. Ecotoxicol Environ Saf 143:236–248

Rehman MZ, Rizwan M, Ali S, Naeem A, Yousaf B, Lui G, Khalid H, Hafeez F, Azhar M (2018) A field study investigating the potential use of phosphorus combined with organic amendments on cadmium accumulation by wheat and subsequent rice. Arab J Geosci 11:1–9

Rehman MZ, Rizwan M, Sohail MI, Ali S, Waris AA, Khalid H, Naeem A, Ahmad HR, Rauf A (2019) Opportunities and challenges in the remediation of metal-contaminated soils by using tobacco (*Nicotiana tabacum* L.): a critical review. Environ Sci Pollut Res 26:18053–18070

Rehman MZ, Waqar M, Bashir S, Rizwan M, Ali S, El Baroudy AAEF, Khalid H, Ayub MA, Usman M, Jahan S (2021) Effect of biochar and compost on cadmium bioavailability and its uptake by wheat–rice cropping system irrigated with untreated sewage water: a field study. Arab J Geosci 14:135

Ren X, Zeng G, Tang L, Wang J, Wan J, Liu Y, Yu J, Yi H, Ye S, Deng R (2018) Sorption, transport and biodegradation – An insight into bioavailability of persistent organic pollutants in soil. Sci Total Environ 610–611:1154–1163

Rizwan M, Ali S, Qayyum MF, Ok YS, Adrees M, Ibrahim M, Zia-ur-Rehman M, Farid M, Abbas F (2017) Effect of metal and metal oxide nanoparticles on growth and physiology of globally important food crops: a critical review. J Hazard Mater 322:2–16

Rizwan M, Ali S, ur Rehman MZ, Rinklebe J, Tsang DCW, Bashir A, Maqbool A, Tack FMG, Ok YS (2018) Cadmium phytoremediation potential of Brassica crop species: a review. Sci Total Environ 631:1175–1191

Rizwan M, Ali S, Rehman MZ, Riaz M, Adrees M, Hussain A, Zahir ZA, Rinklebe J (2021) Effects of nanoparticles on trace element uptake and toxicity in plants: a review. Ecotoxicol Environ Saf 221:112437

Robinson BH, Chiarucci A, Brooks RR, Petit D, Kirkman JH, Gregg PEH, De Dominicis V (1997) The nickel hyperaccumulator plant Alyssum bertolonii as a potential agent for phytoremediation and phytomining of nickel. J Geochem Explor 59:75–86

Rostami S, Azhdarpoor A (2019) The application of plant growth regulators to improve phytoremediation of contaminated soils: a review. Chemosphere 220:818–827

Saha JK, Selladurai R, Coumar MV, Dotaniya ML, Kundu S, Patra AK (2017) Major inorganic pollutants affecting soil and crop quality. In: Soil pollution-an emerging threat to agriculture. Springer, pp 75–104

Sarkar J, Ray S, Chattopadhyay D, Laskar A, Acharya K (2011) Mycogenesis of gold nanoparticles using a phytopathogen Alternaria alternata. Bioprocess Biosyst Eng 35:637–643

Sarma H (2011) Metal hyperaccumulation in plants: a review focusing on phytoremediation technology. J Environ Sci Technol 4:118–138

Scheckel KG, Luxton TP, El Badawy AM, Impellitteri CA, Tolaymat TM (2010) Synchrotron speciation of silver and zinc oxide nanoparticles aged in a kaolin suspension. Environ Sci Technol 44:1307–1312

Schoonover JE, Crim JF (2015) An introduction to soil concepts and the role of soils in watershed management. J Contemp Water Res Educ 154:21–47

Servin AD, White JC (2016) Nanotechnology in agriculture: next steps for understanding engineered nanoparticle exposure and risk. NanoImpact 1:9–12

Servin A, Elmer W, Mukherjee A, De la Torre-Roche R, Hamdi H, White JC, Bindraban P, Dimkpa C (2015) A review of the use of engineered nanomaterials to suppress plant disease and enhance crop yield. J Nanopart Res 17:1–21

Shafigh M, Ghasemi-Fasaei R, Ronaghi A (2016) Influence of plant growth regulators and humic acid on the phytoremediation of lead by maize in a Pb-polluted calcareous soil. Arch Agron Soil Sci 62:1733–1740

Shafigh M, Ghasemi-Fasaei R, Ronaghi A (2017) Influence of plant growth regulators and humic substance on the phytoremediation of nickel in a Ni-polluted soil. J Water Soil 31:1

Shah M, Fawcett D, Sharma S, Tripathy S, Poinern G (2015) Green synthesis of metallic nanoparticles via biological entities. Materials (Basel) 8:7278–7308

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

Shen X, Li S, Zhang H, Chen W, Yang Y, Li J, Tao S, Wang X (2018) Effect of multiwalled carbon nanotubes on uptake of pyrene by cucumber (*Cucumis sativus* L.): mechanistic perspectives. NanoImpact 10:168–176

Sheoran V, Sheoran AS, Poonia P (2016) Factors affecting phytoextraction: a review. Pedosphere 26:148–166

Shimomura M, Sawadaishi T (2001) Bottom-up strategy of materials fabrication: a new trend in nanotechnology of soft materials. Curr Opin Colloid Interface Sci 6:11–16

Singh J, Lee BK (2016) Influence of nano-TiO_2 particles on the bioaccumulation of Cd in soybean plants (*Glycine max*): a possible mechanism for the removal of Cd from the contaminated soil. J Environ Manag 170:88–96

Sohail MI, Waris AA, Ayub MA, Usman M, ur Rehman MZ, Sabir M, Faiz T (2019) Environmental application of nanomaterials: a promise to sustainable future. In: Comprehensive analytical chemistry. Elsevier, pp 1–54

Song B, Zeng G, Gong J, Liang J, Xu P, Liu Z, Zhang Y, Zhang C, Cheng M, Liu Y (2017a) Evaluation methods for assessing effectiveness of in situ remediation of soil and sediment contaminated with organic pollutants and heavy metals. Environ Int 105:43–55

Song B, Zeng G, Gong J, Zhang P, Deng J, Deng C, Cheng M (2017b) Effect of multi-walled carbon nanotubes on phytotoxicity of sediments contaminated by phenanthrene and cadmium. Chemosphere 172:449–458

Song B, Xu P, Zeng G, Gong J, Zhang P, Feng H, Liu Y, Ren X (2018) Carbon nanotube-based environmental technologies: the adopted properties, primary mechanisms, and challenges. Rev Environ Sci Biotechnol 17:571–590

Song B, Xu P, Chen M, Tang W, Zeng G, Gong J, Zhang P, Ye S (2019) Using nanomaterials to facilitate the phytoremediation of contaminated soil. Crit Rev Environ Sci Technol 49:791–824

Soudek P, Petrová Š, Vaňková R, Song J, Vaněk T (2014) Accumulation of heavy metals using Sorghum sp. Chemosphere 104:15–24

Souri Z, Karimi N, Sarmadi M, Rostami E (2017) Salicylic acid nanoparticles (SANPs) improve growth and phytoremediation efficiency of *Isatis cappadocica* Desv., under As stress. IET Nanobiotechnol 11:650–655

Sposito G (2008) The chemistry of soils. Oxford university press

Srivastav A, Yadav KK, Yadav S, Gupta N, Singh JK, Katiyar R, Kumar V (2019) Nano-phytoremediation of pollutants from contaminated soil environment: current scenario and future prospects. In: Phytoremediation: management of environmental contaminants. Springer, Cham, pp 383–401

Su Y, Yan X, Pu Y, Xiao F, Wang D, Yang M (2013) Risks of single-walled carbon nanotubes acting as contaminants-carriers: potential release of phenanthrene in Japanese medaka (*Oryzias latipes*). Environ Sci Technol 47:4704–4710

Su C, Jiang L, Zhang W (2014) A review on heavy metal contamination in the soil worldwide: situation, impact and remediation techniques. Environ Skept Crit 3:24–38

Subramanian KS, Manikandan A, Thirunavukkarasu M, Rahale CS (2015) Nano-fertilizers for balanced crop nutrition. In: Nanotechnologies in food and agriculture. Springer, Cham, pp 69–80

Tangahu BV, Sheikh Abdullah SR, 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 2011:1

Terzi K, Sikinioti-Lock A, Gkelios A, Tzavara D, Skouras A, Aggelopoulos C, Klepetsanis P, Antimisiaris S, Tsakiroglou CD (2016) Mobility of zero valent iron nanoparticles and liposomes in porous media. Colloids Surf A Physicochem Eng Asp 506:711–722

Timmusk S, Seisenbaeva G, Behers L (2018) Titania (TiO_2) nanoparticles enhance the performance of growth-promoting rhizobacteria. Sci Rep 8:617

Torre-Roche RDL, Hawthorne J, Deng Y, Xing B, Cai W, Newman LA, Wang C, Ma X, White JC (2012) Fullerene-enhanced accumulation of p, p'-DDE in agricultural crop species. Environ Sci Technol 46:9315–9323

Tripathi DK, Singh VP, Prasad SM, Chauhan DK, Dubey NK (2015) Silicon nanoparticles (SiNp) alleviate chromium (VI) phytotoxicity in *Pisum sativum* (L.) seedlings. Plant Physiol Biochem 96:189–198

Trujillo-Reyes J, Peralta-Videa JR, Gardea-Torresdey JL (2014) Supported and unsupported nanomaterials for water and soil remediation: are they a useful solution for worldwide pollution? J Hazard Mater 280:487–503

Tudoreanu L, Phillips CJC (2004) Modeling cadmium uptake and accumulation in plants. Adv Agron 84:121–157

Vangronsveld J, Herzig R, Weyens N, Boulet J, Adriaensen K, Ruttens A, Thewys T, Vassilev A, Meers E, Nehnevajova E (2009) Phytoremediation of contaminated soils and groundwater: lessons from the field. Environ Sci Pollut Res 16:765–794

Veisi H, Joshani Z, Karmakar B, Tamoradi T, Heravi MM, Gholami J (2021) Ultrasound assisted synthesis of Pd NPs decorated chitosan-starch functionalized Fe_3O_4 nanocomposite catalyst towards Suzuki-Miyaura coupling and reduction of 4-nitrophenol. Int J Biol Macromol 172:104–113

Venkatachalam P, Jayaraj M, Manikandan R, Geetha N, Rene ER, Sharma NC, Sahi SV (2017) Zinc oxide nanoparticles (ZnONPs) alleviate heavy metal-induced toxicity in Leucaena leucocephala seedlings: a physiochemical analysis. Plant Physiol Biochem 110:59–69

Villalobos M, Escobar-Quiroz IN, Salazar-Camacho C (2014) The influence of particle size and structure on the sorption and oxidation behavior of birnessite: I. Adsorption of As (V) and oxidation of As (III). Geochim Cosmochim Acta 125:564–581

Vítková M, Komárek M, Tejnecký V, Šillerová H (2015) Interactions of nano-oxides with low-molecular-weight organic acids in a contaminated soil. J Hazard Mater 293:7–14

Vítková M, Puschenreiter M, Komárek M (2018) Effect of nano zero-valent iron application on As, Cd, Pb, and Zn availability in the rhizosphere of metal (loid) contaminated soils. Chemosphere 200:217–226

Wan J, Zeng G, Huang D, Hu L, Xu P, Huang C, Deng R, Xue W, Lai C, Zhou C, Zheng K, Ren X, Gong X (2018) Rhamnolipid stabilized nano-chlorapatite: synthesis and enhancement effect on Pb-and Cd-immobilization in polluted sediment. J Hazard Mater 343:332–339

Wang H, Jia Y, Wang S, Zhu H, Wu X (2009) Bioavailability of cadmium adsorbed on various oxides minerals to wetland plant species Phragmites australis. J Hazard Mater 167:641–646

Wang P, Lombi E, Zhao FJ, Kopittke PM (2016a) Nanotechnology: a new opportunity in plant sciences. Trends Plant Sci 21:699–712

Wang X, Liu Y, Zhang H, Shen X, Cai F, Zhang M, Gao Q, Chen W, Wang B, Tao S (2016b) The impact of carbon nanotubes on bioaccumulation and translocation of phenanthrene, 3-CH 3-phenanthrene and 9-NO 2-phenanthrene in maize (*Zea mays*) seedlings. Environ Sci Nano 3:818–829

Watson J-L, Fang T, Dimkpa CO, Britt DW, McLean JE, Jacobson A, Anderson AJ (2015) The phytotoxicity of ZnO nanoparticles on wheat varies with soil properties. Biometals 28:101–112

Wegner K, Pratsinis SE (2005) Gas-phase synthesis of nanoparticles: scale-up and design of flame reactors. Powder Technol 150:117–122

Xiaocan L, Ling X, Qiusheng D, Wei C (2019) Immobilization mechanism of nano - hydroxyapatite on lead in the ryegrass rhizosphere soil under root confinement. Bull Environ Contam Toxicol 103:330–335

Yadu B, Chandrakar V, Korram J, Satnami ML, Kumar M, Keshavkant S (2018) Silver nanoparticle modulates gene expressions, glyoxalase system and oxidative stress markers in fluoride stressed *Cajanus cajan* L. J Hazard Mater 353:44–52

Yamamoto Y, Kobayashi Y, Matsumoto H (2001) Lipid peroxidation is an early symptom triggered by aluminum, but not the primary cause of elongation inhibition in pea roots. Plant Physiol 125:199–208

Yang F, Hong F, You W, Liu C, Gao F, Wu C, Yang P (2006) Influence of nano-anatase TiO2 on the nitrogen metabolism of growing spinach. Biol Trace Elem Res 110:179–190

Yang S-T, Wang X, Jia G, Gu Y, Wang T, Nie H, Ge C, Wang H, Liu Y (2008) Long-term accumulation and low toxicity of single-walled carbon nanotubes in intravenously exposed mice. Toxicol Lett 181:182–189

Yang Y, Liang Y, Ghosh A, Song Y, Chen H, Tang M (2015) Assessment of arbuscular mycorrhizal fungi status and heavy metal accumulation characteristics of tree species in a lead–zinc mine area: potential applications for phytoremediation. Environ Sci Pollut Res 22:13179–13193

Yuan H, Hu S, Huang P, Song H, Wang K, Ruan J, He R, Cui D (2011) Single walled carbon nanotubes exhibit dual-phase regulation to exposed Arabidopsis mesophyll cells. Nanoscale Res Lett 6:44

Zaier H, Ghnaya T, Ghabriche R, Chmingui W, Lakhdar A, Lutts S, Abdelly C (2014) EDTA-enhanced phytoremediation of lead-contaminated soil by the halophyte *Sesuvium portulacastrum*. Environ Sci Pollut Res 21:7607–7615

Zehra A, Sahito ZA, Tong W, Tang L, Hamid Y, Khan MB, Ali Z, Naqvi B, Yang X (2020) Assessment of sunflower germplasm for phytoremediation of lead-polluted soil and production of seed oil and seed meal for human and animal consumption. J Environ Sci 87:24–38

Zhang M, Wang Y, Zhao D, Pan G (2010) Immobilization of arsenic in soils by stabilized nanoscale zero-valent iron, iron sulfide (FeS), and magnetite (Fe_3O_4) particles. Chin Sci Bull 55:365–372

Zhang J, Gong J-L, Zeng G-M, Yang H-C, Zhang P (2017) Carbon nanotube amendment for treating dichlorodiphenyltrichloroethane and hexachlorocyclohexane remaining in Dong-ting Lake sediment—an implication for in-situ remediation. Sci Total Environ 579:283–291

Zhao X, Wang C, Wang D, Hahn H, Fichtner M (2013) Ge-Cu nanoparticles produced by inert gas condensation and their application as anode material for lithium ion batteries. Electrochem Commun 35:116–119

Zhao Z, Sun J, Zhang G, Bai L (2015) The study of microstructure, optical and photocatalytic properties of nanoparticles (NPs)-Cu/TiO_2 films deposited by magnetron sputtering. J Alloys Compd 652:307–312

Zhou Y, Dong C-K, Han L, Yang J, Du X-W (2016) Top-down preparation of active cobalt oxide catalyst. ACS Catal 6:6699–6703

Zhou J, Wang C, Song M, Chen X, Xia W (2021) Simple synthesis of ultrafine amorphous silicon carbide nanoparticles by atmospheric plasmas. Mater Lett 299:130072

Zhu B-K, Fang Y-M, Zhu D, Christie P, Ke X, Zhu Y-G (2018) Exposure to nanoplastics disturbs the gut microbiome in the soil oligochaete *Enchytraeus crypticus*. Environ Pollut 239:408–415

Zuo R, Liu H, Xi Y, Gu Y, Ren D, Yuan X, Huang Y (2020) Nano-SiO2 combined with a surfactant enhanced phenanthrene phytoremediation by *Erigeron annuus* (L.) Pers. Environ Sci Pollut Res 27:20538–20544

Chapter 24
A Systematic Analysis of Nanotechnology Application in Water Contaminations Removal

Madhulika Bhati, Yogesh Nagar, Raghav Sharma, and Himanshi Singh

Abstract This chapter reviews and analyses the implementation of nanotechnology in the purification and treatment of water in various parts of the world. The data is extracted from the bibliographical database "Dimensions" using the keywords, "water purification" and "membrane". VoS viewer which is a software tool for constructing and visualizing bibliographic scientific networks is also used to further analyse the social and conceptual relationships. Using the aforementioned software, a research trend regarding membrane science for water purification indicated the availability of several technological intervention. Out of all the data extracted and reviewed, USA comes out as a key player, leading the world in membrane science applications in the sector of water purification. The research in the USA inclines towards the inclusion of nanotechnology in membranes for improved water selection from different sources. A boom can be observed for some membrane technologies such as Block Co-polymer, Thin-Film Composite (TFC) polyamide membranes, Carbon Nano Tubes (CNT), and graphene oxide, but more modifications and performance data are required for them to be commercialized efficiently. To ease the ecological burden, more sustainable membranes made up of natural polymers like chitin and cellulose are being developed to replace the conventional synthetic membranes. From this analysis, the scope of Nanoparticle technology is presented in fields like water purification, pollutants and also against bacteria, viruses, and microplastics.

Keywords Water purification · Water desalination · VoS · Nano-membrane · Reverse osmosis (RO) · Forward Osmosis (FO)

M. Bhati (✉) · Y. Nagar · R. Sharma · H. Singh
CSIR-National Insitute of Science Communication and Policy Research,
Dr. K.S. Krishnan Marg, Pusa, New Delhi, India
e-mail: madhulikabhati@niscpr.res.in

L. Newman et al. (eds.), *Phytoremediation*, https://doi.org/10.1007/978-3-031-17988-4_24

24.1 Introduction

There are four main issues related to water: Availability, Accessibility, Quality, and Sustainability. This focuses on some of the major problems faced by the people worldwide and the broad status of technology and technology gaps needed to be filled.

Accessibility According to the UN World Water Development report of 2019, the water demand both in the industrial and the domestic zone will increase by 20–30% by 2050. But at present, water stress is experienced by an estimated 2 billion worldwide, with 4 billion people experiencing water shortage at least once a month a year. This decreasing trend of water availability hints at water crises in the coming future.

Quality Quality of water is critical in several sectors like drinking, domestic, recreational, agricultural, and industrial. Therefore, adequate water quality management is extremely necessary to restore the ecosystem balance, ensure public health worldwide and promote socio-economic development. S&T interventions for water quality have to begin with identifying strategies to manage water quality standards. In recent times, efforts have been made to assure access to drinkable water and basic sanitation to reduce the possibility of waterborne diseases. These challenges are further aggravated due to global driving forces such as population growth, climate change, and its related extreme weather events, and increasing water scarcity.

Sustainability For the maintenance of the ecological niche, there is a requirement of a minimal level of water for sustainable growth in the water ecosystem consisting of rivers, lakes, ponds, and groundwater. Due to overexploitation almost all of these resources are constantly threatened by the declining water levels. They are substantially affected by the heavy salt intrusion, surface water contamination, and inadequate time for replenishment. Significant mining and thermo-electricity generation industries withdraw a significant fraction of water available in natural resources. For the USA, in 2000, water withdrawal by the thermo-electricity industry was 3% which is expected to surge up rapidly to 28–49% in 2030 to cater to the increasing energy demands. Such stresses on current water resources make it essential for us to reuse and recycle wastewater. Rapid urbanization and industrialization further threaten water quality and sustainability aspects.

For the sake of reducing the pressure on natural water resources and also meeting the increasing demands for water supply, various technologies have been adapted and are being continuously evolved to treat water with minimal ecological damage. Some technologies which have been extremely successful commercially, are Reverse Osmosis (RO), Forward Osmosis (FO), and Ultrafiltration (UF). In due course, nanotechnology has also become an integral part of such purification technologies, because of its high-efficiency rate. There has also been a rise in the popularity of more ecologically conscious polymer membranes, which are usually biocompatible and made up of materials. To analyse the research trend in water purification in the last decade, a comprehensive analysis has been done using publications extracted from the free Dimension database.

24.2 Methodology

Data elicited from the bibliographical database “Dimensions,” using “water purification” and “membrane” as keywords were used to analyse the research trend in water treatment technologies.

For our study, the keyword, “membrane” and “water purification” were searched on the Dimension platform, for period of 2010–2021. Approximately 4600 documents were retrieved. The top 10% has been analysed to map the research trend in the relevant field. The quantum of publication has increased from 2010 to 2019 as shown in Fig. 24.1. It is evitable from the graph that the highly cited paper was during the period of 2010–2020.

Country-wise publication analysis revealed that the USA is the top player in terms of the number of papers as well as citations received, followed by China and South Korea, respectively (Fig. 24.2).

The paper has done a detailed analysis of the top 1% of papers (~50 articles) published and cited nation in the nanotechnology-based membrane research for water purification. The USA has accounted for 45% of the total publication with the main focus on using electrospinning for manufacturing nano-membranes, cultivating next-generation membranes, and improving the existing technologies for desalinization of contaminated water, oil-water separation, and removal of the micropollutants research domain. Biological remediation like utilization of aquaporins and manufacturing membranes made of Cellulose or Chitin to serve as ecological alternatives to synthetic polymers was also covered extensively.

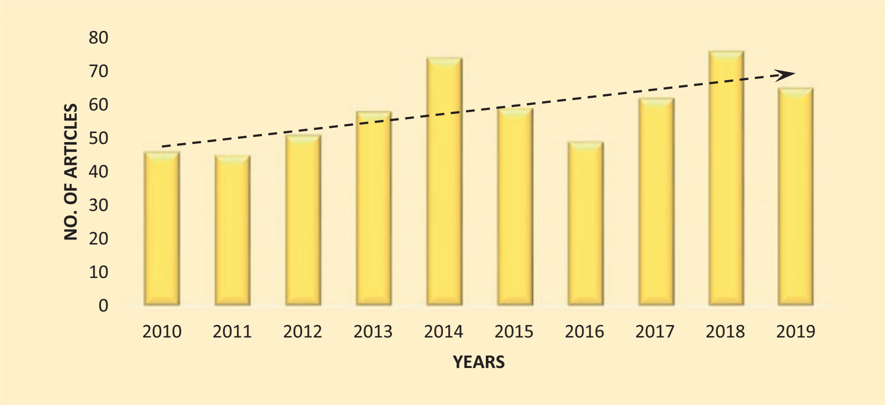


Fig. 24.1 Top 10% of highly cited papers over the years 2010–2020

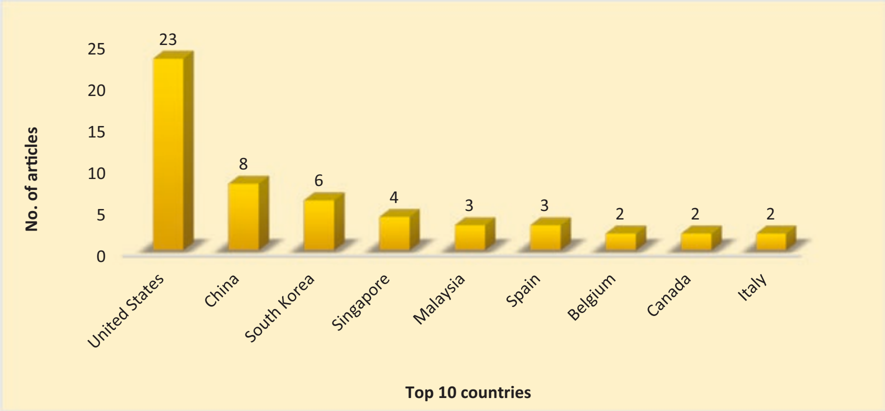


Fig. 24.2 Top 1 per cent highly cited publishing countries

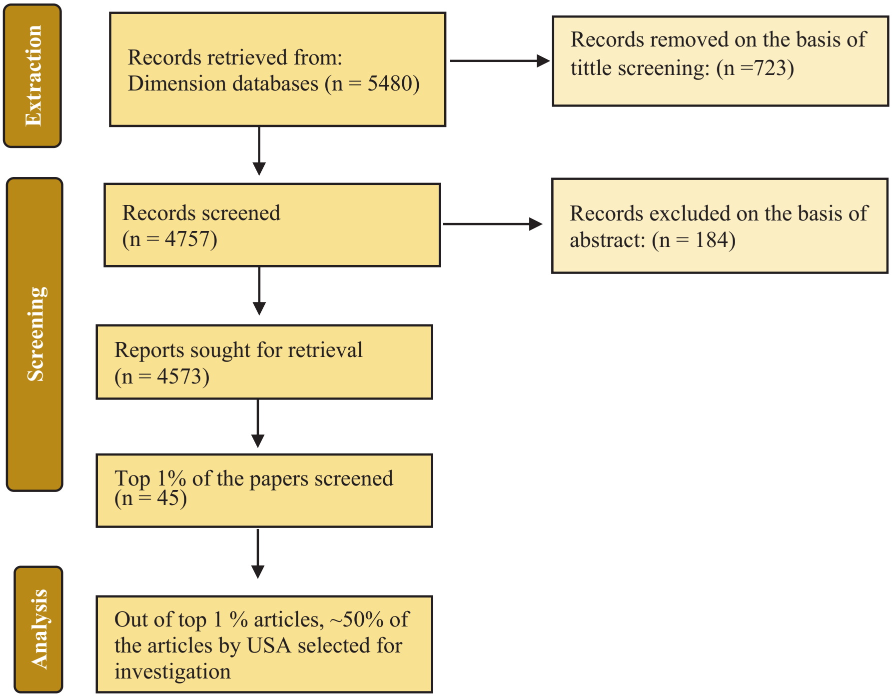


Fig. 24.3 Overview of the methodology followed to screen the articles

VoS viewer visualization tool (Van Eck and Waltman 2010) further analysed the social and conceptual relationship by creating the science map. Analysis was done using organization and authors, citations, bibliographical coupling, and co-authorship as units of analysis. PRISM Flowchart (Page et al. 2021) regarding the methodology is mentioned Fig. 24.3

In Figs. 24.1 and 24.2, the graphs are visualized by network map using full and the fractional counting method. Bibliographical coupling link occurs when two or more documents cite the same/similar research works in their research publication.

In the full counting method, the credit is equally divided among each co-author which results in failure in normalization of the bibliographic coupling among the authors. All the co-authored publications will receive equal citation credit. In such a situation, more co-authors-based research publications will have more bibliographic coupling links which result in providing an advantage to many co-authored publications over the less co-authored publication. The top highly cited paper authored by D. Cohen-Tanugi and JC Grossman (Cohen-Tanugi and Grossman 2012), although had received maximum citations but did not have high bibliographic coupling link strength due to having only two authors, on the other side publication 7 in the list has strong bibliographic linkage due to six co-authors. Therefore, the fractional Counting method is more appropriate to find out a clear picture of the bibliographic coupling strength of individual research outputs.

In fractional counting, all the authors of an article receive fractionated co-publication. The authors of an article receive fractionated co-publication when fractional counting is used. By calculating the number of bibliographic links an author has based on his or her citation quantity, we can calculate their true bibliographic coupling strength. Elimelech Menachem has the highest impact factor due to his multiple articles in the data followed by Cohen-tanaugi. Fractional counting also allows recognition of co-authors like MC Boyce, Nancy G Love, Galit Tal, and Adnan Ali, most of which are overlooked in the full counting method (Matin et al. 2011; Smith et al. 2012; Shi et al. 2014; Rasool et al. 2016).

Besides this, bubble size as well as the distance between the bubbles is also important which is proportional to its relatedness. For example, Elimelech Menachem has contributed to 5 out of 23 (Mi and Elimelech 2010; Phillip et al. 2010; Tiraferri et al. 2011;Shaffer et al. 2013; Werber et al. 2016), and as the core theme of all the papers is related to water desalination by membrane technology (forward osmosis, carbon nanotubes), it is obvious that many of these articles have cited each other. As a result, Elimelech Menachem has high linkage strength with his colleagues as compared to other authors, and thus a higher impact factor, evident by relatively similar size of its bubble in both fractional and full counting methods.

Nancy G Love (Perspectives on anaerobic membrane bioreactor treatment of domestic wastewater: A critical review), Wonjae Choi (Hygro-responsive membranes for effective oil-water separation), and Adnan Ali and Vijay K Thakur (Recent advances in cellulose and chitosan-based membranes for water purification: A concise review) have written articles with different research orientation as compared to the rest of the articles which are based on the use of graphene, carbon nanotubes and nanotechnology for water desalination.

A comprehensive Table 24.1 lists all the top 1 percent articles of the USA and details about the international and inter-organizational collaboration of the USA with its partners. Table 24.1 indicates the impact of research papers on the citation indicator. In addition to the citation metrics, Dimension offers other indicator metrics like Altmetrics Attention Score Rank, which indicates the weighted count of all of the online attention. Altmetrics have been found for individual research output. This includes mentions in public policy documents and references in Wikipedia, mainstream news, social networks, blogs, and more. The inclusion of Altmetrics provides a clear picture of research impact of individual research outputs. It is evident in Table 24.1 that there is a change in the order of the ranking of research papers based on both metrics (citation received by the paper and Altmetrics Attention score rank).

Figure 24.4 shows the significant presence of USA along with the other partner nations. Table 24.1 has shown that the top 1% cited studies in the USA are focused on processes like desalinization, RO, and FO, in which the development of advanced membranes based on nanotechnology are prime by using CNTs, TFN, Graphene Oxide (GO) enhanced Polyamide(PA) and other nanomaterials. Along with this, the problems associated with water filtration like fouling and cleaning of membranes are also getting the focus of most researchers.

24.3 Result and Discussion

The first-generation cellulose-acetate-based membranes were superseded by porous membranes like ultrafiltration (UF), RO, and FO technology and received commercial success. “Phase Inversion Technique”, which is the extraction of the liquid solvent from the polymer solution leaving a thin porous solid membrane is used to form a porous membrane. In RO technology, the water is forced against the osmotic pressure through the membrane with the help of hydraulic pressure, while in FO, the natural osmotic pressure is taken advantage of to induce water flow through the membrane by running a highly saline draw solution on the other side of the membrane. It also has the benefit of low capital over RO as it does not require external pressure and is also relatively prone to less fouling. FO has also been reported to be used in RO pre-treatment by Subramani and Jacangelo (2015) to prevent excess energy usage in desalinating water. In the experiment, seawater is used as a draw solution, and for feed solution, any solution of lower osmotic pressure than the draw solution is used, which results in seawater and favourable for further treatment in RO. Usually, in FO, due to reverse salt flux, the salt concentration of feed solution is increased over time, and osmotic pressure, and water flux is reduced. Phillip et al. (2010), a model was developed to reduce the loss of draw solute into the feed water, and in conclusion, a need for a highly selective layer for high water flux was highlighted. Thin-Film Composite (TFC) polyamide membranes are extensively used as filters for Nanofiltration (NF), RO and FO, and polymer *m*-phenylenediamine (MPD) for RO, FO, and NF, and piperazine (PIP) for NF. These membranes include a non-porous, highly crosslinked selective layer and an underlying porous support layer (usually polysulfone) with a high range for pH concurrence (pH ~2–11) making their use ubiquitous in desalination applications. However, Werber et al. (2016) have also mentioned that the MPD-based TFC membrane used in above mentioned

Table 24.1 Comparison of citation rate and Altmetrics Attention Score Rank of highly cited 1% publication and Collaborations of USA: inter-organization and international

S no.	Tittle	Author	Author's Affiliation	Citation	Altmetric Attention Score rank	International Collaboration	References
1	Water desalination across nanoporous graphene.	Cohen-Tanugi, David; Grossman JC*	Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States	1173	2		Cohen-Tanugi and Grossman (2012)
2	Materials for next-generation desalination and water purification membranes	Werber, Jay R; Osuji, C.; Elimelech, M*	Department of Chemical and Environmental Engineering, Yale University, New Haven, Connecticut 06520–8286, USA; Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States	910	5		Werber et al. (2016)
3	Hygro-responsive membranes for effective oil–water separation	Kota, Arun K;Gibum Kwon; Wonjae Choi;Joseph M. Mabry;Anish Tuteja*	Department of Materials Science and Engineering, University of Michigan, Ann Arbor, Michigan 48109, USA; Department of Mechanical Engineering, University of Texas, Dallas, Richardson, Texas 75080, USA; Rocket Propulsion Division, Air Force Research Laboratory, Edwards Air Force Base, California 93524, USA; Macromolecular Science and Engineering, University of Michigan, Ann Arbor, Michigan 48109, USA.	748	3		Kota et al. (2012)
4	Water purification by membranes: The role of polymer science	Geoffrey M. Geise; Hae-Seung Lee;Daniel J. Miller; Benny D. Freeman, James E. McGrath, Donald R. Paul*	Department of Chemical Engineering, The University of Texas at Austin, Austin, Texas; Department of Chemistry, Macromolecules and Interfaces Institute, Virginia Tech, Blacksburg, Virginia	576	10		Geise et al. (2010)

(continued)

Table 24.1 (continued)

S no.	Tittle	Author	Author's Affiliation	Citation	Altmetric Attention Score rank	International Collaboration	References
5	Reverse draw solute permeation in forward osmosis: modeling and experiments.	Phillip, William A; Yong JS; Elimelech M*	Department of Chemical Engineering, Environmental Engineering Program, P.O. Box 208286, Yale University, New Haven, Connecticut 06520-8286	438	15		Phillip et al. (2010)
6	Advances in Membrane Distillation for Water Desalination and Purification Applications	Camacho, Lucy Mar;Dumée L;Zhang J;Jun-de Li;Duke M; Juan Gomez; Stephen Gray*	Center for Inland Desalination Systems, University of Texas at El Paso, 500 West University Avenue, El Paso, TX 79968, USA; Institute for Frontier Materials, Deakin University, Waurn Ponds Campus, Victoria 3216, Australia; Institute for Sustainability and Innovation, Victoria University, P.O. Box 14428, Melbourne, Victoria 8001, Australia; School of Engineering and Science, Victoria University, P.O. Box 14428, Melbourne, Victoria 8001, Australia; Texas Sustainable Energy Research Institute, University of Texas at San Antonio, 1 UTSA Circle, San Antonio, TX 78249, USA	437	6	Australia	Camacho et al. (2013)
7	Desalination and reuse of high-salinity shale gas produced water: drivers, technologies, and future directions.	Shaffer, Devin L; Arias Chavez LH;Ben-Sasson M; Romero-Vargas Castrillón S; Yip NY; Elimelech M*	Department of Chemical and Environmental Engineering, Yale University, P.O. Box 208286, New Haven, Connecticut 06520-8286, United State	417	4		Shaffer et al. (2013)

8	Nanoporous membranes derived from block copolymers: from drug delivery to water filtration.	Jackson, Elizabeth A; Hillmyer MA*	Department of Chemistry, 207 Pleasant Street SE, Minneapolis, Minnesota 55455-0431	411	8		Jackson and Hillmyer (2010)
9	Emerging desalination technologies for water treatment: A critical review	Subramani, Arun*; Jacangelo JG.	MWH, 300 North Lake Avenue, Suite 400, Pasadena, CA 91101, USA The Johns Hopkins University Bloomberg School of Public Health, Baltimore, MD 21205, USA	397	12		Subramani and Jacangelo (2015)
10	Biofouling in reverse osmosis membranes for seawater desalination: Phenomena and prevention	Matin Asif *; Khan Z; Zaidi S.M.J.; M.C. Boyce	King Fahd University of Petroleum & Minerals, Dhahran, Saudi Arabia b Massachusetts Institute of Technology, Cambridge MA 02139, USA	363	13	Saudi Arabia	Matin et al. (2011)
11	Fouling and cleaning of ultrafiltration membranes: A review	Shi, Xiafu; Tal G; Hankins N P*; Gitis V	Centre for Sustainable Water Engineering, Department of Engineering Science, University of Oxford, Parks Road, Oxford OX1 3PJ, UK; Unit of Environmental Engineering, The Faculty of Engineering Science, Ben-Gurion University of the Negev, PO Box 653, Beer-Sheva 84105, Israel	333	17	Israel, UK	Shi et al. (2014)

(continued)

Table 24.1 (continued)

S no.	Tittle	Author	Author's Affiliation	Citation	Altmetric Attention Score rank	International Collaboration	References
12	Electrospun Nanofibers: New Concepts, Materials, and Applications.	Xue, Jiajia; Xie J;Liu W; Xia Y*	The Wallace H. Coulter Department of Biomedical Engineering, Georgia Institute of Technology and Emory University, Atlanta, Georgia 30332, United States; Department of Surgery-Transplant, Mary and Dick Holland Regenerative Medicine Program, University of Nebraska Medical Center, Omaha, Nebraska 68198, United States ; School of Chemical and Biomolecular Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332, United States ; School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia 30332, United States	332	21		Xue et al. (2017)
13	Cellulose nanomaterials in water treatment technologies.	Carpenter Alexis Wells;deLannoy C F; Wiesner MR*.	Department of Civil and Environmental Engineering, Duke University, Durham, North Carolina 27708, United States; Center for the Environmental Implications of NanoTechnology, Duke University, Durham, North Carolina 27708, United States	322	9		Carpenter et al. (2015)
14	Antibacterial Activity of Ti_3C_2TxMXene.	Kashif Rasool, Mohamed Helal, Adnan Ali, Chang E. Ren, Yury Gogotsi, Khaled A. Mahmoud*	Qatar Environment and Energy Research Institute (QEERI), Hamad Bin Khalifa University (HBKU), P.O. Box 5825, Doha, Qatar; Department of Materials Science and Engineering and A.J. Drexel Nanomaterials Institute, Drexel University, Philadelphia, Pennsylvania 19104, United States	304	11	Qatar	Rasool et al. (2016)

15	Water desalination with a single-layer MoS2 nanopore	Heiranian Mohammad; FarimaniAB; Aluru NR*	Department of Mechanical Science and Engineering, Beckman Institute for Advanced Science and Technology; University of Illinois at Urbana-Champaign, Urbana, Illinois 61801, USA.	297	1		Heiranian et al. (2015)
16	Membrane materials for water purification: design, development, and application	Lee, Anna; Elam Jeffrey W; Darling, Seth B	Center for nanoscale Materials, Argonne National Laboratory,9700 South Cass Avenue,Lemont, Illinois 60439,USA; Energy System Division, Argonne National Laboratory,9700 South Cass Avenue, Lemont, Illinois 60439, USA; Inastitute for Molecular Engineering, University of Chicago, 5801 South Ellis Avenue, Chicago, Illinois 60637, USA.	284	19		Lee et al. (2016)
17	Perspectives on anaerobic membrane bioreactor treatment of domestic wastewater: A critical review	Smith, Adam L; Stadler LB; Love NG; SkerlosSJ; Raskin L*	Department of Civil and Environmental Engineering, University of Michigan, 2350 Hayward Road, Ann Arbor, MI 48109, USA; Department of Mechanical Engineering, University of Michigan, 2350 Hayward Road, Ann Arbor, MI 48109, USA	280	16		Smith et al. (2012)

(continued)

Table 24.1 (continued)

S no.	Tittle	Author	Author's Affiliation	Citation	Altmetric Attention Score rank	International Collaboration	References
18	Surface Modification of Water Purification Membranes	Miller, Daniel J; Daniel R. Dreyer;C. Bielawski; D. Paul; B. Freeman	McKetta Department of Chemical Engineering and Texas Materials Institute, Center for Energy and Environmental Resources, The University of Texas at Austin, 10100 Burnet Road, Building 133, Austin, TX, 78758 USA; Nalco Champion, 3200 Southwest Freeway, Ste. 2700, Houston, TX, 77027 USA; Center for Multidimensional Carbon Materials (CMCM), Institute for Basic Science (IBS), Ulsan National Institute of Science and Technology (UNIST), Ulsan, 44919 Republic of Korea; McKetta Department of Chemical Engineering and Texas Materials Institute, Center for Energy and Environmental Resources, The University of Texas at Austin, 10100 Burnet Road, Building 133, Austin, TX, 78758 USA; McKetta Department of Chemical Engineering and Texas Materials Institute, Center for Energy and Environmental Resources, The University of Texas at Austin, 10100 Burnet Road, Building 133, Austin, TX, 78758 USA	279	7	South Korea	Miller et al. (2017)
19	Graphene oxide (GO) enhanced polyamide (PA) thin-film nanocomposite (TFN) membrane for water purification	Yin, Jun; Guocheng Zhu; Baolin Deng*	Department of Civil & Environmental Engineering, University of Missouri, Columbia, MO 65211, USA; College of Civil Engineering, Hunan University of Science & Technology, Xiangtan, Hunan 411201, China; Department of Chemical Engineering, University of Missouri, Columbia, MO 65211, USA	278	18	China	Yin et al. (2016)

20	Fabrication of a novel thin-film nanocomposite (TFN) membrane containing MCM-41 silica nanoparticles (NPs) for water purification	Yin, Jun;Eun-SikKim; JohnYang; BaolinDeng*	Department of Civil&Environmental Engineering, University of Missouri, Columbia, MO65211, USA; Department of Agriculture and Environmental Sciences, Lincoln University, Jeffersoncity, MO65101, USA c Department of Chemical Engineering, University of Missouri, Columbia, MO65211, USA	274	23		Yin et al. (2012)
21	Covalent binding of single-walled carbon nanotubes to polyamide membranes for antimicrobial surface properties.	Tiraferri, Alberto;Chad D. Vecitis;Menachem Elimelech*	Department of Chemical and Environmental Engineering, Yale University, P.O. Box 208286, New Haven, Connecticut 06520-8286, United States ‡School of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts 02138, United States	258	14		Tiraferri et al. (2011)
22	Recent advances in cellulose and chitosan-based membranes for water purification: A concise review	Thakur, Vijay Kumar; Voicu S I	School of Mechanical and Materials Engineering, Washington State University, Pullman, WA, United States; Faculty of Applied Chemistry and Materials Sciences, University Politehnica from Bucharest, 7 Bucharest 011061, Romania	248	20	Romania	Thakur and Voicu (2016)
23	Gypsum scaling and cleaning in forward osmosis: measurements and mechanisms.	Mi, Baoxia*; M. Eimelech	Department of Civil and Environmental Engineering, The George Washington University, 641 Academic Center, 801 22nd Street, NW, Washington, D.C. 20052; Department of Chemical Engineering, Environmental Engineering Program, P.O. Box 208286, Yale University, New *Haven, Connecticut 06520-8286*	242	22		Mi and Elimelech (2010)

*Corresponding author

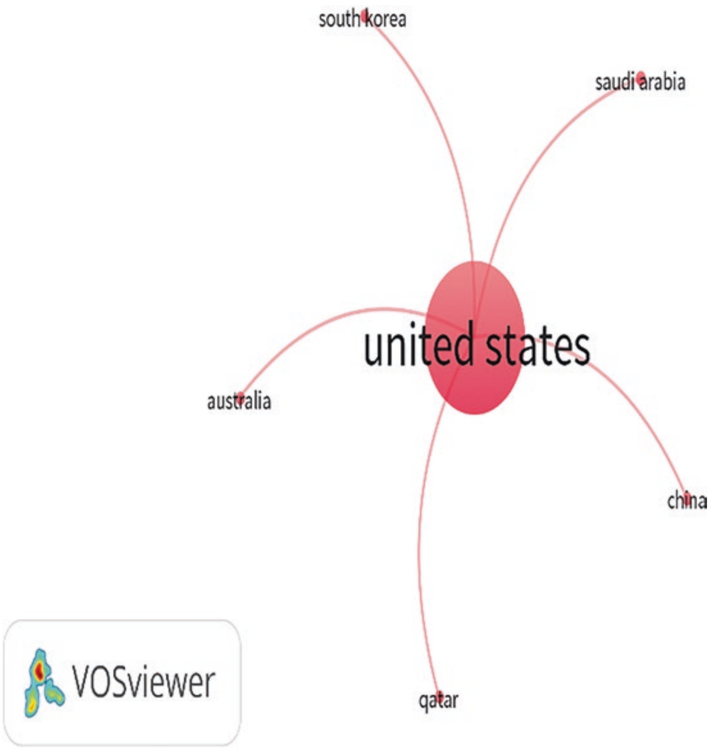


Fig. 24.4 Co-authors between organizations and countries

techniques is prone to membrane fouling as the increased surface area and roughness results in greater foulant–membrane interaction which provides a more significant opportunity for attachment.

Over the years, many efforts have been made to manufacture membrane polymers with the appropriate permeability, selectivity, and thickness qualities. Xue et al. (2017) have proposed the fabrication of nanofibers with desired materials for water purification by electrospinning. The excerpts nanofibers from viscoelastic polymer fluid by using a strong electric field. They have demonstrated porous nanofibres construction by using the method of Polymer-Solvent Phase Separation (rapid cooling by cryogenic liquid before complete curing) and extraction of the polymer formed by the calcination process. It can also be combined with the sol-gel technique to form ceramic and composite nanofibers.

There have also been innovations in designing special water channels that would influence the membrane's water movement. A model of such a water channel has been introduced as Aquaporins. Aquaporins or AQPs, membrane proteins, is a unique water channel found in almost all living organelles. The hourglass shape of the aquaporin allows for faster water permeability and is found to be much more permeable than the existing commercial RO membranes. Incorporation of the functional water channel protein aquaporin Z (AqpZ) into hydrophobic polydimethylsiloxane (PDMS) has been shown by Subramani and Jacangelo (2015) to have a comparatively higher rate of water transport than other commercialized membranes. They offer high permeability than RO membranes and are osmotically driven, rejecting 100% of the solute molecules; however, the knowledge is limited regarding its structural durability and chemical resistance and the production and purification of aquaporin in large quantities. Werber et al. (2016) found that water permeability of the aquaporin-infused membrane rivals that of the TFC membrane, but the instability of the protein AqpZ above storage temp 4 °C after a few months is an added concern.

Controlled polymerization (like electrospinning provides access to a limitless variety of architectural block polymers (Jackson and Hillmyer 2010). Block polymers are hybrid polymers that combine the physical attributes of different elements with ordered structures. High flux membrane is formed by integrating composite membranes with porous support layers and selective block copolymer on top of it. Werber et al. (2016) has highlighted the amalgamation of a self-assembling block copolymer with kinetically limited Phase inversion technique using SNIPS (Self-Assembly with Non-Solvent-Induced Phase Separation) method. It is used to form vertically oriented pores in a thin selective layer at the membrane surface with an integrally formed microporous underlying support layer for a broader pore size distribution. It has recently been used to fabricate a bi-continuous cubic phase with 4-nm pore size. Polymer nanocomposite membranes have been enriched by the incorporation of nanoparticles in the selected polymer. These nanoparticles like silver, titanium, carbon nanotubes, graphene oxide, zeolite, and silicon can alter the membrane's surface properties and influence its flux, permeability, selectivity, and membrane fouling. Subramani and Jacangelo (2015) has discussed conjugation of TFN (Thin-Film Nanocomposite) membrane, with Linde Type A Zeolite (an alumina silicate zeolite that exhibits a three-dimensional pore structure have perpendicular orientation) to increase water transportation. It was also reported that the specific energy consumption for the TFN membranes was 2.24–2.55 kWh/m^2 for fluxes of 11.9–15.3 L m^{-2} h^{-1} and system recovery of 40–55%. Yin et al. (2012) reported an experiment where they included porous MCM-41 Silica having different pore sizes and spherical silica nanoparticles in TFN to study the performance of the membrane. Results indicate that the MCM-41 TFN membrane is optimal as it showed a flux increase of 63.5%. It signifies the role of the hydrophilic porous structure of MCM-41 NPs in allowing a shorter distance for the water molecules to pass through during its permeation. Yin et al. (2016), studied that with Graphene oxide (GO) embedded nanosheets dispersed in TMC hexane, by in-situ interfacial polymerization (IP), in the polyamide thin film (thickness ranging 200–300 nm), under the pressure of 300 psi, the water permeability was 0.198 L/m2hpsi with NaCl rejection of ~93.8%. better permeability compared to nanoparticles consolidated in TFN, GO-TFN was noticed to be relatively better. Lee et al. (2016) indicate, that GO-infused PSU polymers were reported to display enhanced hydrophilicity, water flux, and salt rejection. GO nanosheets polymerized with polydopamine-modified PES membrane had demonstrated higher flux (80 and 276 Lmh/MPa) than that of most commercial nanofiltration membranes. Even though GO-membranes are still in the development stage, they have been found to exhibit a relatively high flux range (80–276 Lmh/MPa) compared to commercially available NF membranes by Rasool et al. (2016). Ti3C2Tx (MXene), 2D carbides, were suggested to be an appropriate alternative to GO in terms of antibacterial properties. The concentration-reliant antibacterial properties were investigated which showed a loss of more than 98% bacterial cell viability at 100 μg/mL concentration of Ti3C2Tx within 4 h of exposure. This emerging compound could pave a path for biofouling preventive (Fig. 24.5).

Like Aquaporin, Carbon NanoTubes (CNTs) also have massive potential as nanochannels in desalination. Subramani and Jacangelo (2015) have reported that the nanotubes can also be made cation/anion-selective by changing their radius. At 4.14 Å, they became cation-selective, and at 5.52 Å, they became anion-selective. Werber et al. (2016), CNTs were found to reject a colloidal gold of 2 nm diameter suggesting the limit of their selectivity. As they do not require hydraulic pressure, CNTs can be a cost-effective alternative but a large surface area membrane to incorporate the highly packaged CNTs is still challenging. Tiraferri et al. (2011), found that single-walled carbon nanotubes (SWNT) imparted anti-bacterial properties when covalently bound to the TFC membranes. The percent loss of *E. coli* viability for the purified and ozonized Single-Walled Carbon Nano Tubes was >95% and significantly higher than that of the purified-only carbon nanotubes (~80%).

Apart from the pore size, when the thickness of the membrane increases, the flux rate decreases, and for this purpose, graphene, a honey-combed structure, ultra-thin membrane with high mechanical strength, is found to be an idyllic membrane for desalination. Cohen-Tanugi and Grossman et al. (2012) reported that the nanopores in single-layered graphene can percolate NaCl salt and filter water at rates 10–100 L/cm^2/day/MPa, which is much more efficient than diffusive RO membranes.

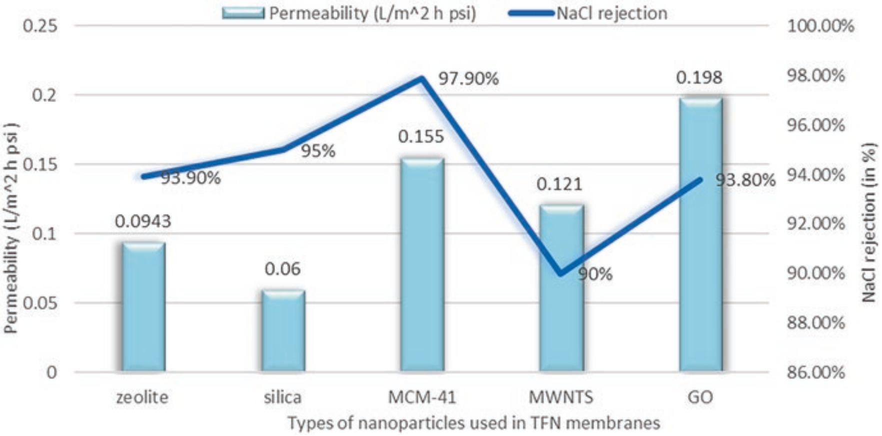


Fig. 24.5 Performance of TFN with different nanoparticles

They further investigated graphene membrane of pore size varied (1.5–62 Å) with the addition of hydrophilic/hydrophobic groups (chemical functionalization) to its boundaries and enhancement of water permeability was observed compared to pore size (~25 Å^2), It was due to hydroxylation as the hydrophilic functional groups increase the water flux. In contrast, hydrogenated pores have better at salt rejection. The salinity of the water was kept at 72 g/L, higher than seawater (~35 g/L) and under pressure ranging from 100 to 200 MPa for more precise results due to ion-pore interaction. The data estimated from the experiment observed that salt ions could pervade the membrane if the diameter is more than 5.5 Å (~47.52 Å^2). Werber et al. (2016) also have similar findings that hydroxylated pores with a size of ~0.45 nm diameter can altogether reject salt and are approximately ~1000 times more water permeable than current TFC-RO membranes.

Graphene membranes are mechanical permanence under pressure and pore dispersal; however, salt rejection is sensitive and still at a bench scale and has not been pertinent at a large scale. Heiranian et al. (2015) have revealed a single Molybdenum disulfide (MoS2) layer with nanopores as a superior substitute to graphene in membranes by allowing 70% more water permeability and requiring very low pressure to achieve desired water flux. The two constituting atoms, molybdenum (Mo) and sulfur (S), provide suppleness to design the edge of the pore and the absence of carbon(like in graphene) makes it resistant to fouling by Chemical Vapor Deposition(CVD). The nanopores of area 20–60 Å^2 are capable of obstructing the ions other than water molecules. In an experiment, the performance in desalinating water of MoS2 atoms, individually (Mo only, and S only) and mixed along with the graphene pore with approximately equivalent pore area were compared as the ion / salt rejection depended only upon the pore size, not the pore type. The pore lines with only Mo atom due to its hydrophilic nature attracted water molecules to the inside and allowed for maximum water permeation. It is followed by the mixed, S atom only and the graphene pore.

The thermal-based technology for desalination is based on phase transition using energy to separate the water from its impurities. Recently the focus has been on combining the thermal phase change with membranes, giving rise to technologies like membrane distillation and pervaporation.

In Membrane Distillation (MD) combination of evaporation processing and membrane technology takes place. The polymers ideal for such filtration have a pore size in the range 0.2–1.0 µm and thickness from 0.04 to 0.25 mm. Polymers like polytetrafluoroethylene (PTFE), polypropylene (PP), and poly vinylidene fluoride (PVDF) are appropriate for membrane distillation. The modified Hollow Fibre membrane offers high surface area but low flux) and Flat Sheet membrane has higher flux as compared to the Hollow Membrane and is made up of a thin active layer and a porous support layer (Camacho et al. 2013). Although it consumes low energy overall (~10.3 kWh/m^3) and promises to reject salt ions by 100% till now, only pilot plant research has been performed. Pervaporation offers a rejection of salt by 100% while consuming very low energy. The water concoction is separated based on preferential removal because of attraction between similar molecules and rapid diffusion through the membrane. Materials like polyvinyl alcohol (PVA) polymer are ideal for Pervaporation because of their extreme hydrophilic nature (due to hydroxyl-rich groups) and film-forming tendency. The issue of low water flux can be overcome by the addition of silica nanoparticles to increase water diffusion and flux rate (Subramani and Jacangelo 2015).

Shaffer et al. (2013) have emphasized about the case study of irresponsible discharge of Marcellus Shale produced water (with total dissolved solids (TDS) range between ~8000 and 360,000 mg/L), into the Monongahela River raising its TDS by 40,000 mg/L, above the safe water quality standard (500 mg/L). It is of utmost insistence to treat such contaminated water. Till now the most successful technologies to treat high salinity brines on a pilot scale are Mechanical Vapor Compression method (most developed), FO, and MD. However, the functioning and maintenance cost of industrial plants with such technology are very high, indicating the need for a better eco-friendly and cost-effective alternative shortly.

The downside of polymeric membranes is their inherent hydrophobicity causes high fouling tendency and has an adverse impact on durability as well as overall operation cost. The water often gets entombed beneath oil and against the membrane, preventing oil permeation, and hence membrane gets fouled by oil during demulsification. Kota et al. (2012) have demonstrated for the first time a continuous, purely gravity-driven capillary force-based separation (CFS), which offers efficient segregation of the surfactant-stabilized emulsions. The apparatus uses both super hydrophilic and oleophobic meshes and parallelly runs two CFS operations with a separation efficiency of 99.9% in saline and non-saline emulsions. This economic and ecologically friendly innovation has potential applications in wastewater treatment plants, and mass oil spill purification.

Fouling is exacerbated by the build-up of organic macromolecules, inorganic particles, and microorganisms on the membrane surface and causes reduced flux. Shi et al. (2014) investigated the possible treason to fouling in UF due to adsorption (due to specific interactions between solutes/particles and the membrane), pore blocking, and cake or gel formation. In the absence of a permeation flux, a monolayer of solutes is formed on the surface of a membrane almost instantaneously. Domestic Waste Water DWW treatment by AnMBRs (Anaerobic Membrane Reactors) was found effective in averting long-term membrane fouling; Smith et al. (2012) used a method without sulphate-rich chemicals in AnMBRs. Other fouling treatment methods include conventional physical (hydraulic flushing/rinsing, backwash), chemical (acids, oxidants, surfactants, enzymes), or combined methods (chemically enhanced backwashing, CEB), as well as unconventional methods such as ultrasonic and electric cleaning.

However, excess exposure of the polymeric membrane to such methods usually leads to their early disintegration ultimately. Mi and Elimelech (2010) in the FO (occurence10% higher than in RO) and RO membranes found >96% recovery in water flux with no additional chemical requirement using cellulose acetate (CA) membrane and gypsum particle probe making it a promising solution for reversible gypsum scaling. This long-term exposure to membranes causes wear and tear and increases the capital in manufacture; purchasing such membranes repeatedly leads to more waste harmful to the environment. Biofouling is prompted by the unwanted growth biofilm (an assemblage of self-sufficient microbial cells that forms immutable association with the surface of polymeric substances which cannot be eliminated by gentle rinsing) in the membrane surface over time, which compels higher operating pressure, more regular chemical cleaning leading to a shorter membrane life. Even though pre-treatment can significantly reduce crystalline, organic, and particulate fouling, it is not sufficient to completely treat biofouling, persistent pathogens can still thrive and relocate despite almost all of their population being disintegrated by pretreatment. Matin et al. (2011) mentioned a survey in an earlier study across 70 US reverse osmosis membrane installations, having consistent problems with membrane biofouling, leading to a decreased flux rate and an increase in energy consumption. Although the molecular basis of flux decline is not well understood, they have assumed it to be due to water transport impedance (hydraulic resistance) caused by the biofilm rather than to some modification of the inherent transport characteristics of the separation polymer. They have also identified the Biofilm Enhanced Osmotic Pressure (BEOP) originating from the bacterial cell component of the biofilm as the leading cause of the increase in the salt passage (fouled with dead cells showed a reduction of about 5–6%). The decrease in salt rejection may be biodegradation or biodeterioration of the RO membrane.

Membrane surface roughness increases fouling due to the accumulation of foulants in gorges that prevent them from being trapped between cross-current shear forces. Multivalent ions (like Ca2+) in the feed solution can cross-link with the charged foulants by electrostatic force, Membrane properties like surface plasmon resonance (used to measure the adsorption of the self-assembled foulants), surface wettability (manipulated using various functional groups) are some of the future aspects of membrane research to reduce fouling. In a study, Miller et al. (2017) discovered that hydrophilic functional groups offered ideal resistance against the adhesion of detergents, bacteria, and other small macromolecules to the membrane surface. They have also reviewed the role of polydopamine as a coating on the membrane as it makes the surfaces hydrophilic, without changing its surface geometry. Significant conversions of surface hydrophilicity have been reported in earlier studies on using polydopamine on hydrophobic surfaces such as PVDF (polyvinylidene fluoride), PTFE (polytetrafluoroethylene), PET (polyethylene terephthalate), and polyimide in making the surface strength extremely high and more sustainable and resistant to mechanical, chemical, and electrochemical degradation They can only be removed by using strong alkaline or oxidizing solutions, showing good corrosion resistance.

An ecological alternative of bioremediation for such synthetic polymeric membranes Cellulose and Chitin based membrane. Carpenter et al. (2015) showed that cellulose nanomaterial (CN) exhibits a large potential for a water purification membrane due to its unique characteristics like inherent fibrous structure, physical properties low production cost, biocompatibility, and ecologically sound source. They have also compared CN with CNT (Table 24.2) based on their properties, and it is

Table 24.2 Comparison of properties between CNs and CNTs (Carpenter et al. 2015)

Properties	CNs	CNTs (single-walled)
Diameter	5–70 nm	0.4–2 nm
Young's modulus	50–143 GPa	0.32–1.47 TPa
Optical activity	Transparent/iridescent films	None
Energy requirement	500–2300 kW h t^{-1}	278,000–250,200,000 kW h t^{-1}
Cost	\$1/g (dry), \$5/g (slurry)	\$80–280/g
Ecotoxicity	Low toxicity, some proinflammatory cytokines	Oxidative stress and inflammation; inhalation and dermal exposure are high risk
Disposal	Biodegradable by organisms with cellulase enzyme	Persistent/non-degradable
Source	Wood, cotton, hemp, flax, wheat straw, algae	Fossil fuels

evident that although CN does not offer many robust membranes, they are low in toxicity and manufacturing cost.

The conjugation of amine groups on CN surfaces allowed them to absorb 98% anionic chromate at 12.5 mg/g concentration, and bacteria-derived CNs successfully absorbed Pb^{2+}, Mn^{2+}, and Cr^{3+}. Another bio-renewable, water- and acetic acid-soluble polymer is chitosan. Thakur and Voicu (2016) have proposed the removal of heavy metals dissolved in the water bodies by manufacturing polyacrylamide-chitosan polymer an successfully removed 43.35 mg/g of Cu^{2+}, 63.67 mg/g of Pb^{2+} and 263.9 mg/g of Hg^{2+} y at pH 5. The TFC membrane coated with a thin composite layer of chitosan/graphene oxide, when exposed to brackish water, showed an increase in the water flux to 61.5 L/m^2h with a salt rejection of 95.6%.

24.4 Conclusion

The USA is currently leading the domain of membrane science in the sector of water purification in the world, according to the resources analysed from Dimension and VoS Viewer. The focus of research in the USA is inclining towards the inclusion of nanotechnology in membranes for a more refined selection of water from various sources. There has been a boost in the pilot scales for different membrane technologies working on block co-polymer, TFC, CNT, and graphene oxide, but more modifications and performance data are required for them to be commercialized efficiently. Environmental problems are also being kept in mind leading to the development of more sustainable membranes made up of natural polymers like chitin and cellulose to replace the conventional synthetic membranes to ease the ecological burden. It is evident from the research analysis that the future is the age of membrane science, not limited to only water purification against pollutants but also against bacteria, viruses, and microplastics as well as air purification.

References

Camacho LM, Dumée L, Zhang J, Li JD, Duke M, Gomez J, Gray S (2013) Advances in membrane distillation for water desalination and purification applications. Water 5(1):94–196

Carpenter AW, de Lannoy CF, Wiesner MR (2015) Cellulose nanomaterials in water treatment technologies. Environ Sci Technol 49(9):5277–5287

Cohen-Tanugi D, Grossman JC (2012) Water desalination across nanoporous graphene. Nano Lett 12(7):3602–3608

Geise GM, Lee HS, Miller DJ, Freeman BD, McGrath JE, Paul DR (2010) Water purification by membranes: the role of polymer science. J Polym Sci B Polym Phys 48(15):1685–1718

Heiranian M, Farimani AB, Aluru NR (2015) Water desalination with a single-layer MoS2 nanopore. Nat Commun 6(1):1–6

Jackson EA, Hillmyer MA (2010) Nanoporous membranes derived from block copolymers: from drug delivery to water filtration. ACS Nano 4(7):3548–3553

Kota AK, Kwon G, Choi W, Mabry JM, Tuteja A (2012) Hygro-responsive membranes for effective oil–water separation. Nat Commun 3(1):1–8

Lee A, Elam JW, Darling SB (2016) Membrane materials for water purification: design, development, and application. Environ Sci Water Res Technol 2(1):17–42

Matin A, Khan Z, Zaidi SM, Boyce MC (2011) Biofouling in reverse osmosis membranes for seawater desalination: phenomena and prevention. Desalination 281:1–6

Mi B, Elimelech M (2010) Gypsum scaling and cleaning in forward osmosis: measurements and mechanisms. Environ Sci Technol 44(6):2022–2028

Miller DJ, Dreyer DR, Bielawski CW, Paul DR, Freeman BD (2017) Surface modification of water purification membranes. Angew Chem Int Ed 56(17):4662–4711

Page MJ, McKenzie JE, Bossuyt PM, Boutron I, Hoffmann TC, Mulrow CD, Shamseer L, Tetzlaff JM, Akl EA, Brennan SE, Chou R (2021) The PRISMA 2020 statement: an updated guideline for reporting systematic reviews. Int J Surg 88:105906

Phillip WA, Yong JS, Elimelech M (2010) Reverse draw solute permeation in forward osmosis: modeling and experiments. Environ Sci Technol 44(13):5170–5176

Rasool K, Helal M, Ali A, Ren CE, Gogotsi Y, Mahmoud KA (2016) Antibacterial activity of Ti_3C_2T x MXene. ACS Nano 10(3):3674–3684

Shaffer DL, Arias Chavez LH, Ben-Sasson M, Romero-Vargas Castrillón S, Yip NY, Elimelech M (2013) Desalination and reuse of high-salinity shale gas produced water: drivers, technologies, and future directions. Environ Sci Technol 47(17):9569–9583

Shi X, Tal G, Hankins NP, Gitis V (2014) Fouling and cleaning of ultrafiltration membranes: a review. J Water Process Eng 1:121–138

Smith AL, Stadler LB, Love NG, Skerlos SJ, Raskin L (2012) Perspectives on anaerobic membrane bioreactor treatment of domestic wastewater: a critical review. Bioresour Technol 122:149–159

Subramani A, Jacangelo JG (2015) Emerging desalination technologies for water treatment: a critical review. Water Res 75:164–187

Thakur VK, Voicu SI (2016) Recent advances in cellulose and chitosan based membranes for water purification: a concise review. Carbohydr Polym 146:148–165

Tiraferri A, Vecitis CD, Elimelech M (2011) Covalent binding of single-walled carbon nanotubes to polyamide membranes for antimicrobial surface properties. ACS Appl Mater Interfaces 3(8):2869–2877

Van Eck NJ, Waltman L (2010) VOSViewer: visualizing scientific landscapes [software]. Version 1:15

Werber JR, Osuji CO, Elimelech M (2016) Materials for next-generation desalination and water purification membranes. Nat Rev Mater 1(5):1–5

Xue J, Xie J, Liu W, Xia Y (2017) Electrospun nanofibers: new concepts, materials, and applications. Acc Chem Res 50(8):1976–1987

Yin J, Kim ES, Yang J, Deng B (2012) Fabrication of a novel thin-film nanocomposite (TFN) membrane containing MCM-41 silica nanoparticles (NPs) for water purification. J Membr Sci 423:238–246

Yin J, Zhu G, Deng B (2016) Graphene oxide (GO) enhanced polyamide (PA) thin-film nanocomposite (TFN) membrane for water purification. Desalination 379:93–101

Chapter 25
Nanoparticles-Based Management of Cadmium Toxicity in Crop Plants

C. O. Ogunkunle, M. A. Jimoh, E. F. Adegboye, A. B. Rufai, O. A. Olatunji, G. O. Okunlola, and C. O. Adenipekun

Abstract Cadmium is an important soil pollutant and poses serious challenges to crop production due to its significant toxicity to crop plants. However, crop plants possess several homeostatic cellular processes or mechanisms that can regulate or detoxify high Cd concentrations to mitigate their toxicity to cells and tissues. These cellular processes can be enhanced or promoted by the exogenous application of nanoparticles due to their ability to cross cellular barriers because of their specific physical and chemical features. Therefore, this chapter presents an overview of recent advances regarding the use of nanoparticles in the alleviation of Cd toxicity in crop plants. Additionally, the mechanisms of alleviation of Cd toxicity by exogenously-applied nanoparticles were explored to better understand the regulation of Cd toxicity in crop plants in the presence of nanoparticles.

Keywords Nanoparticles · Cadmium toxicity · Crop health · Alleviation · Oxidative stress · Immobilization

---

C. O. Ogunkunle (✉)
Environmental Botany Unit, Department of Plant Biology, P. M. B. 1515, University of Ilorin, Ilorin, Nigeria

Department of Plant Biology, Osun State University, Osogbo, Nigeria
e-mail: ogunkunle.co@unilorin.edu.ng

M. A. Jimoh · A. B. Rufai · O. A. Olatunji · G. O. Okunlola
Department of Plant Biology, Osun State University, Osogbo, Nigeria

E. F. Adegboye
Environmental Botany Unit, Department of Plant Biology, P. M. B. 1515, University of Ilorin, Ilorin, Nigeria

C. O. Adenipekun
Plant Physiology Unit, Department of Botany, University of Ibadan, Ibadan, Nigeria

L. Newman et al. (eds.), *Phytoremediation*, https://doi.org/10.1007/978-3-031-17988-4_25

25.1 Introduction: Cadmium Toxicity to Plants

Cadmium is considered a major non-biodegradable pollutant of great environmental concerns in many regions of the world (Nedelkoska and Doran 2000; Ogunkunle et al. 2020a), and a known threat to crop production and global food security (Irshad et al. 2020; Javaid et al. 2020; Youssef et al. 2021). Cadmium toxicity has been reported to cause overproduction of ROS which in turn leads to damage and destruction to plant cell biomolecules, membranes as well as organelles (Abbas et al. 2017). In addition, abundant reports exist in the literature that excess Cd in soils can greatly alter the transport and uptake of essential minerals like Ca, P, Mg, K and Mn, and render them unavailable for plants' roots (Guo et al. 2007; Kinay 2018; Metwally et al. 2005; Zhang et al. 2019). Cadmium toxicity can lead to decreased photosynthesis and carbon metabolisms which lead to reduced growth and development of crop organs (Fig. 25.1).

In soils polluted with Cd, roots are the primary point of contact and uptake of Cd in crop plants The quantity of Cd absorbed and bioaccumulated in the root tips is usually proportional to the degree of cell damage. Cadmium has been reported to induce chromosomal aberration and disrupt mitosis in root tips (Tran and Popova 2013; Shi et al. 2016). Root length, surface area and root tip number have also been reported to decrease in Cd-stressed crop plants (Lu et al. 2013). In leaves, photosynthetic activity is the first point of attack by Cd toxicity with resultant effects on the levels of chlorophylls a and b. The cadmium-induced decline in chlorophylls and carotenoid concentration, according to Qian et al. (2009) could be explained by Cd toxicity action on enzymes involved in pigment synthesis. The first symptom of Cd toxicity in crop plants is chlorosis of the leaves due to impairment in the biosynthesis pathway of photosynthetic pigments (Carrier et al. 2003). In addition, Cd can strongly interact with Fe leading to enzymatic degradation and uptake reduction of

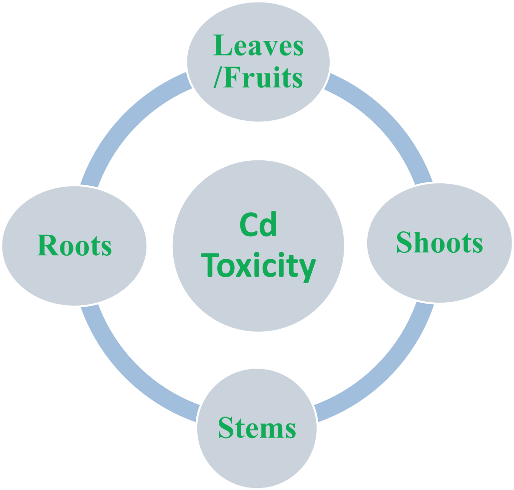


Fig. 25.1 Tissue parts of crop plants affected by cadmium toxicity

Fe in leaves of crop plants (Vassilev et al. 2002). Several reports in the literature have supported the assertion that Cd toxicity decreased levels of chlorophyll pigments in leaves of crop plants (Ben et al. 2009; Delpérée and Lutts 2008; Ekmekci et al. 2008; Fagioni and Zolla 2009; López-Millán et al. 2008; Rizwan et al. 2016a).

25.2 Nanoparticles in Sustainable Agriculture

Agriculture in any economy is one of the primary pillars that provide a sustainable and better life for its populace. Presently, the field of agriculture is faced with a lot of challenges, including climate change, and contamination of water bodies and soils with several harmful environmental pollutants (e.g., heavy metals, oil spills, pesticides, herbicides, and fertilizers). In efforts to combat these challenges, newer agricultural practices, technologies, and strategies are continuously been introduced by experts. Right now, agricultural scientists have realized that smart innovation like nanotechnology is strongly needed for agricultural growth to combat the global challenges of climate change and food security. In light of this, the use of nanoparticles-based products has been recently introduced to improve modern agricultural practices and has been advocated for the enhancement of agricultural productivity (Akanbi-Gada et al. 2019; Ogunkunle et al. 2018; Ogunkunle et al. 2022). Modern agriculture is gradually metamorphosing into precision agriculture through the aid of new-age materials (nanoparticles) to achieve maximum productivity (Mittal et al. 2020).

The adoption of nanoparticles (<100 nm) in remediating contaminated agricultural soils and enhancing crop productivity has gained greater attention in recent times (Ogunkunle et al. 2021). Nanoparticles (NPs) are considered so important in crop production because of the intrinsic properties they possess. The small particle size coupled with the large surface area of NPs bestowed greater binding phases for inorganic contaminants such as heavy metals (HMs) (Wang et al. 2012) and penetrating capacity which enables them to penetrate plant cells and tissues easily, and also promote greater adsorption with an improved target delivery of desirable agronomic substances (Kashyap et al. 2015). Though NPs seem to be a double-edged sword in their uses in crop production, the merits of their applications outweigh the demerits. And the impacts of NPs on crop plants chiefly depend on properties such as the NPs-type, concentration, surface area, particle size, and most importantly the species of crop plants treated with the NPs (Akbari et al. 2011). For instance, Jacob et al. (2013) observed that TiO_2-NPs were able to modify the enzymatic antioxidant defense of kidney beans whereas the same TiO_2-NPs negatively affected the rate of H_2O absorption and transpiration in corn plants. Youssef et al. (2021) also reported that hermatite-NPs at 500 mg/kg were most beneficial and reduced Cd toxicity to maize plants while higher concentrations of the same NPs became toxic.

25.3 Nanoparticles-Induced Alleviation of Cd Toxicity in Crop Plants

The continuous presence of Cd in soil ecosystems or agricultural soils poses serious global environmental issues due to concerns about its effects on crop productivity and the food chain with implications on human health. According to the literature, several techniques exist at present to ameliorate/reduce the negative impact of HMs in the soil ecosystem, and among these techniques, the use of NPs has proved effective and efficient (Ahmad et al. 2019; Jiang et al. 2021). The application of NPs is an innovative and effective strategy in alleviating HM-induced toxicity stress in plants (Gunjan et al. 2014; Tripathi et al. 2015; Rizwan et al. 2019a), and particularly Cd (Tafazoli et al. 2017).

25.3.1 Nanoparticles-Mediated Modification of Cd Uptakes in Roots of Crop Plants

Increased accumulation of heavy metals (HMs) such as Cd in environmental compartments of the ecosystem portends serious ecological and human health implications. This is so important and of great concern, because the majority of HMs are non-biodegradable unlike organic contaminants, and increased release of them usually results in long-term soil ecotoxicity (Adriano et al. 2004; Sharma and Pandey 2014). Several studies mentioned in the literature have affirmed the potential of NPs to restrict or reduce the root uptake of Cd in crop plants under Cd stress. For instance, astaxanthin nanoparticles (Zeshan et al. 2021) and ZnO-NPs (Khan et al. 2019) applied to wheat plants were able to reduce the root uptake of Cd when compared to control. Also, the exposure of rice plants under Cd stress to both TiO_2-NPs and Si-NPs showed restricted Cd uptake to the above-ground biomass (Rizwan et al. 2019c). Similarly, Singh et al. (2016) reported that Cd toxicity in soybean was limited by TiO_2-NPs due to reduced uptake by roots, and similarly reported in rice (Ji et al. 2017).

In the roots of *Brassica chinensis* exposed to Cd-contaminated soil, Li and Huang (2014) reported that nanoparticle hydroxyapatite (nHAP) was able to decrease Cd uptake by roots, and the transport to shoots. It is also important to note that the ameliorative role of NPs on HMs toxicity in crop plants is largely dependent on crop types/species as opined by Adrees et al. (2020) and Hussain et al. (2021). This was observed in the study of Lyu et al. (2018) where the comparative effects of modified nano-scale black carbon were applied to Cd-contaminated soil, and both ryegrass and red beet were grown on the contaminated soil. The authors reported that the NPs increased the dry weight of ryegrass while there was no significant increase in red beet leaves. In addition, Wang et al. (2016a, b) explained that foliar application of Si-NPs to conventional and hybrid rice cultivars cultured in contaminated soil presented varied Cd and other HMs uptake. However, all the described are laboratory and greenhouse experiments, and the only field-scale study (Hussain et al. 2021) involved the application of multi-NPs of ZnO-NPs, Si-NPs, and Fe-NPs) to reduce Cd toxicity in wheat grown on aged Cd-contaminated field. Hussain et al. (2018) and Hussain et al. (2019c) in their studies on Cd-stressed wheat also found that ZnO-NPs and Fe-NPs, both foliar-applied and soil-applied were able to decrease the uptake of Cd and subsequently reduced the Cd concentrations in the roots, shoots, and grains. The authors affirmed that the decreasing trend of Cd in the wheat tissues was further promoted when the NPs' treatments were increased either as foliar spray or in soil.

25.3.2 Nanoparticles-Mediated Amelioration of Cd-Induced Toxicity

Tripathi et al. (2015) have asserted inter alia NPs, engineered NPs are the most effective in the alleviation of metal-induced toxicity in plants (Table 25.1). This may be possible due to their affinity for metals as a result of their smaller sizes and large surface area which make them penetrate metal-contaminated environments easily.

25.3.2.1 Modulation of Mineral Elements

Most of the HMs are toxic at high concentrations to crop plants due to their potential to competitively impair the uptake of most of the essential mineral elements needed by crop plants for growth and development at root surfaces (Keller et al. 2015; Rizwan et al. 2016a). In a recent study by Zeshan et al. (2021), astaxanthin nanoparticles (Ast-NPs) were found to improve the nutrient profile of Cd-stressed wheat seedlings. The level of N, P, K^+, and Ca^{2+} was significantly increased by 32%, 44%, 25%, and 84%, respectively. The Ast-NPs were also found to reprogram the ionic homeostasis of the plant by improving the levels of K^+ and Ca^{2+} by 51% and 46%, and $K^{+/}Na^+$ and Ca^{2+}/Na^+ ratios by 60% and 56%, respectively. Wang et al. (2015) found that application of foliar spray of SiO_2-NPs - improved the root uptake and shoot transport of Mg and Zn in 20-d old stressed rice seedlings. In a similar experiment, Si-NPs were reported to enhance the root uptake of S, Mg, P, and K in wheat under Cd stress (Ali et al. 2019; Hussain et al. 2019a).

25.3.2.2 Enhancement of Growth (Biomass)

In wheat exposed to Cd stress, Hussain et al. (2019c) reported that both foliar-applied and soil-applied Fe-NPs were able to alleviate the toxicity and made the plant healthy. The authors reported a higher number of tillers and spikes length in Fe-NPs-treated Cd-stressed wheat plants. Furthermore, the authors also found that

Table 25.1 Some nanoparticles and alleviation endpoints of Cd toxicity in different plant species

Nanoparticles	Concentration	Route of exposure	Plant species	Alleviation endpoint	References
ZnO-NPs	75 ml/l	Hoagland solution	Cotton (*Gossypium hirsutum* L.)	Up-regulated chlorophyll *a*, *b* and carotenoids in leaf Increased activity of SOD, CAT, POX and APX	Priyanka et al. (2021)
Si-NPs	300–1200 mg/l	Seed priming	Wheat (*Triticum aestivum*)	Enhanced antioxidant enzyme activities Reduced level of oxidative stress, Decreased Cd load in grains	Hussain et al. (2019b)
Hermatite-NPs	500 mg/kg	Soil	Maize (Zea mays)	Increased fresh biomass Alleviated Cd-induced DNA damage Enhanced GTS%	Youssef et al. (2021)
TiO_2-NPs	10–1000 mg/l	Hydroponic	Rice seedlings (*Oryza sativa*)	Increased root length, plant height and fresh weight Net photosynthetic rate and chlorophyll contents Reduced oxidative stress	Ji et al. (2017)
Ast-NPs	100 mg/l	Hydroponic	Wheat (*Triticum aestivum*)	Reduced Cd uptake by roots by 54% Reduced translocation to leaves by 29%	Zeshan et al. (2021)
TiO_2-NPs	100 mg/kg	Foliar	Cowpea (*Vigna unguiculata*)	Promoted chlorophyll contents Reduced Cd contents of roots, shoots, and grains Promoted stress enzymes in roots and leaves Increased Zn, Mn, and Co levels in seeds	Ogunkunle et al. (2020a)
Si-NPs	300–1200 mg/kg	Soil	Wheat (*Triticum aestivum*)	Enhanced activity of SOD and POD	Ali et al. (2019)

(continued)

Table 25.1 (continued)

Nanoparticles	Concentration	Route of exposure	Plant species	Alleviation endpoint	References
Fe_3O_4-NPs	2000 mg/l	Hydroponic	Wheat (*Triticum aestivum*)	Enhanced the plant growth, Increased SOD and POD activities in shoots and roots Decreased MDA contents in seedlings	Konate et al. (2017)
TiO_2-NPs	100 mg/kg	Soil	Cowpea (*Vigna unguiculata*)	APX and CAT activity promoted Reduced MDA content Reduced Cd partitioning in roots and leaves	Ogunkunle et al. (2020b)
SiO_2-NPs	2.5 mM	Foliar spray	Rice (*Oryza sativa*)	Increased the biomass Decreased Cd in shoot and roots Decreased MDA contents Increased GSH, SOD activities in shoots and roots	Wang et al. (2015)
TiO_2-NPs	100 mg/l	Foliar spray	Wheat (*Triticum aestivum*)	Decreased Cd concentrations in shoots, roots, and grains Enhanced the plant biomass and grain yield	Irshad et al. (2021)
SiO_2-NPs	5–25 mM	Foliar spray	Rice (*Oryza sativa*)	Decreased Cd in grains Increased K, Mg, Fe in grains Reduced Cd translocation to roots to other plant parts	Chen et al. (2018)
ZnO-NPs	25–100 mg/kg	Soil	Wheat (*Triticum aestivum*)	Promoted tissue dry biomass Reduced oxidative Reduced Cd tissue accumulation	Khan et al. (2019)
Ag-NPs	25 mg/kg	Soil	Yellow lupin (*Lupinus luteus*)	Enhanced activity of GPX Promoted metallothionein expression	Jaskulak et al. (2019)

(continued)

Table 25.1 (continued)

Nanoparticles	Concentration	Route of exposure	Plant species	Alleviation endpoint	References
Fe-NPs	Not available	Soil	Rice (*Oryza sativa*)	Increased rice biomass	Sebastian et al. (2019)
Fe-NPs	500–8000 mg/kg	Soil	Wheat (*Triticum aestivum*)	Decreased Cd concentration in tissues	Lopez-Luna et al. (2016)
ZnO-NPs Fe_3O_4-NPs	ZnO: 25–100 mg/L Fe_3O_4: 5–20 mg/l	Seed priming	Wheat (*Triticum aestivum*)	Increased content of chlorophyll contents Promoted tissue biomass and nutrients Reduced Cd toxicity by decreasing oxidative stress	Rizwan et al. (2019a)
Fe-NPs	25–100 mg/kg	Soil	Wheat (*Triticum aestivum*)	Increased photosynthesis Decreased Cd concentration in tissues	Adrees et al. (2020)
Nano-scale hydroxyapatite	5–30 g/kg	Soil	Pakchoi (*Brassica chinensis*	Reduction of Cd in shoots Decrease the level of MDA Increased activities of SOD, CAT, and POD	Li and Huang (2014).
ZnO-NPs	50–100 mg/l	Foliar	Maize (*Zea mays*)	Improved root and shoot dry biomass – Increased chlorophyll content Reduced MDA, H_2O_2, and Cd concentration	Rizwan et al. (2019b)
CeO_2-NPs	100 mg/l	Hydroponic	Soybean (*Glycine max*)	Decreased Cd in shoots	Rossi et al. (2018)
TiO_2-NPs	100–300 mg/kg	Soil	Soybean (*Glycine max*)	Increase biomass Increase chlorophyll, protein contents in leaf, Decreased MDA contents in leaf	Singh and Lee (2016)
ZnO-NPs	0–100 ppm	Soil & Foliar	Wheat (*Triticum aestivum*)	Increased wheat growth, yield Improved Zn biofortification Reduced Cd in wheat grains	Hussain et al. (2018)

the Fe-NP application linearly enhanced the dry biomasses of the shoot, roots, and spikes (Hussain et al. 2019c). Similarly, Konate et al. (2017) had previously reported that the application of Fe_3O_4-NPs to wheat seedlings through a hydroponic medium increased root and shoot length in the presence of Cd stress. The use ZnO-NPs has also been reported to effectively alleviate Cd stress in crops and improve growth parameters. Hussain et al. (2018) in their study on wheat plants found that ZnO-NPs, either applied through soil or by foliar treatment did improve the plant height and spike length. The authors also recorded that the shoot length of wheat was also enhanced by at least 21% and 10% in foliar- and soil-treated wheat plants, respectively. Similarly, shoot dry biomass and root dry biomass were increased by both foliar and soil-applied ZnO-NPs by at least 42% and 43%, respectively (Hussain et al. 2018). In rice, Zhang et al. (2019) found that the application of ZnO-NPs to Cd-stressed rice improved the plant's height at both tillering and booting stages. Similarly, the authors reported significant improvement in the root biomass, shoot biomass, ear biomass, and total biomass of the rice plants upon supplementation with ZnO-NPs after Cd stress.

The use of TiO_2-NPs as ameliorative strategy for Cd toxicity in crops has also been largely documented. Ji et al. (2017) explained that plant height was improved after exposure to TiO_2-NPs, indicating that the addition of TiO_2-NPs reduced the damage of Cd stress to rice seedlings. Lian et al. (2020) also showed that maize under Cd stress when exposed to foliar-applied TiO_2-NPs at 100 and 200 mg/l inhibited Cd absorption and later increased the biomass of maize plants. Similarly, nano-TiO_2 particles have been found to improve growth and biomass of Cd-stressed soybean plants (Singh and Lee 2016). In a recent study, Irshad et al. (2021) reported that TiO_2-NPs applied through the foliar route improved growth attributes (plant height and spike length), straw, and grain yield in wheat plants.

25.3.2.3 Improvement of Leaf Health

Nanoparticles have been noted to improve/enhance the growth and development of (crop) plants that are under HM stress due to their ability to improve photosynthetic activities (Fatemi et al. 2021; Zhou et al. 2021). In a pot experiment by Adrees et al. (2020) involving wheat exposed to Cd stress, Fe-NPs were found to improve photosynthesis in the leaves of the plant. This should be noted as a very important alleviation as the photosynthetic activities of plants are the first point of attack by Cd. In another study involving foliar spray of SiO_2-NPs to rice exposed to 20 μM Cd, it was found that the NPs increased the concentrations of chlorophylls a and b (Wang et al. 2015). Similarly in a recent study, Zeshan et al. (2021) found that astaxanthin nanoparticles (Ast-NPs) were able to alleviate Cd stress in wheat by improving chlorophyll contents, net photosynthetic rate, transpiration rate, stomatal conductance, and intracellular CO_2 concentration by 21%, 31%, 19%, 55%, and 5%, respectively, when compared to Cd-stressed plants. The NPs were also found to maintain the normal structure of chloroplasts with enlarged starch grain and reduction in osmiophilic plastoglobuli (Zeshan et al. 2021).

Hussain et al. (2019c) reported that photosynthetic activities of wheat plants under Cd stress were improved upon both foliar- and soil-applied Fe-NPs application. The authors reported the highest photosynthetic rate of 102% and 90% in foliar spray and soil treatment, respectively at 20 mg/l and 20 mg/kg applications of Fe-NPs (Hussain et al. 2019c). As regards the stomatal conductance in the study, an increase of 116% was recorded for foliar-applied Fe-NPs and 105% for soil application, respectively for 20 mg/l and 20 mg/kg applications. Sebastian et al. (2018) also applied Fe-NPs to rice under Cd toxicity and reported that the chlorophyll concentrations in the plants were enhanced.

In addition, the literature has provided information on Cd-toxicity alleviation by ZnO-NPs in the leaves of crop plants. Hussain et al. (2018) exposed Cd-stressed wheat to ZnO-NPs application via soil medium and recorded improved chlorophyll a and carotenoids of about 138% and 111%, respectively. The transpiration rate, photosynthetic rate, and stomatal conductance of Cd-stressed wheat plants were also reportedly improved upon the application of ZnO-NPs via foliar and soil applications (Hussain et al. 2018). A similar report of an increase in chlorophyll a, b and carotenoids by ZnO-NPs was obtained in the study of Venkatachalam et al. (2016) where an increment of 133.7%, 139.2%, and 132.4% was obtained, respectively. Ag-NPs produced through green synthesis have also been found to ameliorate the Cd toxicity (0.5 mg/kg) by enhancing chlorophyll a, b and carotenoids by 43.10%, 46.81%, and 3.91%, respectively in *Moringa oleifera* (Azeez et al. 2019).

25.3.2.4 Improvement of Nutritional Quality of Crops

The decrease in Cd concentration in crop plants exposed to NPs treatments may be due to the improved nutrition occasioned by the dilution effect in plants. Rizwan et al. (2019a) used seed priming with Fe-NPs to reduce grain Cd contents in wheat plants and found that the Cd level was below the recommended threshold (0.2 mg/kg) for cereals. Similarly, Hussain et al. (2019c) reported that foliar-applied Fe-NPs at 15 mg/l and soil-applied Fe-NPs at 20 mg/kg also reduced wheat grain Cd to a level suitable for consumption. Recently, Irshad et al. (2021) studied the effects of foliar-applied TiO_2-NPs on Cd contents in wheat plants and reported that Cd contents in straw, roots, and grains were significantly reduced by nanoparticles application. The authors reported that the Cd concentration of straw was reduced by at least 13%, 11% in roots, and 38% in grains. It was further reported that the foliar-applied TiO_2-NPs significantly reduced the human risk index of Cd, thereby making the grains suitable for consumption (Irshad et al. 2021).

25.4 Mechanisms of Nanoparticles-Mediated Amelioration of Cd-Induced Toxicity in Crop Plants

25.4.1 Reduction in Soil Cd Bioavailability

The major mode of action of NPs in ameliorating or alleviating HMs toxicity in the soil environment is by changing metal speciation through surface adsorption (Ding et al. 2017; Feizi et al. 2018; Huang et al. 2018) or converting labile forms to stable forms (Vithanage et al. 2017; Zhao et al. 2018). Cadmium adsorption to NPs was observed by Nasiri et al. (2013) and Tafazoli et al. (2017) when zero-valent iron nanoparticles (nzFe-NPs) were applied to remediate Cd in soil. It was found that nZFe-NPs reduced Cd bioavailability by sorbing to iron (hydr)oxide shell which involves standard redox potential. The adsorption of Cd on nanoparticles‘surfaces due to their large surface area assists in minimizing Cd toxicity through the reduction in the bioavailability of Cd in soil. Several studies in the literature have also affirmed the efficacy of Fe-NPs and Fe_3O_4-NPs in reducing Cd bioavailability in soil by immobilization through the adsorption process (Liu et al. 2008; Watanabe et al. 2009; Hussain et al. 2019c; Sebastian et al. 2019). Watanabe et al. (2009) suggested that the iron plaque formed from the oxidation of Fe^{2+} to Fe^{3+} absorbs Cd on its surface, thereby reducing the bioavailability and toxicity of Cd. Houben and Sonnet (2010) reported the reduction of Cd concentration in soil by 45%-63% through the application of powdered Fe-NPs due to reduced leaching of Cd. Similarly, Nasiri et al. (2013) and Rizwan et al. (2019a) found zero-valent iron- and ZnO-NPs useful in the reduction of Cd bioavailability in soil. Other NPs that have been proved to be effective in the immobilization of Cd in soil by sorbing Cd to their particle surface are ZnO-NPs and Si-NPs (Adrees et al. 2020; Khan et al. 2019).

In converting the labile form of Cd to a stable form by NPs, modified black carbon NPs were applied to Cd-spiked soil and exposed to ryegrass and red beet (Lyu et al. 2018). The authors reported that the DTPA-extractable, carbonate, and exchangeable fractions of rhizospheric-Cd of both crops were significantly reduced.

25.4.2 Modification of Homeostasis

Plants, in general, have evolved several mechanisms of homeostasis that assist in limiting uptake and accumulation of Cd in addition to modifications of transporter proteins and detoxification in cells and tissues (Fig. 25.2). Nanoparticles have been reported as a key agent in the modification of plants' homeostasis under detrimental stress conditions by regulating some physiological and biochemical processes in plants' cells/tissues such as H_2O acquisition, CO_2 fixation, nitrogen metabolism, and antioxidant systems (Tripathi et al. 2015; Wei and Wang 2013).

25.4.2.1 Changes in the Distribution of Tissue Cd

Rizwan et al. (2021) reported that NPs can alleviate the toxicity of HMs (Cd) in plants by altering or modifying their distribution in plants' tissues. One way of alleviating Cd toxicity is by immobilizing Cd ions in the rhizosphere, thereby restricting the uptake and transport. Hussain et al. (2019c) have found that Fe-NPs could immobilize Cd ions and restrict the uptake by wheat roots. The restriction of uptake and transport of Cd is not restricted to soil application of NPs but also foliar application. Chen et al. (2018) reported that foliar application of Si-NPs to rice grown on the field was able to reduce Cd uptake by roots and its translocation to upper nodes and grains. Similarly, Rizwan et al. (2019b) found similar results when maize under Cd stress was treated with foliar-applied ZnO-NPs, and translocation of Cd to aerial parts was reduced. The above observations may be possible because NPs can

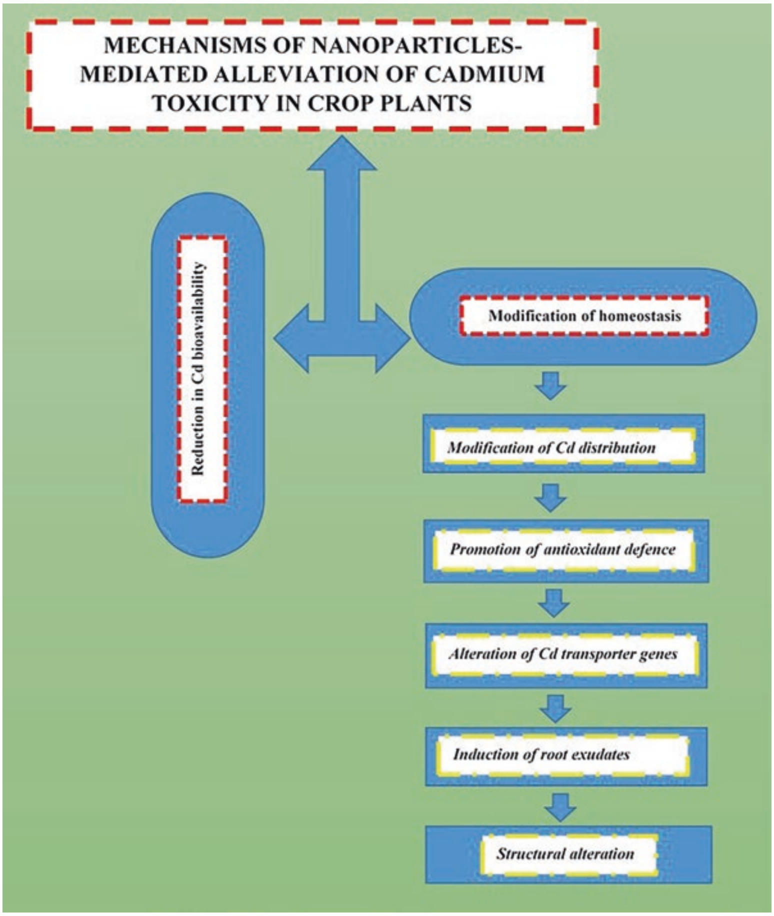


Fig. 25.2 Mechanisms of alleviation of Cd-toxicity by nanoparticles in crop plants

modify the distribution of HMs at subcellular levels in plants experiencing HM stress (Rizwan et al. 2021). In addition, the presence of apoplastic barriers in plant roots which serve the physiological function of controlling H_2O flow and O_2 in plants (Chao-Dong et al. 2013) has been suggested as catalyst reduction in Cd bio-accumulation in *Glycine max* by decreasing the amount of Cd root uptake (Rossi et al. 2017).

25.4.2.2 Enhancement of Antioxidant Defense Systems

There are a plethora of studies in the literature confirming the potential of HMs in excess to cause increased generation of ROS and electrolyte leakage leading to lipid peroxidation and oxidative stress in plants. Similarly, several studies have confirmed the potential of several NPs to increase the tolerance and ability of plants against HM-induced stress by improving the antioxidant defense system (Ali et al. 2019; Ji et al. 2017; Jiang et al. 2021; Ogunkunle et al. 2020a, b, c; Rizwan et al. 2019a, c; Tripathi et al. 2016;). This potential of NPs depends on concentrations and types of NPs and the duration of exposure of plants (Fatemi et al. 2021; Hussain et al. 2021). It is also important to note that several direct effects of NPs on antioxidant enzymes in plants have been noted but there has not been a distinct relationship between the effect and properties of NPs in literature (Rico et al. 2015; Tripathi et al. 2015). However, a recent study (Zeshan et al. 2021) has identified the role of genes expressing antioxidants. The authors reported that the application of astaxanthin-NPs significantly up-regulated the expression of genes (*TaSOD* and *TaPOD*) for antioxidants in wheat plants. The authors affirmed the role of the NPs in the regulation of plant antioxidant mechanisms by promoting defense-related genes for Cd-stress recovery.

One mode of action of NPs in alleviating HM-induced stress is the scavenging ability of NPs to reduce ROS generation. Boghossian et al. (2013) found out in CeO_2-NPs-treated rice seedlings that the NPs were able to scavenge toxic radicals (O_2^- and HO^-) and reduced H_2O_2 concentration. This was attributed to the surface lattice of the NPs which enabled them to alternate between the +4 and +3 oxidation state, thereby scavenging the radicals. Several other studies have also affirmed the scavenging ability of CeO_2-NPs in stressed plants (Gomez-Garay et al. 2014; Rico et al. 2013a, b; Xia et al. 2008). Nano-zero-valent iron has also been proven to be effective in promoting the antioxidant defense system of the plant under HM-stressed conditions. In a study by Gong et al. (2017), ramie Cd-stressed seedling was subjected to nZVI treatment and found that 100 mg nZVI/kg was able to reduce H_2O_2 generation and decreased MDA content in the seedling.

It is interesting to know that many of NPs possess the ability to mimic the activity of natural enzymes in plants especially NPs such as CeO_2-NPs, Fe_3O_4-NPs, and Co_3O_4-NPs that have been proved to mimic catalase and peroxidase activities in plants, and CuO-NPs for peroxidase activity (Wei and Wang 2013). Foliar-applied CeO_2-NPs has also proved effective in stimulating antioxidant defense system in rice exposed to hydroponically applied $CdCl_2$ (Wang et al. 2019) and also inhibited Cd bioaccumulation in the tissues. Similarly, Hussain et al. (2019c) found both foliar- and soil-applied Fe-NPs effective in stimulating the activity of SOD and POD in wheat plants exposed to Cd stress.

The role of TiO_2-NPs in alleviating HM-induced stress by enhancing the antioxidant defense system of plants has also been comprehensively studied. For example, reports have shown that TiO_2-NPs enhanced the activities of several antioxidant enzymes (CAT, SOD, and APX) in cowpea (Ogunkunle et al. 2020b), (SOD and POD) wheat (Irshad et al. 2021), and (SOD, CAT, APX, and GPX) in spinach (Lei et al. 2008), thereby conferring tolerance under HM-induced stress. Hong et al. (2005) and Ji et al. (2017) reported that TiO_2-NPs were able to reduce the generation of reactive oxygen free radicals by improving antioxidant enzyme activities and reduced malondialdehyde (MDA) in spinach and rice seedlings, respectively. In Cd-treated soybean, the application of TiO_2-NPs was able to alleviate toxicity by reducing the generation of proline and lipid peroxidation and enhancing photosynthetic activities (Singh and Lee 2016). Similarly, investigations on Cd-treated spinach have revealed that the application of TiO_2-NPs was able to mitigate oxidative stress by reducing H_2O_2 generation and MDA and increasing antioxidant activities of SOD, GPX, CAT, and APX (Zheng et al. 2008). Foliar-applied TiO_2-NPs were also found to increase the activities of GST and SOD, and at the same time up-regulated alanine, aspartame, and galactose to ameliorate Cd toxicity to maize (Lain et al. 2020). Silica nanoparticles (SiO_2-NPs) have also been found to be effective in alleviating Cd toxicity by promoting increased activity of GSH and SOD in shoots and roots of rice when compared to Cd-treated rice (Wang et al. 2015).

25.4.2.3 Modification of Expression of Cd Transport Genes

Heavy metals such as Cd toxicity are a major abiotic stressor that promotes the production of binding proteins involved in the activation of stress-response genes in plants (Rico et al. 2015). The entrance of Cd into the plant's cell can modify protein functions in plants by increasing protein biosynthesis through metal ion release. Several of these proteins are constituents of metal transporters (such as ZIP, HMA, CDF, phytochelatins, and NRAMP) involved in maintaining the homeostasis of HMs in plant cells (Ovecka and Takac 2014). Cadmium ion is a known toxic trace element that enters through the metal transporters such as Fe transporters into plant cells (Hall and Williams 2003). So, when externally applied nanoparticles containing mineral elements such as Fe are involved, the Fe ion competes with Cd ion in the roots during uptake, and thereby reducing the tendency for Cd uptake. Another mechanism could be the inhibition of Fe-related genes by supplementation of Fe-containing NPs which will subsequently reduce/decrease Cd uptake as observed in rice by Chen et al. (2017). Similarly, Cui et al. (2017) in a study on the effect of silica nanoparticles on Cd toxicity in rice cells reported that the mechanism of detoxification of Cd by Si-NPs was by inhibition of gene expression of Cd uptake and transport *(OsLCT1 and OsNramp5). They* also found that the gene expression of Cd transport into the vacuole (*OsHMA3*) was enhanced by the Si-NPs. This latter observation may be an evolved mechanism by rice to prevent Cd toxicity in the rice cells since Cd ions stored in the vacuoles will be rendered inactive in plant cytosols. Recently, Zeshan et al. (2021) found that astaxanthin-NPs negatively regulated the expression of Cd transporters (*TaHMA2* and *TaHMA3*) in wheat plants when compared to Cd-stressed plants to reduce Cd uptake and translocation to the aboveground parts. Recently, Youssef et al. (2021) found that Cd stress upregulated expression for PCNA1 and PCNA2 genes in both roots and shoots of maize seedlings whereas, the application of hermatite-NPs at 500 mg/kg to the Cd-stressed plants significantly reduced the expressions of both PCNAI and PCNA2. The authors opined that the presence of hermatite-NPs reduced DNA damage occasioned by Cd toxicity in the plants.

25.4.2.4 Increased Induction of Root Exudates or Complexants

The application of nanoparticles to soil has also been reported to alleviate Cd toxicity to plants by stimulating the secretion of organic ligands and complexants in the root rhizosphere. This has been reported to modify metal mobility and uptake by crop plants (Adrees et al. 2015a; Keller et al. 2015; Rizwan et al. 2016b). Rossi et al. (2018) reported CeO_2-NPs increase root exudates in the presence of Cd which was likely responsible for Cd complexation in the root rhizosphere of soybean plants and reduced the shoot Cd concentration. Also, Cui et al. (2017) used Si-NPs to alleviate Cd toxicity in rice and reported that one of the mechanisms of alleviation is the formation of Si- complexes on the cell walls which bound with Cd and reduced the transport of Cd into the rice cells.

25.4.2.5 Structural Alteration of Crop Plants

The structural integrity of crop plants can be affected by Cd toxicity which may consequentially affect productivity in terms of biomass weight (dry and wet weights). For instance, there was the disintegration of root epidermis seedlings of carrots and tomato plants under Cd stress (Wang et al. 2012), and alteration in root cells (nuclei, vacuoles, and shape) in radish exposed to $CdCl_2$ for 5 days (Manesh et al. 2018). However, exogenously applied NPs, either through soil or foliar routes was found to be effective in alleviating such structural damages imposed by Cd toxicity in crop plants. In a study by Wang et al. (2012), Cd stress endpoints in form of reduced root diameter and disintegrated root epidermis in cucumber and tomato seedlings were alleviated by the application of hydroxyapatite-NPs, Fe_3O_4-NPs, a-Fe_2O_3-NPs, and g-Fe_2O-NPs to Cd-spiked soil, respectively. The authors opined that the reduction in phytotoxicity was occasioned by the formation of precipitation of applied NPs on root surfaces of test plants. Also, Rossi et al. (2017) in their study found that CeO_2-NPs amended the effect of Cd toxicity on the apoplastic barrier in roots of soybean by shortening the apoplastic barriers which is a form of tolerance adaptation under HM stress (Adrees et al. 2015b).

25.5 Conclusion

This chapter advanced the knowledge of nanoparticle-induced tolerance to cadmium stress in crop plants. The explored works of literature have shown a plethora of evidence that nanoparticles can induce positive physiological and genetic modification in crop plants as responses to mitigate Cd toxicity. The available information in literature has also presented the enhancement of gene expression genes for antioxidants and transporter proteins, structural alteration of plant tissues, and increased root exudates/complexants as parts of the mechanism of alleviation of Cd toxicity in crop plants.

References

Abbas T, Rizwan M, Ali S, Adrees M, Zia-ur-Rehman M, Qayyum MF, Murtaza G (2017) Effect of biochar on alleviation of cadmium toxicity in wheat (*Triticum aestivum* L.) grown on Cd-contaminated saline soil. Environ Sci Pollut Res 25:25668–22568

Adrees M, Ali S, Rizwan M, Ibrahim M, Abbas F, Farid M, Rehman MZ, Irshad MK, Bharwana SA (2015a) The effect of excess copper on growth and physiology of important food crops: a review. Environ Sci Pollut Res 22:8148–8162

Adrees M, Ali S, Rizwan M, Rehman MZ, Ibrahim M, Abbas F, Farid M, Qayyum MF, Irshad MK (2015b) Mechanisms of silicon-mediated alleviation of heavy metal toxicity in plants: a review. Ecotoxicol Environ Saf 119:186–197

Adrees M, Khan ZS, Ali S, Hafeez M, Khalid S, ur Rehman MZ, Hussain A, Hussain K, SAS C, Rizwan M (2020) Simultaneous mitigation of cadmium and drought stress in wheat by soil application of iron nanoparticles. Chemosphere 238:124681. https://doi.org/10.1016/j.chemosphere.2019.124681

Adriano DC, Wenzel WW, Vangronsveld J, Bolan NS (2004) Role of assisted natural remediation in environmental cleanup. Geoderma 122:121–142

Ahmad B, Zaid A, Jaleel H, Khan MMA, Ghorbanpour M (2019) Nanotechnology for phytoremediation of heavy metals: mechanisms of nanomaterial-mediated alleviation of toxic metals. In: Ghorbhanpour M, Wani SH (eds) Advances in phytonanotechnology. Academic Press, pp 316–322. https://doi.org/10.1016/B978-0-12-815322-2.00014-6

Akanbi-Gada M, Ogunkunle CO, Vishwarkama V, Viswanathan K, Fatoba PO (2019) Phytotoxicity of nano-zinc oxide to tomato plant (*Solanum lycopersicum* L.): Zn uptake, stress enzymes response and influence on on-enzymatic antioxidants in fruits. Environ Technol Innov 14. https://doi.org/10.1016/j.eti.2019.100325

Akbari B, Tavandashti MP, Zandrahimi M (2011) Particle size characterization of nanoparticles- a practical approach. Iran J Mater Sci Eng 8:48–56

Ali S, Rizwan M, Hussain A, ur Rehman MZ, Ali B, Yousaf B, Wijaya L, Alyemeni MN, Ahmad P (2019) Silicon nanoparticles enhanced the growth and reduced the cadmium accumulation in grains of wheat (*Triticum aestivum* L.). Plant Physiol Biochem 140:1–8

Azeez L, Adejumo AL, Lateef A, Adebisi SA, Adetoro RO, Adewuyi SO, Tijani KO, Olaoye S (2019) Zero-valent silver nanoparticles attenuate Cd and Pb toxicities on *Moringa oleifera* via immobilization and induction of phytochemicals. Plant Physiol Biochem 139:283–292

Ben A, Charles G, Hourmant A, Ben J, Branchard M (2009) Physiological behaviour of four rapeseed cultivar (*Brassica napus L.*) submitted to metal stress. C R Biol 332(4):363–370

Boghossian AA, Sen F, Gibbons BM, Sen S, Faltermeier SM, Giraldo JP, Zhang CT, Zhang J, Heller DA, Strano MS (2013) Application of nanoparticle antioxidants to enable hyperstable chloroplasts for solar energy harvesting. Adv Energy Mater 3:881–893

Carrier P, Baryla A, Havaux M (2003) Cadmium distribution and microlocalization in oilseed rape (*Brassica napus*) after long-term growth on cadmium-contaminated soil. Planta 216:939–950

Chao-Dong Y, Xia Z, Guo-Feng L, Jun-Wei Z, Man-Zhu B, Zhi-Xiang Z (2013) Progress on the structure and physiological functions of apoplastic barriers in root. Bull Bot Res 33:114–119

Chen Z, Tang YT, Yao AJ, Cao J, Wu ZH, Peng ZR, Wang SZ, Xiao S, Baker AJ, Qiu RL (2017) Mitigation of Cd accumulation in paddy rice (*Oryza sativa* L.) by Fe fertilization. Environ Pollut 231:549–559

Chen R, Zhang C, Zhao Y, Huang Y, Liu Z (2018) Foliar application with nano-silicon reduced cadmium accumulation in grains by inhibiting cadmium translocation in rice plants. Environ Sci Pollut Res 25:2361–2368

Cui J, Liu T, Li F, Yi J, Liu C, Yu H (2017) Silica nanoparticles alleviate cadmium toxicity in rice cells: mechanisms and size effects. Environ Pollut 228:363–369

Delpérée C, Lutts L (2008) Growth inhibition occurs independently of cell mortality in tomato (*Solanum lycopersicum*) exposed to high cadmium concentrations. J Integr Plant Biol 50(3):300–310

Ding L, Li J, Liu W, Zuo Q, Liang SX (2017) Influence of nano-hydroxyapatite on the metal bioavailability, plant metal accumulation and root exudates of ryegrass for phytoremediation in lead-polluted soil. Int J Environ Res Pub Health 14:1–9

Ekmekçi Y, Tanyolaç D, Ayhan B (2008) Effects of cadmium on antioxidant enzyme and photosynthetic activities in leaves of two maize cultivars. J Plant Physiol 165:600–611

Fagioni M, Zolla L (2009) Does the different proteomic profile found in apical and basal leaves of spinach reveal a strategy of this plant toward cadmium pollution response? J Proteomic Res 8(5):2519–2529

Fatemi H, Pour BE, Rizwan M (2021) Foliar application of silicon nanoparticles affected the growth, vitamin C, flavonoid, and antioxidant enzyme activities of coriander (*Coriandrum sativum* L.) plants grown in lead (Pb)-spiked soil. Environ Sci Pollut Res 28:1417–1425

Feizi M, Jalali M, Renella G (2018) Nanoparticles and modified clays influenced distribution of heavy metals fractions in a light-textured soil amended with sewage sludges. J Hazard Mater 343:208–219

Gomez-Garay A, Pintos B, Manzanera JA, Lobo C, Villalobos N, Martín L (2014) Uptake of CeO2 nanoparticles and its effect on growth of *Medicago arborea* in vitro plantlets. Biol Trace Elem Res 161:143–150

Gong X, Huang D, Liu Y, Zeng G, Wang R, Wan J, Zhang C, Cheng M, Qin X, Xue W (2017) Stabilized nanoscale zerovalent iron-mediated cadmium accumulation and oxidative damage of *Boehmeria nivea* (L.) Gaudich cultivated in cadmium contaminated sediments. Environ Sci Technol 51:11308–11316

Gunjan B, Zaidi MGH, Sandeep A (2014) Impact of gold nanoparticles on physiological and biochemical characteristics of *Brassica juncea*. J Plant Biochem Physiol 2:1–6

Guo TR, Zhang GP, Zhou MX, Wu FB, Chen JX (2007) Influence of aluminum and cadmium stresses on mineral nutrition and root exudates in two barley cultivars. Pedosphere 17:505–512

Hall JL, Williams LE (2003) Transition metal transporters in plants. J Exp Bot 54(393):2601–2613

Hong FS, Yang P, Gao FQ, Liu C, Zheng L, Zhou J (2005) Effect of nano-anatase TiO_2 on spectral characterization of photosystem II particles from spinach. Chem Res Chin Univ 21:196–200

Houben D, Sonnet P (2010) Leaching and phytoavailability of zinc and cadmium in a contaminated soil treated with zero-valent iron. In: Proceedings of the 19th World Congress of Soil Science, Soil Solutions for a Changing World. pp 1–6

Huang D, Deng R, Wan J, Zeng G, Xue W, Wen X, Zhou C, Hu L, Liu X, Xu P, Guo X (2018) Remediation of lead-contaminated sediment by biochar-supported nano-chlorapatite: accompanied with the change of available phosphorus and organic matters. J Hazard Mater 348:109–116. https://doi.org/10.1016/j.jhazmat.2018.01.024

Hussain A, Ali S, Rizwan M, ur Rehman MZ, Javed MR, Imran M, Chatha SAS, Nazir R (2018) Zinc oxide nanoparticles alter the wheat physiological response and reduce the cadmium uptake by plants. Environ Pollut 242:1518–1526

Hussain A, Rizwan M, Ali Q, Ali S (2019a) Seed priming with silicon nanoparticles improved the biomass and yield while reduced the oxidative stress and cadmium concentration in wheat grains. Environ Sci Pollut Res 26:7579–7588

Hussain A, Oves M, Alajmi MF, Hussain I, Amir S, Ahmed J, Rehman MT, El- Seedi HR, Ali I (2019b) Biogenesis of ZnO nanoparticles using *Pandanus odorifer* leaf extract: anticancer and antimicrobial activities. RSC Adv 9:15357–15369

Hussain A, Ali S, Rizwan M, ur Rehman MZ, Qayyum MF, Wang H, Rinklebe J (2019c) Responses of wheat (Triticum aestivum) plants grown in a Cd contaminated soil to the application of iron oxide nanoparticles. Ecotoxicol Environ Saf 173:156–164

Hussain A, Rizwan M, Ali S, ur Rehman MZ, Qayyum MF, Nawaz R, Ahmad A, Asrar M, Ahmad SR, Alsahli AA, Alyemeni MN (2021) Combined use of different nanoparticles effectively decreased cadmium (Cd) concentration in grains of wheat grown in a field contaminated with Cd. Ecotoxicol Environ Saf 215:112139

Irshad HMK, Noman A, Alhaithloul H, Adeel M, Yukui R, Shah T, Zhu S, Shang J (2020) Goethite-modified biochar ameliorates the growth of rice (*Oryza sativa* L.) plants by suppressing Cd and As-induced oxidative stress in Cd and As co-contaminated paddy soil. Sci Total Environ 137086

Irshad MA, Rehman MZ, Anwar-ul-Haq M, Rizwan M, Nawaz R, Shakoor MB, Wijaya L, Alyemeni MN, Ahmad P, Ali S (2021) Effect of green and chemically synthesized titanium dioxide nanoparticles on cadmium accumulation in wheat grains and potential dietary health risk: a field investigation. J Hazard Mater 415:1–9

Jacob DL, Borchardt JD, Navaratnam L, Otte ML, Bezbaruah AN (2013) Uptake and translocation of Ti from nanoparticles in crops and wetland plants. Int J Phytoremediation 15:142–153

Jaskulak M, Rorat A, Grobelak A, Chaabene Z, Kacprzak M, Vandenbulcke F (2019) Bioaccumulation, antioxidative response, and metallothionein expression in Lupinus luteus L. Exposed to heavy metals and silver nanoparticles. Environ Sci Pollut Res 26:16040–16052

Javaid S (2020) Heavy metals stress, mechanism and remediation techniques in rice (Oryza sativa L.): a review. Pure Appl Biol 9

Ji Y, Zhou Y, Ma C, Feng Y, Hao Y, Rui Y, Wu W, Gui X, Han Y, Wang Y, Xing B (2017) Jointed toxicity of TiO_2-NPs and Cd to rice seedlings: NPs alleviated Cd toxicity and Cd promoted NPs uptake. Plant Physiol Biochem 110:82–93

Jiang M, Wang J, Rui M, Yang L, Shen J, Chu H, Song S, Chen Y (2021) OsFTIP7 determines metallic oxide nanoparticles response and tolerance by regulating auxin biosynthesis in rice. J Hazard Mater 403:123946

Kashyap PL, Xiang X, Heiden P (2015) Chitosan nanoparticle based delivery systems for sustainable agriculture. Int J Biol Macromol 77:36–51

Keller C, Rizwan M, Davidian JC, Pokrovsky OS, Bovet N, Chaurand P, Meunier JD (2015) Effect of silicon on wheat seedlings (*Triticum turgidum* L.) grown in hydroponics and exposed to 0 to 30 μM Cu. Planta 241:847–860

Khan ZS, Rizwan M, Hafeez M, Ali S, Javed MR, Adrees M (2019) The accumulation of cadmium in wheat (Triticum aestivum) as influenced by zinc oxide nanoparticles and soil moisture conditions. Environ Sci Pollut Res 26:19859–19870

Kinay A (2018) Effects of cadmium on nicotine, reducing sugars and phenolic contents of Basma tobacco variety. Fresenius Environ Bull 27:9195–9202

Konate A, He X, Zhang Z, Ma Y, Zhang P, Alugongo GM, Rui Y (2017) Magnetic (Fe_3O_4) nanoparticles reduce heavy metals uptake and mitigate their toxicity in wheat seedling. Sustain 9:1–16

Lei Z, Mingyu S, Xiao W, Chao L, Chunxiang Q, Liang C, Hao H, Xiaoqing L, Fashui H (2008) Antioxidant stress is promoted by nano-anatase in spinach chloroplasts under UV-B radiation. Biol Trace Elem Res 21:69–79

Li Z, Huang J (2014) Effects of nanoparticle hydroxyapatite on growth and antioxidant system in pakchoi (*Brassica chinensis* L.) from cadmium-contaminated soil. J Nanomater:1–7

Lian J, Zhao L, Wu J, Xiong H, Bao Y, Zeb A, Tang J, Liu W (2020) Foliar spray of TiO_2 nanoparticles prevails over root application in reducing Cd accumulation and mitigating Cd-induced phytotoxicity in maize (*Zea mays* L.). Chemosphere 239(124794)

Liu JH, Inoue H, Moriguchi T (2008) Salt stress-mediated changes in free polyamine titers and expression of genes responsible for polyamine biosynthesis of apple in vitro shoots. Environ Exp Bot 62:28–35

Lopez-Luna J, Silva-Silva MJ, Martinez-Vargas S, Mijangos-Ricardez OF, Gonz'alez-Ch'avez MC, Solís-Domínguez FA, Cuevas-Díaz MC (2016) Magnetite nanoparticle (NP) uptake by wheat plants and its effect on cadmium and chromium toxicological behavior. Sci Total Environ 565:941–950

López-Millán A-F, Sagardoy R, Solanas M, Abadía A, Abadía J (2008) Cadmium toxicity in tomato (*Lycopersicon esculentum*) plants grown in hydroponics. Environ Exp Bot 65:376–385

Lu Z, Zhang Z, Su Y, Liu C, Shi G (2013) Cultivar variation in morphological response of peanut roots to cadmium stress and its relation to cadmium accumulation. Ecotoxicol Environ Saf 91:147–155

Lyu Y, Yu Y, Li T, Cheng J (2018) Rhizosphere effects of *Lolium perenne* L. and *Beta vulgaris* var. *cicla* L. on the immobilization of Cd by modified nanoscale black carbon in contaminated soil. J Soils Sedim 18:1–11

Manesh RR, Grassi G, Bergami E, Marques-Santos LF, Faleri C, Liberatori G, Corsi I (2018) Co-exposure to titanium dioxide nanoparticles does not affect cadmium toxicity in radish seeds (*Raphanus sativus*). Ecotoxicol Environ Saf 148:359–366

Metwally A, Safronova VI, Belimov AA, Dietz KJ (2005) Genotypic variation of the response to cadmium toxicity in *Pisum sativum* L. J Exp Bot 56:167–178

Mittal D, Kaur G, Singh P, Yadav K, Ali SA (2020) Nanoparticle-based sustainable agriculture and food science: recent advances and future outlook. Front Nanotechnol 2:579954

Nasiri J, Gholami A, Panahpour E (2013) Removal of cadmium from soil resources using stabilized zero-valent iron nanoparticles. J Civil Eng Urban 3:338–341

Nedelkoska TV, Doran PM (2000) Characteristics of metal uptake by plants species with potential for phytoremediation and phytomining. Miner Eng 13:549–561

Ogunkunle CO, Jimoh MA, Asogwa NT, Viswanathan K, Vishwakarma V, Fatoba PO (2018) Effects of manufactured nano-copper on copper uptake, bioaccumulation and enzyme activities in cowpea grown on soil substrate. Ecotoxicol Environ Saf 155:86–93. https://doi.org/10.1016/j.ecoenv.2018.02.070

Ogunkunle CO, Gambari H, Agbaje F, Okoro HK, Asogwa NT, Vishwakarma V, Fatoba PO (2020a) Effect of low-dose nano titanium dioxide intervention on Cd uptake and stress enzymes activity in Cd-stressed cowpea [*Vigna unguiculata* (L.) Walp] plants. Bull Environ Contam Toxicol 104(5):619–626

Ogunkunle CO, Odulaja DA, Akande FO, Varun M, Vishwakarma V, Fatoba PO (2020b) Cadmium toxicity in cowpea: effect of foliar intervention of nano-TiO_2 on tissue Cd bioaccumulation, stress enzymes and potential dietary health risk. J Biotechnol 310:54–61

Ogunkunle CO, Ahmed El-Imam AM, Bassey E, Vishwakarma V, Fatoba PO (2020c) Co-application of indigenous arbuscular mycorrhizal fungi and nano-TiO_2 reduced Cd uptake and oxidative stress in pre-flowering cowpea plants. Environ Technol Innov 20:101163. https://doi.org/10.1016/j.eti.2020.101163

Ogunkunle CO, Oyedeji S, Okoro HK, Adimula V (2021) Interaction of nanoparticles with soil. In: Amrane A, Mohan D, Nguyen TA, Assad AA, Yasin G (eds) Nanomaterials for soil remediation, vol 6, pp 101–132. https://doi.org/10.1016/B978-0-12-822891-3.00006-2

Ogunkunle CO, Jimoh MA, Oyedeji S, Varun M, Okunlola GO (2022) Engineered nanomaterial-mediated changes in the growth and development of agricuktural crops. In: Ghorbanpour M, Shahid MA (eds) Nano-enabled agrochemicals in agriculture, vol 20, pp 345–376

Ovecka M, Takac T (2014) Managing heavy metal toxicity stress in plants: biological and biotechnological tools. Biotechnol Adv 32:73–86

Priyanka N, Geetha N, Manish T, Sahi SV, Venkatachalam P (2021) Zinc oxide nanocatalyst mediates cadmium and lead toxicity tolerance mechanism by differential regulation of photosynthetic machinery and antioxidant enzymes level in cotton seedlings. Toxicol Rep 8:295–302

Qian H, Li J, Sun L, Chen W, Sheng GD, Liu W (2009) Combined effect of copper and cadmium on *Chlorella vulgaris* growth and photosynthesis-related gene transcription. Aquat Toxicol 94:56–61

Rico CM, Hong J, Morales MI, Zhao L, Barrios AC, Zhang JY, Peralta-Videa JR, Gardea-Torresdey JL (2013a) Effect of cerium oxide nanoparticles on rice: a study involving the antioxidant defense system and in vivo fluorescence imaging. Environ Sci Technol 47:5635–5642

Rico CM, Morales MI, McCreary R, Castillo-Michel H, Barrios AC, Hong J, Tafoya A, Lee WY, Varela-Ramirez A, Peralta-Videa JR, Gardea-Torresdey JL (2013b) Cerium oxide nanoparticles modify the antioxidative stress enzyme activities and macromolecule composition in rice seedlings. Environ Sci Technol 47:14110–14118

Rico CM, Peralta-Videa JR, Gardea-Torresdey JL (2015) Chemistry, biochemistry of nanoparticles, and their role in antioxidant defense system in plants. In: Nanotechnology and plant sciences. Springer International Publishing. pp 1-17

Rizwan M, Ali S, Abbas T, Rehman MZ, Hannan F, Keller C, Al-Wabel MI, Ok YS (2016a) Cadmium minimization in wheat: a critical review. Ecotoxicol Environ Saf 130:43–53

Rizwan M, Ali S, Adrees M, Rizvi H, Rehman MZ, Hannan F, Qayyum MF, Hafeez F, OK YS. (2016b) Cadmium stress in rice: toxic effects, tolerance mechanisms and management: a critical review. Environ Sci Pollut Res 23:17859–17879

Rizwan M, Ali S, Ali B, Adrees M, Arshad M, Hussain A, ur Rehman MZ, Waris AA. (2019a) Zinc and iron oxide nanoparticles improved the plant growth and reduced the oxidative stress and cadmium concentration in wheat. Chemosphere 214:269–277

Rizwan M, Ali S, ur Rehman MZ, Adrees M, Arshad M, Qayyum MF, Ali L, Hussain A, SAS C, Imran M (2019b) Alleviation of cadmium accumulation in maize (Zea mays L.) by foliar spray of zinc oxide nanoparticles and biochar to contaminated soil. Environ Pollut 248:358–367

Rizwan M, Ali S, ur Rehman MZ, Malik S, Adrees M, Qayyum MF, Alamri SA, Alyemeni MN, Ahmad P (2019c) Effect of foliar applications of silicon and titanium dioxide nanoparticles on growth, oxidative stress, and cadmium accumulation by rice (*Oryza sativa*). Acta Physiol Plant 41:1–10. https://doi.org/10.1007/s11738-019-2828-7

Rizwan M, Ali S, ur Rehman MZ, Riaz M, Adrees M, Hussain A, Zahir ZA, Rinklebe J (2021) Effects of nanoparticles on trace element uptake and toxicity in plants: a review. Ecotoxicol Environ Saf 221:112437. https://doi.org/10.1016/j.ecoenv.2021.112437

Rossi L, Zhang W, Schwab AP, Ma X (2017) Uptake, uptake, accumulation, and in planta distribution of coexisting cerium oxide nanoparticles and cadmium in *Glycine max* (L.). Merr Environ Sci Technol 51:12815–12824

Rossi L, Sharifan H, Zhang W, Schwab AP, Ma X (2018) Mutual effects and in planta accumulation of co-existing cerium oxide nanoparticles and cadmium in hydroponically grown soybean (*Glycine max* (L.) Merr.). Environ Sci Nano 5:150–157

Sebastian A, Nangia A, Prasad MNV (2018) A green synthetic route to phenolics fabricated magnetite nanoparticles from coconut husk extract: implications to treat metal contaminated water and heavy metal stress in *Oryza sativa* L. J Clean Prod 174:355–366

Sebastian A, Nangia A, Prasad MNV (2019) Cadmium and sodium adsorption properties of magnetite nanoparticles synthesized from *Hevea brasiliensis* Muell. Arg. bark: relevance in amelioration of metal stress in rice. J Hazard Mater 371:261272

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

Shi Q, Wang J, Zou J, Jiang Z, Wu H, Wang J, Jiang W, Liu D (2016) Cadmium localization and its toxic effects on root tips of barley. Zemdirbyste-Agriculture 103(2):151–158

Singh J, Lee BK (2016) Influence of nano-TiO2 particles on the bioaccumulation of Cd in soybean plants (*Glycine max*): a possible mechanism for the removal of Cd from the contaminated soil. J Environ Manag 170:88–96

Tafazoli M, Hojjati SM, Biparva P, Kooch Y, Lamersdorf N (2017) Reduction of soil heavy metal bioavailability by nanoparticles and cellulosic wastes improved the biomass of tree seedlings. J Plant Nutr Soil Sci 180:683–693

Tran TA, Popova LP (2013) Functions and toxicity of cadmium in plants: recent advances and future prospects. Turk J Bot 37:1–13

Tripathi DK, Singh VP, Prasad SM, Chauhan DK, Dubey NK, Rai AK (2015) Silicon-mediated alleviation of Cr(VI) toxicity in wheat seedlings as evidenced by chlorophyll florescence, laser induced breakdown spectroscopy and anatomical changes. Ecotoxicol Environ Saf 113:133–144

Tripathi DK, Singh S, Singh VP, Prasad SM, Chauhan DK, Dubey NK (2016) Silicon nanoparticles more efficiently alleviate arsenate toxicity than silicon in maize cultivar and hybrid differing in arsenate tolerance. Front Environ Sci 4:1–14

Vassilev A, Vangronsveld J, Yordanov I (2002) Cadmium phytoextraction: present state, biological backgrounds and research needs. Bulgarian J Plant Physiol 28(3-4):68–95

Venkatachalam P, Jayaraj M, Manikandan R, Geetha N, Rene ER, Sharma NC, Sahi SV (2016) Zinc oxide nanoparticles (ZnO NPs) alleviate heavy metal-induced toxicity in *Leucaena leucocephala* seedlings: a physiochemical analysis. Plant Physiol et Biochem. https://doi.org/10.1016/j.plaphy.2016.08.022

Vithanage M, Herath I, Almaroai YA, Rajapaksha AU, Huang L, Sung JK, Lee SS, Ok YS (2017) Effects of carbon nanotube and biochar on bioavailability of Pb, Cu and Sb in multi-metal contaminated soil. Environ Geochem Health 39:1409–1420

Wang M, Chen L, Chen S, Ma Y (2012) Alleviation of cadmium-induced root growth inhibition in crop seedlings by nanoparticles. Ecotoxicol Environ Saf 79:48–54

Wang S, Wang F, Gao S (2015) Foliar application with nano-silicon alleviates Cd toxicity in rice seedlings. Environ Sci Pollut Res 22:2837–2845

Wang S, Wang F, Gao S, Wang X (2016a) Heavy metal accumulation in different rice cultivars as influenced by foliar application of nano-silicon. Water Air Soil Pollut 227:1–13

Wang ST, Liu HL, Liu W, Zuo QQ (2016b) Effect of low-molecular-weight organic acids on nano-hydroxyapatite adsorption of cadmium and lead. J Biomater Tissue Eng 6:433–439

Wang Y, Wang L, Ma C, Wang K, Hao Y, Chen Q, Mo Y, Rui Y (2019) Effects of cerium oxide on rice seedlings as affected by co-exposure of cadmium and salt. Environ Pollut 252:1087–1096

Watanabe T, Murata Y, Nakamura T, Sakai Y, Osaki M (2009) Effect of zero-valent iron application on cadmium uptake in rice plants grown in cadmium-contaminated soils. J Plant Nutr 32:1164–1172

Wei H, Wang E (2013) Nanomaterials with enzyme-like characteristics (nanozymes): next-generation artificial enzymes. Chem Soc Rev 42:6060–6093

Xia T, Kovochich M, Liong M, Mädler L, Gilbert B, Shi H, Yeh JI, Zink JI, Nel AE (2008) Comparison of the mechanism of toxicity of zinc oxide and cerium oxide nanoparticles based on dissolution and oxidative stress properties. ACS Nano 2:2121–2134

Youssef OA, Tammam AA, El-Bakatoushi RF, Alframawy AM, Emara MM, El-Sadek LM (2021) Uptake of hematite nanoparticles in maize and their role in cell cycle dynamics, PCNA expression and mitigation of cadmium stress. Plant Biol. https://doi.org/10.1111/plb.13315

Zeshan A, Abdullah M, Adil MF, Wei D, Noma A, Ahmed T, Sehar S, Ouyang Y, Shamsi IH (2021) Improvement of morpho-physiological, ultrastructural and nutritional profiles in wheat seedlings through astaxanthin nanoparticles alleviating the cadmium toxicity. J Hazard Mater. https://doi.org/10.1016/j.jhazmat.2021.126511

Zhang F, Liu M, Li Y, Che Y, Xiao Y (2019) Effects of arbuscular mycorrhizal fungi, biochar and cadmium on the yield and element uptake of *Medicago sativa*. Sci Total Environ 655:1150–1158

Zhao C, Ren S, Zuo Q, Wang S, Zhou Y, Liu W, Liang S (2018) Effect of nanohydroxyapatite on cadmium leaching and environmental risks under simulated acid rain. Sci Total Environ 627:553–560

Zheng L, Su M, Wu X, Liu C, qu C, Huang H, Liu X, Fashui H (2008) Antioxidant stress is promoted by nano-anatase in spinch chloroplasts under UV-B radiation. Biol Trace Elem Res 121(1):69–79

Zhou P, Adeel M, Shakoor N, Guo M, Hao Y, Azeem I, Li M, Liu M, Rui Y (2021) Application of nanoparticles alleviates heavy metals stress and promotes plant. Growth Overv Nanomater 11:1–18

Chapter 26
Heavy Metal Remediation by Nanotechnology

Shafia Maryam and Alvina Gul

Abstract Heavy metal extraction from the earth leads to contamination in water bodies. Through water heavy metals are absorbed by living organisms. Beyond a certain threshold, these heavy metals are toxic and lead to mutagenicity and carcinogenicity. Nanomaterials are microscopic particles of size ranging between 1 and 100 nm. Nanoparticles have various unique characteristics such as conductive, catalytic, magnetic, optical, and mechanical properties. The absorption, of heavy metals by nanomaterials is an efficient method of heavy metal remediation from wastewater. Various heavy metal ions such as Cu, Zn, Ni, Co, Mn, Mg, and Fe are either absorbed by nanostructures or converted to less toxic compounds. Nanoparticles efficiently utilized up till now for heavy metal remediation are carbon nanotubes, fullerenes, graphene oxide nanoparticles, nanometal oxides, iron oxide nanoparticles, nanobots, polymeric nanoparticles, silicon nanoparticles, nanofilters, biogenic nanoparticles along with various microbes. Until now all of these have been analyzed for in vitro analysis. The results indicate that the use of these nanoparticles for remediation of specific heavy metal ions is a witness that nanotechnology is a safe and efficient strategy for bioremediation. In vitro and in vivo trials are needed for the bioremediation of waste water.

Keywords Heavy metals · Bioremediation · Nanotechnology · Polycyclic aromatic hydrocarbons · Nano-adsorbents

26.1 Introduction to Heavy Metals

Heavy metals (HMs) are constituents of the earth's crust and are extracted for chemical, paint, glass, paper, leather tanning, textile printing, fertilizers, pharmaceuticals, petroleum refining industries, along with various others. Natural sources for heavy

---

S. Maryam · A. Gul (✉)
Atta ur Rahman School of Applied Biosciences (ASAB), National University of Sciences and Technology (NUST), Islamabad, Pakistan
e-mail: alvina_gul@asab.nust.edu.pk

L. Newman et al. (eds.), *Phytoremediation*, https://doi.org/10.1007/978-3-031-17988-4_26

metal release in the environment are volcanoes, erosion of metal-containing rocks, geothermal activity, and degassing. These anthropogenic sources of water pollution have serious adverse effects and consequences for the food chain. The most common metal ores extracted include iron, arsenic, lead, gold, silver, and nickel. Extracted by mining heavy metal ores in open pits effect their close environment. Wind along with water transports these to environments, disrupting the stable functioning of the ecosystem. Heavy metals are also emitted by nature through forest fires and volcanic eruptions. Water bodies are crucial for industry, farmland irrigation, and domestic uses. At present water bodies in the vicinity of these industries are heavily polluted with metal contaminants. Heavy metals due to their high stability and solubility seep through the soil and persist in water. The presence of heavy metals in ground water is attributed to the diffusion of contaminants usually organic pollutants to the soil. The organic pollutants from wastewater enhance the seepage ability of heavy metals. This has devastating consequences for ground water reservoirs. Wastewater effluents effect both the quality and availability of ground water. Untreated wastewater is colored, frothy, and highly toxic. The quality of industrial wastewater is studied by comparison with standards of quality.

A large proportion of water on the planet is ground water. Ground water is a source of drinking water for various populations. One-third of the global population consumes ground water for domestic, agricultural, and industrial uses (International Association of Hydrogeologists 2020). Wastewater contaminating water bodies is attributed to an increase in anthropogenic activities. Multiplication of industrial products is a major factor in the three-fold destruction of aquatic life. Life exists around water bodies and contamination of water bodies impacts every particle touched by water. Heavy metal contamination in water bodies has serious consequences and adverse effects on communities dependent upon water bodies. Metals have incomplete d orbitals that form complexes with organic compounds. The binding with calcium, manganese, magnesium, copper, and zinc may be positive as they essentially become cofactors for binding in complex reactions, the same cannot be stated for binding to mercury, cadmium, and silver. These compounds persist, accumulate, and absorb in cells. In both intracellular and extracellular space these bind to proteins and other organic compounds. As a result metal uptake in living organisms is very simple and common in the water. A very simple uptake system understood is magnesium. Gram-negative bacteria, *Saccharomyces cerevisiae* along with various other microbes possess a non-specific uptake system called CorA. Along with magnesium, nickel, cobalt, zinc, and manganese are transported into the microbes. Arsenate is transported by phosphate inorganic transport, while chromate is transported by a sulfate transport system (Nies 1999).

Heavy metals are more persistent than organic contaminants. HMs have a persistent ecotoxicological impact on the food chain. HMs accumulate overtime and are absorbed by humans through inhalation, oral ingestion, or skin exposure. Metals such as Cu, Zn, Ni, Co, Mn, Mg, and Fe along with various others including essential minerals are required for a healthy diet. In contrast, mercury, lead, and cadmium are not required for human consumption. Metals in basic and neutral pH are not toxic due to their insolubility. Metals are absorbed in agricultural produce through which they enter the stomach and are converted to stable oxidation states. Metals form complexes with other compounds and proteins. These complex compounds by the bloodstream and are distributed all over the human body. Heavy metals beyond threshold concentration form complexes in cellular organelles. HMs are nonbiodegradable and as a result, are not removed from the human system. HM poisoning at a mild concentration causes diarrhea, depression, pneumonia, paralysis, vomiting, and gastrointestinal disorders. Toxicity at extreme concentrations leads to mutagenicity, neurotoxicity, and carcinogenicity. Metal toxicity is directly proportional to low pH. Low pH and change in speciation, as well as charge influence metal binding at the biological surface. Low pH increases the availability of free metal ions and free oxygen ions bind to metal ions to produce highly toxic oxyradicals. Oxyradicals along with hydroxyl radicals and superoxide anion are persistent and highly cytotoxic. Oxyradical breakdown requires stronger agents.

Water is an essential requirement of life. The previous decade is remembered for the explosive contamination of water bodies. While urbanization and industrialization are marked as the main perpetrators, careful management of anthropogenic activities can solve this crisis. Pollution in water bodies is a global challenge. The pollution level has staggered to 40% of all lakes and rivers on this planet. The five most common sources of metal deposition common all over the world include rock weathering, manufacturing, pesticides, and fertilizers (Zhou et al. 2020). Heavy metal pollution in water bodies was prioritized in policy formulation process beginning in the 1970s (Babich and Stotzky 1985; European Community 1991; Mortvedt 1996; Duan and Tan 2013). From the 1970s to 2017 the pollution level from single metal contamination has changed to mixed metal contamination, which further complicates the process of cleaning waterways. Multiple or mixed metal contamination requires a detailed study of types of metals contaminating water bodies. The next requirement is developing an environmentally friendly, yet effective strategy for remediation.

One solution discovered in nature is microbial bioremediation. Microbes are resistant to change in the environment and adapt to stress. Ancient bacterial strains are reported to have thermophilic as well as halophilic potential. Microbes found in toxic environments have evolved to tolerate and survive heavy metal toxicity. Bacteria are efficient reducers of metal ions. Metal ions are converted to crystals or simpler compounds (Iravani and Varma 2020). Microbes with metabolic diversity are a candidate for waste clean-up. Along with microbes, plants and animals are also involved in environment cleaning. Rainbow trout were studied and demonstrated 55% tolerance to Na ions by sulphydryl-rich protein (Laurén and McDonald 1987). Sulphydryl protein binds and detoxifies metals. It also stimulates metallothionein and supports the microbe's ability to tolerate exposure to metal contamination (Pascoe and Beattie 1979). It is reported that heavy metal interferes with metabolic processes in microbes and hinders the breakdown of organic biomass by microbes. These interferences were reported with mutations. Microbes with metal resistance are used as candidates for wastewater clean-ups and are reported in the literature.

26.2 Polycyclic Aromatic Hydrocarbons (PAHs)

Polycyclic aromatic hydrocarbons (Fig. 26.1) are organic Di benzene ring fused pollutants. With high hydrophobicity and low bioavailability, these are resistant to degradation with highly carcinogenic, mutagenic, and teratogenic capabilities. These compounds persist in the environment and accumulate in the environment. PAHs are accumulated in wastewater by anthropogenic activities and are absorbed by living organisms. PAHs are increasingly toxic with increasing molecular weight. The persistence of these complex chemicals is causing disasters and damaging the ecosystems. Removal of PAHs by bioremediation is an economical and safe method. PAH bind with metallic ions to gain stability and strength. This further increases their toxic potential.

Polycyclic hydrocarbons are removed from the environment by either partitioning them in non-aqueous phase liquids or absorb by sequestration in soil. Activated carbon in liquid-phase adsorption to remove PAHs from contaminated wastewater. The most popular method to remove PAHs is silica gel. Nanoparticles from poly(ethylene) glycol-modified urethane acrylate (PMUA) precursor chain mineralize phenanthrene and enhance biodegradation (Tungittiplakorn et al. 2005). Amphiphilic polyurethane (APU) nanoparticles degrade PAH. Nanoparticles produced from polyurethane acrylate are ionomer (UAA) or poly (ethylene glycol)-modified urethane acrylate (PMUA) precursor chains that are cross-linked in water through emulsification. Particles as colloids in size 17–97 nm have enhanced desorption and transport comparable to surfactant micelles. APU particles with hydrophobic interiors have a high affinity for PHEN and promote its mobility in soil. Size change influences the bioremediation property of APU nanoparticles (Tungittiplakorn et al. 2004). Nanoscale zero-valent iron with hydrogen peroxide removes PAHs from aqueous samples with oil (Haneef et al. 2020).

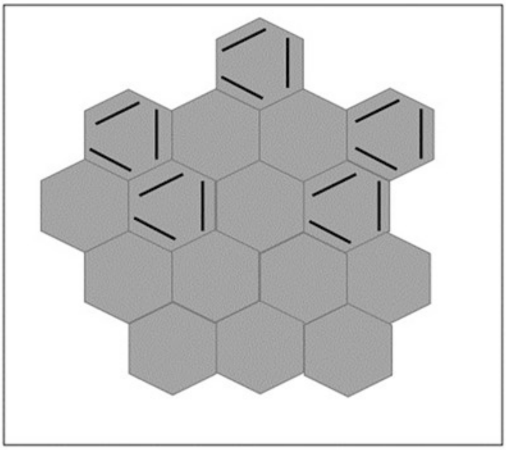


Fig. 26.1 Multiple aromatic rings fused to produce polycyclic aromatic hydrocarbon

26.3 Conventional Treatments

The quality of water impacts human and ecosystem health. With an increase in water pollution water resources need to be protected. The impure polluted water with noxious contamination is degraded by chemical coagulation, photocatalytic degradation, solvent extraction, chemical precipitation, reverse osmosis, electrochemical treatment, ion exchange along with various other methods. These strategies have been used over time individually as well as in combination. Among all these methods adsorption of heavy metal compounds is reported to be an efficient and economical method. Pollution caused by heavy metals is decreased by three strategies. The first strategy states to decrease the availability and mobility of these toxins. Once concentrated and separated these toxins can be removed from the water body. The next strategy employed is directly degrading the contaminant. While the last strategy is filtering every ounce of water to remove toxic ions and compounds. These strategies are successful and have not over time proved to be economically reliable and efficient for wastewater remediation. The problem with all these techniques and approaches begin with the incomplete removal of waste from contaminated water. With various heavy metal ions still in aqueous samples, it is toxic to all life around it. Another issue relating to these treatments is cost. These techniques require installation, operation, maintenance, labor, and resources at a massive scale. It is not practical to apply these techniques in developing or underdeveloped countries. The most important and damaging aspect for the effectivity of these techniques is environment. These high-budget techniques end up damaging the ecosystem more than saving it. A more practical approach considered for this use was adsorption by biological sources such as biopolymers, microbes, and nanotechnology. Researchers are trying to develop technology to keep heavy metal contamination away from water ways and clean and clear already contaminated water bodies. This task is harder in developing and underdeveloped countries. With limited resources and a higher level of contamination. The above-mentioned strategies fail in various parts of the world especially Africa, India, the Far East, and the Middle East. The third world primarily suffers due to these problems. An out-of-the-box solution is needed to sort remediation of waterways as many populated cities in the world are already starving with loss of drinking water.

26.4 Bioremediation

Environment influences all life around it in both negative and positive forms. A healthy environment raises healthy offsprings while a contaminated environment damages the entire ecosystem. With changing times land is not an abundant resource and any site left contaminated is creating a global crisis in various parts of the world. Contamination and pollution are plagues that cannot be contained within borders. Contaminated sites are a potential threat to human health and the ecosystem. This makes the need to clear contaminated zones holistically, economically, and efficiently even more important. With human civilization reaching its pinnacle it is necessary to sort out a permanent solution for wastewater. Climate change and its devastation have brought mankind to confront problems created in the environment. Waste sites by conventional approach were cleaned by digging a landfill to fill with contaminated waste. This was a short-term solution with high cost and maintenance. The next approach adopted was to destroy pollutants completely by various techniques such as incineration along with chemical decomposition. Both these techniques are complex and expensive and were neither practical nor economical for long-term steps to clear contamination. The new approach applied after these failed attempts were bioremediation. Bioremediation is the biological degradation of organic waste in controlled conditions until the concentration level of toxic compounds is below the threshold. Bioremediation employs microbes such as bacteria, fungi, or plants to degrade compounds. Bioremediation is an economical, efficient approach to a clean environment. It proves to be the most environmentally friendly approach while all other approaches proved to be damaging to the environment.

26.5 Nanoparticles

Nanotechnology is a relevantly new technology utilized to resolve problems that previously could not be solved. Nanotechnology is a revolution in modern science with development in energy, medicine, electronics, and space sciences. Nanotechnology is the foundation of new materials of nanometer size. Nanomaterials are microscopic particles of size ranging between 1 and 100 nm (10^{-9} m). Nanoparticles are not visible to the human eye and require high-resolution equipment for investigation such as scanning electron microscopy Field Emission Scanning Electron Microscope (FESEM), Tunneling Electron Microscope (TEM), Atomic Force Microscopy (AFM) along with various other techniques. Nanoparticles possess distinct specific physical-chemical properties as compared to bulk materials. Nanoparticles have various unique properties such as conductive, catalytic, magnetic, optical, and mechanical properties. Particles on conversion to nano state have a threefold enhanced capacity. A conductor of light, heat or current becomes a stronger conductor. This unique aspect is the reason behind extensive applications of nanotechnology. Nanotechnology today is used for biomedical sciences, electrical engineering, imaging to many more fields. With outstanding results and a reputation to solve complex problems nanotechnology was a go-to candidate for environment cleaning.

Nanoparticles are produced by two approaches: Top-down and Bottom-up. In a top-down approach, materials undergo a reduction in form and size to reach the nanoscale. Opposite to the top-down approach nanoparticles can be produced by building small particles and monomers to the nanoscale. The bottom-up approach controls the size, shape, surface morphology, and conformation of nanoparticles.

Nanoparticles with a specific shape, size, and distribution are achieved by optimizing synthesis protocol, along with identifying reducing agents, stabilizers, optimum temperature, optimum pH along with time duration for production of nanoparticles.

26.6 Nanotechnology for Bioremediation

Nanotechnology with exceptional development is a solution to various complicated problems. Nanotechnology is employed to reduce pollutant concentration in the environment. Nanoparticles are used as renewable reagents to replace toxic agents in product manufacturing. One such example is nano-based home lighting to reduce electricity consumption by 10% and carbon emissions by 200 million tons per year (*National Nanotechnology Initiative: The Initiative and Its Implementation Plan* 2001). Nanocatalysts are efficient for providing specificity for compound. Zeolites or aluminosilicates are used for separations and catalysis. These selectively oxidize hydrocarbons such as toluene or benzaldehyde. Zeolites as part of nanostructures initiate low energy oxidation in visible light (Panov et al. 2000).

Nanoparticles exhibit unique reactivity that is unusual with crystal and lattice structures. In situ remediation of chlorinated organic solvents produces undesired by-products, namely, vinyl chlorides and dichloroethylene. Nanoparticles provide this advantage in bioremediation, with zero by-products production (Elliott and Zhang 2001). Nanoparticles also find a unique prospect as sensors of organic contamination. Zinc oxide nanoparticles are sensors as well as photocatalysts for chlorinated phenols (Kamat et al. 2002). Nanoparticle surfaces are modified and coated with organic and inorganic dyes to enhance photocatalysis. The matrix of carbon nanoparticles with zeolites was deployed with ex situ slurry reactors for treatment of contaminated water (Ponder et al. 2000). Iron, zinc, palladium, and silver nanoparticles reduce contaminants such as PCBs, organochlorine, pesticides, and halogenated solvents (Zhang et al. 1998). Metallic nanoparticles reduce recalcitrant contaminants such as anions, radionucleotides and heavy metals (Fig. 26.2).

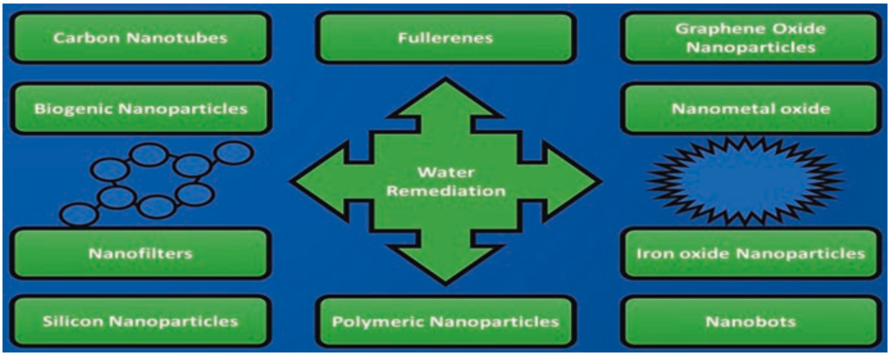


Fig. 26.2 Heavy metal remediation strategies by nanotechnology

Nanotechnology is a zero-chlorine option for water purification. Chlorine is a carcinogenic by-product and has devastating consequences. Various previous studies are a witness to the capacity of microbes and plants immobilizing heavy metals in aqueous samples. Nanotechnology uses oxidation process for degradation of pollutants ranging from pesticides, pharmaceuticals, endocrine receptors, cosmetics and other synthetic products. Nanoparticles are produced by synthetic and natural methods (Ali et al. 2018).

26.7 Nano-Adsorbents

The absorption, of heavy metals by nanomaterials is an efficient method of heavy metal remediation from wastewater. Many nano sorbents have already been commercialized and are employed to clear water bodies. Pollutants are absorbed on the surface by covalent and non-covalent bonding. Nanoparticles are engineered with large surface areas and small intraparticle distance to facilitate diffusion (Kalfa et al. 2009). Nanoparticle surfaces are modified to absorb contaminants. Active absorption sites are created on these nanomaterials by increasing surface energy on basis of size-dependent surface structure along with pore size. These contaminants can then be desorbed by modulating the pH and temperature of the solution. Nanomaterials with the ability to desorb contaminants are economical and recycled again (Saikia et al. 2011, 2013; Saha et al. 2011). Nano-adsorbents consist of different nanomaterials and are broadly classified into various categories like metallic nanoparticles, nanostructured mixed oxides, magnetic nanoparticles, and metallic oxide nanoparticles (Al_2O_3, TiO_2, MnO_2, ZrO_2, ZnO, MgO, CeO_2), based on their role in the adsorption process (Gupta et al. 2015). Another new series used is carbonaceous nanomaterials (CNMs) which include carbon nanotubes, carbon nanoparticles, and carbon nanosheets that have also been assimilated into these categories. Absorbents need to be packaged, transported, and stored after absorbing heavy metals. The synthesis of absorbents is designed to combine various functional extensions upon the nanomaterials to achieve high performance.

Nanoparticles due to their small size have a large surface area. This enhances the adsorption capacity on the metal surface of persistent inorganic pollutants. Nano-adsorbents have two main properties listed innate surface and external functionalization. Nano-adsorbents are designed for physical, chemical, and material properties along with surface structure, size, and composition. Nanobiotechnology is used for bioremediation. Nanoparticles form on cell wall surfaces by enzymes reducing metal ions to positively charged particles. The particles aggregate by using specific enzymes such as NADH-dependent reductive along with nitrate-dependent reductive. Adsorption is recorded to be faster with rising temperature, due to the high diffusion rate which facilitates ion exchange between compounds. The ionic strength of compounds also influences bioremediation. The presence of chloride ions produces stable complexes with heavy metals with high solubility (Ferraz and Lourençlo 2000).

26.8 Carbon Nanoparticles

Nanoparticles with carbon have been constructed with various strategies. Carbon nanoparticles are classified as nanotubes, graphene, graphene oxide, and fullerenes. Carbon nanoparticles are easy to modify by both chemical and physical methods. Along with easy modification, their extraordinary electrical and thermal abilities make them a strong contestant for bioremediation. Two carbon-based nanomaterials used for wastewater remediation are carbon nanotubes-based and graphene-based nanomaterials (Dresselhaus and Terrones 2013; Smith and Rodrigues 2015). Hg^{2+} can be removed by multiwalled carbon nanotubes (MWCNTs) modified with different geometrical dimensions (El-Sheikh et al. 2011). Multi-walled carbon nanotubes were modified with sulfur to create nano assembly of two-layered hydroxide crystals on the surface of the nanosphere.

26.9 Carbon Nanotubes

Carbon nanotubes (CNTs) are layered rolled-up graphene sheets. These are single-wall as well as multiwalled structures with diameters from 1 nm to several nanometers in size. With large surface area and specific porosity, heavy metals absorb in the cervices of nanotubes. With a large surface area, carbon nanotubes are highly efficient in wastewater treatment compared with other carbon nanomaterials. Surface modification further improves this efficiency. Raw CNTs are not absorbent without acid treatment to clean the surface of CNT and modify it with functional groups to enhance the absorbance of heavy metals (Al-Khaldi et al. 2015; Al-Hakami et al. 2013; Renou et al. 2008; Ren et al. 2011). Metal oxides such as iron oxide or manganese oxide are grafted upon the CNT surface (Tang et al. 2012; Chan et al. 2012). The absorption mechanism along with affinity to certain metals depends upon properties such as pH, temperature, and contact time between metals and CNT (Li et al. 2005; Lu and Liu 2006; Ren et al. 2013). The pH reported for maximum removal of Cu^{2+} is 7, Zn^{2+} is 3, and for Cr^{6+} is 5 (Ren et al. 2013; Lu and Chiu 2006). Li et al. (2005) conducted a study to determine the optimum contact time for Pb^{2+}. For 10 mgL^{-1} 20 min are required. While for 20 mgL^{-1} the time duration prolongs to 50 mins (Li et al. 2005). The grafting of functional groups is achieved by surface utilizing plasma, along with adsorption strategies by electron affinity. CNTs remain physically and chemically stable. Their mechanical and magnetic properties help bind heavy metals (Ihsanullah et al. 2016). Yet this technology has only been used in lab-scale projects due to cost constraints along with concerns over the environment (Hlihor et al. 2017; SenthilKumar et al. 2011). CNT efficiently absorbs heavy metal ions such as As^{3+}, As^{3+}, Th^{4+}, Eu^{3+}, Sr^{2+}, U^{6+}, Cu^{2+}, Ni^{2+}, Cd^{2+}, Pb^{2+}, and Cr^{6+}. Surface Modifications by chemicals improve the absorbance capacity of CNTs (Gupta et al. 2016).

26.10 Fullerenes

Fullerenes are closed pentagonal and hexagonal ring structures assembled as soccer balls. Hydrophobic in nature, fullerenes have high electron affinity, surface area, and surface-to-volume ratio. Heavy metal contamination binds to fullerenes due to its unique physicochemical properties. Fullerenes absorb charged ions between carbon nanoclusters. Hydrophobic functionalized fullerenes have been used in killing pathogenic aqueous microbes by photocatalytic reaction (Brunet et al. 2009). Nanocomposite-polystyrene film removed Cu^{2+} from wastewater. The initial removal was reported higher with gradual decline until an isotherm equilibrium was established. Converting fullerenes to fabrics or biofilms decreases hydrophobicity which renders fullerenes less effective in clearing heavy metal remediation (Alekseeva et al. 2016). Activated carbons modified with fullerenes enhance the metal ion absorption capacity of activated carbon (Samonin et al. 2008).

26.11 Graphene Oxide Nanocomposites

Graphene oxide is a chemically active compound with high oxidation capacity. The high oxidation capacity has a surface with carboxy, epoxy, and hydroxyl groups. Graphene oxide with low electric capacity and high surface modification with the functional capacity to remove heavy metal particles in the wastewater. Graphene oxide is used as a modified absorbent, membrane filter, and photocatalyst to clear wastewater of heavy metal contamination. Graphene oxides were modified with triotylamine absorbed 99.4% Cr^{4+} in 1 h (Kumar et al. 2013). Synthetic Nanocomposites modified with iron oxide removed arsenic and magnetite from polluted water (Chandra et al. 2010). Modified with TiO_2, ZnO, Cu_2O, and iron oxides graphene oxide nanoparticles are three times more efficient in degrading dyes from wastewater. Cr^{4+} is reduced to less toxic trivalent Cr^{3+} by ZnO and TiO_2 nanocomposite (Li et al. 2012). Through covalent grafting polymeric compounds are bonded to graphic oxide nanocomposites. Trioctylamine-modified graphene oxide nanocomposites have a high absorption capacity for Cr^{4+} along with various others (Kumar et al. 2013). Thiographene modified with lipase is reported to have 16% ester bond cleavage. Immobilized enzymes bonded to thiographene have heterogenous enzymatic capacity. Hydrolytic and oxidoreductase reactions by enzymes degrade compounds to simpler forms (Sturala et al. 2019).

26.12 Nanometal Oxides

Nanosized metal oxides include iron oxide, manganese oxide, aluminum oxide, and titanium oxide. The efficiency of these nanoparticles is dependent on size, shape, stability, and dispersibility. Nanoparticle synthesis is classified into two categories one is the physical approach (Inert gas condensation, severe plastic deformation, high-energy ball milling, and ultrasound shot peening), and the other being, Chemical approach (microemulsion, chemical co-precipitation, chemical vapor condensation, pulse electrodeposition, liquid, and gas-phase reduction along with various other methods). Heavy metals are in cationic forms at neutral to low pH. At higher pH hydroxides are formed with anions that cause the oxidation of metals such as Chromium (Joseph et al. 2019). Chromium from its stable form of Cr (III) transforms to Cr (VI) (Pantsar-Kallio et al. 2001). Furthermore, negatively charged nanoparticles readily react with positively charged heavy metals with high pH.

Zinc oxide (ZnO) nanoparticles with photocatalysis with high oxidizing power with a characteristic band gap in UV spectral region. ZnO nanoparticles adsorb heavy metals and are structured as nano-plates, microspheres, nanorods, and other assemblies. Zinc oxide nano-plates and porous nano-sheet remove Cu^{2+} (Wang et al. 2010). Copper nanostructures are synthesized with biomass and have excellent catalyzing capacity. Zero-valent copper nanoparticles with sodium borohydride were employed as a catalyst for dichloromethanation and dichlorination of contaminated ground water. The analysis proved a 90% surge in the reduction of dichloromethane (Huang et al. 2012). Copper oxide nanoparticles prepared by leaf extract of *Psidium guajava* were spherical, mono-dispersed nanoparticles with 93% degradation efficiency against Nile blue and 81% against reactive yellow 160 dyes. These dyes are carcinogenic and block sunlight. Exposure to these is a menace for aquatic as well as human life (Singh et al. 2019). Platinum and palladium cell-supported nanoparticles produced by *Desulfovibrio vulgaris* are efficient reducers of various pharmaceutical products such as ciprofloxacin, sulfamethoxazole, ibuprofen, and 17β-estradiol (Martins et al. 2017). Biogenic manganese oxide nanoparticles were prepared with *Pseudomonas putida.* In in situ trials, the nanoparticles removed estrone and 26% dichlofenac (Furgal et al. 2015). Gold nanoparticles attached to sodium borohydrate and *E. coli* K12 cells efficiently disintegrate 4-nitrophenol (Kumar et al. 2013). Nano silver has been used for the purification of water for use in drinking (Liu et al. 2014; Kim et al. 2012). Nano silver is used for the preparation of anti-bacterial fouling membranes to purify water.

26.13 Iron Oxide Nanoparticles

Iron possesses potent magnetism and catalytic ability along with high reactivity. Iron oxide nanoparticles are synthesized with ease and with a high surface-area-to-volume ratio for use in bioremediation. Surface modification along with strong magnetic ability is compatible to absorb metallic contaminants efficiently from wastewater. Iron oxide in nature exists as magnetite (Fe_3O_4) along with maghemite (γ-Fe_2O_3), and hematite (α-Fe_2O_3) (Cornell and Schwertmann 1996). Nanoparticles produced with iron exhibit magnetism and are superparamagnetic. These ferromagnetic materials with large surface area and low toxicity are used for biomedical applications. These nanoparticles are relatively easy to modify and have low toxicity with high biocompatibility with the environment. Some common strategies to produce magnetic nanoparticles are liquid phase methods, two-phase methods (microemulsion), aerosol method, polyols method, sonolysis, and hydrothermal and sol-gel method.

To remove Cu from aqueous solutions FeO adsorbents with a pollutant removal rate of 149.25 mg g^{-1} (Grossl et al. 1994; Schwertmann and Taylor 1979). The surface of FeO was modified with humic, polyacrylic acid, amino, and alginic functional groups. For removal of copper and chromium magnetic nanoparticles were employed. The surface of nanoparticles was amino-functionalization and showed a removal rate of 11.24 and 12.4 mg g^{-1}(Huang and Chen 2009). Nickel-ferrite nanoparticles synthesized by co-precipitation were used to absorb and heavy metal contamination from synthetic wastewater samples. Optimum removal parameters reported were pH 3–7, dose and contact time respectively 10, 20, 30, 40, 50 mg for 30-, 60-, 90- and 120-min. Removal efficiency for Cr^{4+}, Pb^{2+}, and Cd^{2+} were reported 89%, 79%, and 87%, respectively (Khoso et al. 2021).

Nanoscale zerovalent iron (nZVI) is a reducing agent for groundwater remediation. nZVI removes contaminants such as halogenated, nitrogenous, phenolic, inorganic compounds along with radioactive compounds and heavy metal compounds. Electrons are transferred from Fe^0 through which organic pollutants are removed from the water. Small size with a large surface area makes them efficient candidates for water remediation. Pollutants such as polychlorinated pollutants, organic and inorganic ions, and anions along with dissolved heavy metals are dissolved by nZVI due to their exceptional characteristics. nZVI nanoparticles are modified with large surface areas yet small to absorb heavy metal ions. Surface modifications upon these include emulsification with other techniques. Under anaerobic conditions, Fe_0 is oxidized to Fe^{2+} in aqueous environments. Fe^{2+} is oxidized to $Fe(OH)_3$ with high pH to remove heavy metals such as chromium in water bodies. Organic compounds are oxidized to produce O_2 by Hydrogen peroxide. Hydrogen peroxide in combination with ferric ions produces hydroxyl radicals that bind metal ions. Iron nanomaterials due to redox potential and large surface area remove heavy metals from water (Li et al. 2003). Additives such as are aminopropyltrimethoxysilane modified to the surface of Fe_2O_3 to enhance the absorption of certain heavy metals (Palimi et al. 2014).

26.14 Polymeric Nanoparticles

Polymeric Nanoparticles along with nano-clays, nanofibers, and aerogels are used for the bioremediation of heavy metals. Polymeric membranes are used for the desalination of wastewater. Polymeric nanoparticles used for water purification are a long-term solution. The adsorption properties of nanoparticles are manipulated by varying the following properties. The pore size of polymeric nanoparticles can be controlled which enhances adaptability. Other membrane properties are modified by selecting specific additives, coagulants, and monomers to enhance adsorption properties (Goh and Ismail 2018; Yin and Deng 2015).

Chitosan for its absorbent properties is used to absorb heavy metals. Chitosan was modified with poly (acrylic acid) to produce magnetic chitosan for the uptake of Pb^{2+}. The maximum absorption capacity recorded was 204.89 mg/g in 1 h 10 min. The efficiency recorded was 96% removal efficiency (Hu et al. 2020). Magnetic γ-Fe_2O_3 were embedded with chitosan/cellulose beads to absorb heavy metals. The maximum absorption recorded for Cu^{2+}, Cd^{2+}, and Pb^{2+} were found as 88.21, 61.12, and 45.86, respectively (Luo et al. 2015). A study by Ahmadi et al. 2017 reported γ-Fe_3O_4 modified with chitosan absorbed more Cd^{2+} than pure chitosan or γ-Fe_3O_4. Amino groups and hydroxyl groups from chitosan act as active sites, along with oxygen atoms of γ-Fe_3O_4 to absorb Cd^{2+}. Magnetic modification by grafting chitosan enhances the adsorption capacity of nanomaterials. Properties affecting nanoparticles efficiency to absorb heavy metals is shape, size, state, crystallinity, structure, solubility, chemical composition, surface chemistry along with agglomeration rate.

26.15 Silicon Nanoparticles

Besides this, different silicon-based nanomaterials are also used as nano-adsorbents such as silicon nanotubes, silicon nanoparticles, and silicon nanosheets. Silicon dioxide nanoparticles coated with fungal biomass removed cadmium from wastewater (Ali et al. 2019). Silicon dioxide nanoparticles by Langmuir isotherm calculations are reported to absorb 93.6% Cr^{4+} in optimal conditions and 88.6% efficiency rate with a real sample (Ranandeh Kalankesh et al. 2015). Silica gel is a strong absorbent that adsorbs acenaphthene (Hall et al. 2009). Silica gels with entrapped yeast and bacteria have been used for environment cleanup. Silicon nanowires with boron doping hold functional amine and oxide groups on the surface. These nanowires are sensitive to pH changes along with the detection of pharmaceuticals such as streptavidin, even at picomolar concentrations (Cui et al. 2001). Strontium ions are absorbed by silica pellets coated with zirconium phosphate (Jiao et al. 2021).

26.16 Nanobots

Micro/nanobots are used to remove contamination. These auto-propelled nanoparticles convert contaminants to non-toxic compounds based on surface chemistry. Nanobots can be operated by guided motion to monitor water bodies. They detect external stimuli. They are economical, energy-saving water treatment options for mega-scale bioremediation projects (Shivalkar et al. 2021). Nanomaterials incorporated in nanomotors assist in faster electron transfer to increase the catalytic activity and velocity of nanomotors. Nanobots produced by the fabrication of pollen grains remove Hg^{2+} (Maric et al. 2020). Platinum-coated tubular halloysite nano clay nanomotors remediate Zn^{2+} and Cd^{2+} from water samples (Maric et al. 2018).

Nano and microrobots have enhanced sensing and biosensing capacity. With the minute size and easy-to-control nanoparticles in microfluidic chips to sense heavy metals in motion. These are ideal candidates for microenvironmental sensing. Self-propelled nanomotors have efficient use for sensing and removing pollutants. Nanoparticles were constructed with platinum and iron oxide, with a bilayer of titanium oxide. Silica coating made it an efficient absorbent of pollutants. The bubble-propelled nanomotor absorbs three times metals in comparison to any standard Titanium oxide tube (Liang et al. 2018). Nanomotors constructed with metal-organic frameworks are tailored with functional structures to bind metal ions on active sites. The specific pore site with bubble propulsion and large surface area is efficient to remediate heavy metals (Khezri and Pumera 2019). Nanomotors are propelled by artificial motion such as light-stimulated nanomotors. TiO_2 along with various other metal oxides. Micromotors constructed with platinum catalysts quench hydroxyl radicals along with O_2 bubbles to detect glutathione cysteine and methionine (Zhao et al. 2013). Nanopiezocatalysts are composed of bismuth ferrite degraded organic pollutants in presence of UV-visible light (Mushtaq 2019). Nanojets are autonomously propelled, high-efficiency jets prepared with nanoclay. Tubular halloysite nanoclay jets efficiently detect and remove metal ions from contaminated water samples. Most metal ions removed included (Hg^{2+} and Pb^{2+}, Zn^{2+} and Cd^{2+}). (Maric et al. 2019).

26.17 Nanofiltration

Nanomembranes have barriers with properties based on applications. Nanomembranes vary by pore size, surface hydrophobicity, roughness, and chemical stability. Pore size determines the permeability of membranes, while surface hydrophobicity affects membrane fouling characteristics. Nanofiltration removes pollutants by the size-exclusion mechanism. The process is sensitive to variations in pH, temperature, pressure, and membrane chemistry along with the concentration of the incoming feed. Research proves increase in pressure leads to higher removal of metals such as Pb^{2+} (93%) and Ni^{2+} (86%) (Hosseini et al. 2016; Maher et al. 2014).

Along with size nanofilters remove pollutants by charge exclusion. Nanofiltration membranes have charged surfaces. Based on the materials of membranes the charge varies. Materials such as piperazine (PIP) give a negative charge, while poly(amidoamine) (PAMAM) along with polyethyleneimine (PEI) are positively charged (Zhu et al. 2014). Two enhanced efficiencies for heavy metal removal double-layered membranes are used. One such example is polybenzimidazole (PBI) and polyethersulfone (PES). This combination efficiently removed 95% Cd^{2+} along with Co^{2+} (Cheng et al. 2011). Another research Zhu et al. (2015) proved a 99.2% removal rate of copper, cadmium, and arsenic by PAMAM nanomembrane. A study by Al-Rashdi et al. (2013) used NF270 membranes prepared by polyamide for metal remediation. The membrane is a thin piperazine-based microporous polysulfone layer with a positively charged surface when the solution pH is lower than 3.3–4. The study revealed that the NF270 membrane prepared for metal ions removal that constant pH with 1000 mg.L^{-1} cause 100% removal of Cu ions through a nano filter. Increasing the concentration of ions reduces the filtration rate to 58%. The order of metal absorption revealed was $Cu^{2+} > Cd^{2+} > As^{3+} > Mn^{2+} > Pb^{2+}$. Sulfonyl and amide groups are incorporated in a dual functionality organic framework. The combination of various chemicals enhanced the absorption of various heavy metals. TMU-81 nano filter was reported to have a significantly high enhancement of Cd (II), Cu (II) along with Cr (II) in an aqueous environment. Reshaping TMU-81 to a network structure increased pore size to provide a metal-organic framework. To enhance the economic potential of TMU-81 as a multifunctional remediation filter, recycling by pyrolysis is applied. Pyrolysis at 800 °C with argon gas can recover metal-carbon hybrids (Esrafili et al. 2021).

26.18 Microfiltration and Ultrafiltration

Microfiltration along with ultrafiltration trap heavy metals, colloids with suspended particles. Heavy metals are attached to the polymeric ligands of these filters. Particulates and metal matters are dissolved by membrane filters. With increased permeability, selectivity and anti-fouling efficiency membrane technology have effectively cleared bioremediation. Nanomembranes' efficiency has been enhanced by the use of organic, inorganic, and polymeric particles to remove heavy metals and fouling in aqueous bodies. Metal ions by electrostatic attraction are trapped in the ultrafilter (Barakat 2011). The polymeric ligands most applicable are poly(acrylic) acids (PAAs), carboxyl methylcellulose (CMC), polyvinyl ethyleneimine (PEI), and poly(acrylic) acid sodium salts (PAASS). Polymeric ligands are reusable and decrease operating costs. For specific removal of certain metals, the parameters of polymeric ligands are adjusted according to the molecular weight, chemical and mechanical stability, solubility, and low toxicity (Qiu and Mao 2013). The pH of the solution affects the membrane charge of polymeric ligands, which may cause ionic rejection for certain metals (Lam et al. 2018). Environmental conditions along with pH are constantly monitored and controlled during the process. It was reported that higher pH causes sedimentation by hydroxide formation (Lam et al. 2018; Crini et al. 2017). Nanomembranes are used for both secondary as well as tertiary treatment of wastewater. Nanomembranes are coated with titanium. Titanium due to its photocatalytic capacity degrades organic contaminants and microbes when exposed to UV light (Li et al. 2008; Danion et al. 2004).

An effective membrane developed for water filtration is called a mixed matrix membrane (MMM). Nanomaterials are mixed with polymers, thin films, and porous matrices along with nanocomposites are called mixed matrix membranes (Kim et al. 2007). These membranes effectively separate agitated fillers in the matrix.

Thin film composites present in these MMMs separate small molecules by reverse osmosis and other diffusion mechanisms (Jeong et al. 2007; Lind et al. 2009).

26.19 Biogenic Nanoparticles

Biogenic nanoparticles are used for the diagnosis of various chronic diseases. Biogenic nanoparticles are produced by reducing silver particles with supernatants of bacterial cultures. Bacterial nanoparticle size is optimized by adjusting size and morphology by adjusting the time of reaction (Kapahi and Sachdeva 2019). Microbes in an anaerobic environment remove recalcitrant pollutants, along with electricity generation from wastewater. Heavy metals are absorbed into the biological membranes by passive transport. Accumulation of heavy metals in cells disrupts metabolic pathways in cells, leading to apoptosis (Klaus-Joerger et al. 2001).

Production of biogenic nanoparticles begins with mixing extracts with metallic salts in solution. The salt is reduced into mono or divalent ions. This is indicated by the change in color. This process proceeds zerovalent state, eventually to nucleation of reduced metal nanoparticles. Nanoparticles are charged and amalgamate together to form larger compounds. These large masses lose the essential properties that make nanoparticles unique. Nanoparticles are capped with synthetic chemicals to stabilize nanoparticles in nano conformations. The chemicals used include sodium borohydrate, hydrazine hydrate, amines, and thiols. These synthetic chemicals are a threat to ecosystem stability. Ethical concerns ban the release of nanoparticles coated with harmful chemicals in the environment. The research then shifted to using biochemicals to coat nanoparticles. Biological compounds with reduced capacity can replace synthetic chemicals. Polyphenols, peptides, amino acids along with other bioactive compounds from living organisms. Plants and microbes are biofactories with nutrients that can be used as capping agents.

Plant extracts are used to reduce metallic salts for the production of nanoparticles. Nanoparticles are produced with Fe, Zn, Au, Ag, Pd, Cu, Mn, and many other metals. Biogenic nanoparticles ionize heavy metal compounds on the cell wall. By various enzymatic reactions, biotransformation of heavy metal compounds produced metallothioneins along with other exopolysaccharides around the cell wall. Along with ionization bacteria also utilize various other techniques to reduce metal bioremediation. Biosorption and bioaccumulation of heavy metals by living biomass is a viable solution for clearing the water of toxic heavy metals. Change in the oxidation state of metals facilitates deposition upon microbial membranes. Nanomicrobes are efficient in the biosorption and degradation of contaminants due to their large surface area. Microbes with high catalysis are efficient sorbents and degraders of metal ions.

26.20 Nano Cellulose

Lignocellulosic biomass is the dry matter of plants. Plant cells are composed of two different polymers, cellulose, and lignin. The composition of these two polymers varies in all plant types but, cellulose is a major component of lignocellulosic biomass in the plant cell wall. Cellulose is composed of repeating units of anhydro-d-glucose units linked together in a linear chain. These monomers are composed of hydroxyl groups that form strong inter and intramolecular hydrogen bond networks. The alignment of glucose with varied hydrogen bonding networks, leads to differentiating allomorphs of cellulose. Yet essentially cellulose is composed of carbon, glucose, and hydroxyl groups. Nanocellulose fibers are less than 100 nm in diameter to many micrometers in length. Their properties include high tensile, mechanical, and thermal strength and are exceptionally stronger than Kevlar fibers. Their biosorbent properties, green biomaterial status, and abundance in nature make them a potential candidate for metal ion extraction. Nanocellulose provides more active sites for the surface binding of metal ions. Hydroxyl groups on nanocellulose surface immobilize metal ions while hydrophobicity of nanocellulose reduces the risk of biofouling in an aqueous medium. These hydroxyl groups are also modified with amino, aldehyde, carboxyl, sulfate, phosphate, thiol, and any other groups. It is also resistant to biological degradation due to its high crystallinity. Operational hindrances involved with nanocellulose include low absorption capacity in long term, due to agglomeration, immobilization, and cost-effectiveness. Carboxy cellulose nanofibers are an effective medium to remove Cd^{2+}(Sharma et al. 2018).

26.21 Yeast

Yeast is a model organism for simple eukaryotes Yeasts are active agents for various food products such as bread, wine, and beer. Yeasts are simple eukaryotes and ideal candidates for genome modification along with accessibility in gene cloning. Yeasts have the absorbent capacity, are easy to grow, and with a strong mechanism for biosorption to remove metal ions. Baker's yeast (*Saccharomyces cerevisiae*) removes Pb, Au, Co, Cu, and Fe along with various other cations (Dhankhar et al. 2011; Simmons et al. 1995; Wang and Chen 2006). In yeast oxidoreductases along with quinone facilitate nanoparticle formation. Glutathione contributes to the detoxification and bioreduction of free radicals and xenobiotics (Roy et al. 2015). Bioremediation of phenol and ethanol was recorded with non-biodegradable polymers produced with coaxial electrospinning upon yeast core. The yeast utilized was *Candida tropicalis* (Letnik et al. 2015).

26.22 Fungus

Fungus has unique capacity to withstand stress conditions of moisture, pH, and nutrients. Fungus absorbs heavy metals in their food bodies. The fungal cell wall composed of chitin, proteins, glucans, lipids, and polysaccharides has various functional groups. These functional groups such as hydroxyl, carboxyl, amino, phosphate, or sulfate form complexes with metal ions (Remacle 1990). Fungi secrete proteins with extracellular hydrolyzing capacity. Fungus hydrolyzes metal halides in acidic conditions. Cationic proteins in fungus reduce metals to nanoparticles. *Fusarium oxysporum* was utilized to produce nanoparticles. α-NaDPH-dependent nitrate reductase with peptides was capping agents on silver nanoparticles (Ahmad et al. 2003). Quinine and derivatives of naphthoquinone have proved to be productive in nanoparticle production (Moghaddam 2010) Zirconium, silica, and titanium ions have already been utilized for production of biogenic nanoparticles.

26.23 Algae

Algae are autotrophic organisms known to be the most efficient photosynthates on the planet. Three algal phyla are reported to possess metal ion biosorption capacity. These include brown, green, and red algae (Phaeophyta, Rhodophyta, and Chlorophyta). Algal proteins possess active functional groups such as amine, carboxyl, hydroxyl, sulfate, and phosphate. These proteins form metal complexes (Romera et al. 2007). Algae nanoparticles are alternative bioremediation for the safe removal of heavy metal ions. Algae produce nanoparticles both extra and intracellularly. Nanoparticles produced by algal extracts from *Chlorella pyrenoidosa* have intrinsic crystallinity along with surface stabilization along with functional moieties to degrade wastewater contaminants (Aziz et al. 2015). *Chlorella vulgaris* nanoparticles are produced with various metal salts TiO_2, ZnO, NiO, CuO, and Fe_2O_3. These biogenic nanoparticles have bioremediation activity (Adochite and Andronic 2021). Sugar polymers present in algae extracts prevent the agglomeration of nanoparticles. Three brown seaweeds *Petalonia fascia*, *Colpomenia sinuosa,* and *Padina pavonica* aqueous extracts were used as reductants for iron oxide nanoparticles. The application of nanoparticles using seaweed extracts could be alternative safe bioremediation of wastewaters. Currently, iron oxide nanoparticles are used to reduce nitrogen and phosphorus and reduce the blooming of harmful algae; little information about this issue has been reported (El-Sheekh et al. 2021).

26.24 Cyanobacteria

Cyanobacteria or blue-green algae are called the most efficient photosynthates on the planet. Efficient absorption of heavy metals by Cyanobacteria is reported in the literature. Two species of cyanobacteria *Nostoc calcicola* HH-12 and *Chroococcus* sp. were investigated for absorbing Cr^{4+} from samples of heavy metal-contaminated water sampled from the premises of the Textile Industry (Anjana et al. 2007). Spirulina is documented for absorbing high proportions of Pb^{2+} and Zn^{2+} from water samples (Aneja et al. 2010; Zinicovscaia et al. 2015). Gold is accumulated in cell walls in chloride solution. Chloride promotes the precipitation of amorphous gold-sulfide compounds in cell walls and cell surfaces near platelets (Lengke et al. 2006). Cyanobacteria possess the ease to modify with changing environmental conditions. One effective technique employed is the formation of an exopolysaccharide biofilm. Heavy metals are absorbed to the unique anionic heteropolysaccharides. The exopolysaccharide biofilm is formed by a combination of proteins expressed by specific genes in cyanobacteria. As a result, different species of cyanobacteria absorb different combinations and different ratios of heavy metals (Potnis et al. 2021).

26.25 Bacteria

Bacteria ubiquitously exist in the environment. Bacteria are efficient bio absorbers of pollutants. Bacteria possess a mechanism for resistance to metal ions. (Mustapha and Halimoon 2015). Bacterial biomass efficiently absorbs heavy metals such as Cu, Zn, Pb, Cd, and Cr. Bacterial cell wall with high anionic functional groups such as peptidoglycan, teichoic acids, lipopolysaccharides, phospholipids, and teichuronic acids has metal binding capacity. The interactions with heavy metals are facilitated by various functional groups including carboxyl, hydroxyl, amine and phosphate. (Sherbet 1978). Bacteria enrich the stable complex of gold compounds (Lengke and Southam 2006). ZnS nanoparticles are stabilized by *Rhodobacter sphaeroides* immobilized cultures. ATP Sulfurylase with sulfate permease and phospho adenosine phosphosulfate reductase facilitates the production of nanoparticles. The particle size is optimized by culture time and its immobilization upon the beads (Bai et al. 2006). Antibacterial activity of nanocomposites immobilized with bacterial composites. Copper phosphate hybrid nanoflowers in presence of *Pseudomonas aeruginosa* dissolute Cu^{2+} with catalytic efficiency (Gao et al. 2020). With gamma proteobacteria and actinobacteria, biodegradable membranes are prepared for the bioremediation of crude oil (Catania et al. 2020).

26.26 Recommendations

Waste from various sources discharged in water bodies has been treated in in vitro experiments. Most investigations gave fruitful results with nanomaterials effectively degrading heavy metal. The same is reported with biomass. Yet until these strategies are commercialized, the environment cannot be cleared of hazardous toxins. For wastewater bioremediation, a feasible, sustainable, and systematic strategy is urgently needed. It is necessary to ensure coordination at all necessary levels from research institutes, governing institutes, commerce, and the public itself. Research

Table 26.1 Contaminated water bodies analyzed by multivariant statistics

Sr. No.	Water bodies under study	References
1.	Durgapur city in West Bengal	Saha and Paul (2019)
2.	Yangtze River in China	Wu et al. (2009)
3.	Gosainkunda lakes in Nepal	Rupakheti et al. (2017)
4.	Port Jackson and in Australia	Jahan and Strezov (2017)
5.	Botany	Jahan and Strezov (2017)
6.	Kembla	Jahan and Strezov (2017)
7.	Newcastle	Jahan and Strezov (2017)
8.	Yamba	Jahan and Strezov (2017)
9.	Eden	Jahan and Strezov (2017)
10.	Khanpur Lake in Pakistan	Iqbal and Shah (2013)

is needed to understand the molecular as well as the biochemical mechanism for the synthesis of green nanoparticles. It is predicted that enzymes stabilize nanoparticles. By coding genes that produce these enzymes, commercial-scale production of nanobiogenic nanoparticles on an industrial scale. National censuses are needed in different industrial zones to understand Heavy metal distribution in the environment. There is a need to develop an efficient management plan to protect water ecosystems. Local managers along with community leaders need guidance on potential contamination risks and dissemination of waste (Daily 2000; Mitchell 2006; Richter et al. 2018). To spread awareness about environmental contamination tools are employed for processing and analyzing information. The information has to be conveyed to leaders, managers, technicians, and the general public (Kumar et al. 2018, 2020). There is a need to develop an index to assess the spatial distribution of heavy metals in aquatic environments. Various multivariant statistics have been used to determine HM concentration in various rivers and water bodies. Some such examples are stated below (Table 26.1).

Water contamination in vulnerable populations leads to a sanitation crisis. Sewerage discharge in this polluted water causes problems with personal hygiene and preparation of food (Chaggu et al. 2002; Qadir et al. 2010).

26.27 Conclusion

Heavy metal contamination in water bodies is a serious threat to life. Aquatic habitats exposed to industrial and domestic wastes contaminate the surrounding environment as toxins seep through the water. Nanotechnology in recent years has proved to be an effective strategy to stabilize the ecosystem and assist in the elimination of pollutants from water bodies. Nanomaterials bind heavy metals and remove heavy metal ions. Metal biosorption by abundant biomass has economic benefits. In large-scale fermenters waste by-products are generated using microbes such as algae, yeast, fungus, and bacteria The metal binding capacity of these microbes is attributed to the efficient binding functional group present on the outer membranes along with proteins released by these microbes to convert metal ions to fewer toxic isomers.

References

Adochite C, Andronic L (2021) Aquatic toxicity of photocatalyst nanoparticles to green microalgae Chlorella vulgaris. Water 13(1):77

Ahmad A, Mukherjee P, Senapati S, Mandal D, Khan MI, Kumar R, Sastry M (2003) Extracellular biosynthesis of silver nanoparticles using the fungus Fusarium oxysporum. Colloids Surf B 28(4):313–318

Ahmadi M, Niari MH, Kakavandi B (2017) Development of maghemite nanoparticles supported on cross-linked chitosan (γ-Fe2O3@ CS) as a recoverable mesoporous magnetic composite for effective heavy metals removal. J Mol Liq 248:184–196

Alekseeva OV, Bagrovskaya NA, Noskov AV (2016) Sorption of heavy metal ions by fullerene and polystyrene/fullerene film compositions. Prot Metals Phys Chem Surf 52(3):443–447

Al-Hakami SM, Khalil AB, Laoui T, Atieh MA (2013) Fast disinfection of Escherichia coli bacteria using carbon nanotubes interaction with microwave radiation. Bioinorg Chem Appl 2013:458943

Ali I, Alharbi OM, Tkachev A, Galunin E, Burakov A, Grachev VA (2018) Water treatment by new-generation graphene materials: hope for bright future. Environ Sci Pollut Res 25(8):7315–7329

Ali EAM, Sayed MA, Abdel-Rahman TM, Hussein AM, Hussein R (2019) Bioremediation of waste water from cadmium pollution using silicon dioxide nanoparticles and fungal biomasses. J Pure Appl Microbiol 13(3):1561–1570

Al-Khaldi FA, Abusharkh B, Khaled M, Atieh MA, Nasser MS, Saleh TA, Agarwal S, Tyagi I, Gupta VK (2015) Adsorptive removal of cadmium (II) ions from liquid phase using acid modified carbon-based adsorbents. J Mol Liq 204:255–263

Al-Rashdi BAM, Johnson DJ, Hilal N (2013) Removal of heavy metal ions by nanofiltration. Desalination 315:2–17

Aneja RK, Chaudhary G, Ahluwalia SS, Goyal D (2010) Biosorption of Pb 2+ and Zn 2+ by nonliving biomass of Spirulina sp. Indian J Microbiol 50(4):438–442

Anjana K, Kaushik A, Kiran B, Nisha R (2007) Biosorption of Cr (VI) by immobilized biomass of two indigenous strains of cyanobacteria isolated from metal contaminated soil. J Hazard Mater 148(1–2):383–386

Aziz N, Faraz M, Pandey R, Shakir M, Fatma T, Varma A, Barman I, Prasad R (2015) Facile algae-derived route to biogenic silver nanoparticles: synthesis, antibacterial, and photocatalytic properties. Langmuir 31(42):11605–11612

Babich H, Stotzky G (1985) Heavy metal toxicity to microbe-mediated ecologic processes: a review and potential application to regulatory policies. Environ Res 36(1):111–137

Bai HJ, Zhang ZM, Gong J (2006) Biological synthesis of semiconductor zinc sulfide nanoparticles by immobilized Rhodobacter sphaeroides. Biotechnol Lett 28(14):1135–1139

Barakat MA (2011) New trends in removing heavy metals from industrial wastewater. Arab J Chem 4(4):361–377

Brunet L, Lyon DY, Hotze EM, Alvarez PJ, Wiesner MR (2009) Comparative photoactivity and antibacterial properties of C60 fullerenes and titanium dioxide nanoparticles. Environ Sci Technol 43(12):4355–4360

Catania V, Lopresti F, Cappello S, Scaffaro R, Quatrini P (2020) Innovative, ecofriendly biosorbent-biodegrading biofilms for bioremediation of oil-contaminated water. New Biotechnol 58:25–31

Chaggu E, Mashauri D, Van Buuren J, Sanders W, Lettinga G (2002) Excreta disposal in Dar-es-Salaam. Environ Manag 30(5):0609–0620

Chan LS, Cheung WH, Allen SJ, McKay G (2012) Error analysis of adsorption isotherm models for acid dyes onto bamboo derived activated carbon. Chin J Chem Eng 20(3):535–542

Chandra V, Park J, Chun Y, Lee JW, Hwang IC, Kim KS (2010) Water-dispersible magnetite-reduced graphene oxide composites for arsenic removal. ACS Nano 4(7):3979–3986

Cheng S, Oatley DL, Williams PM, Wright CJ (2011) Positively charged nanofiltration membranes: review of current fabrication methods and introduction of a novel approach. Adv Colloid Interf Sci 164(1–2):12–20

Cornell RM, Schwertmann U (1996) The iron oxides: structures, properties, reactions, occurrences and uses. VCH Verlagsgesellshaft GMBH, Weinheim, pp 533–559

Crini G, Morin-Crini N, Fatin-Rouge N, Deon S, Fievet P (2017) Metal removal from aqueous media by polymer-assisted ultrafiltration with chitosan. Arab J Chem 10:S3826–S3839

Cui Y, Wei Q, Park H, Lieber CM (2001) Nanowire nanosensors for highly sensitive and selective detection of biological and chemical species. Science 293(5533):1289–1292

Daily GC (2000) Management objectives for the protection of ecosystem services. Environ Sci Pol 3(6):333–339

Danion A, Disdier J, Guillard C, Abdelmalek F, Jaffrezic-Renault N (2004) Characterization and study of a single-TiO2-coated optical fiber reactor. Appl Catal B Environ 52(3):213–223

Dhankhar R, Hooda A, Solanki R, Sainger PA (2011) Saccharomyces cerevisiae: a potential biosorbent for biosorption of uranium. Int J Eng Sci Technol 3(6):467–491

Directive, E.U.W (1991) Council Directive of 21. May 1991 concerning urban waste water treatment (91/271/EEC). J Eur Commun 34:40

Dresselhaus MS, Terrones M (2013) Carbon-based nanomaterials from a historical perspective. Proc IEEE 101(7):1522–1535

Duan J, Tan J (2013) Atmospheric heavy metals and arsenic in China: situation, sources and control policies. Atmos Environ 74:93–101

Elliott DW, Zhang WX (2001) Field assessment of nanoscale bimetallic particles for groundwater treatment. Environ Sci Technol 35(24):4922–4926

El-Sheekh MM, El-Kassas HY, Shams El-Din NG, Eissa DI, El-Sherbiny BA (2021) Green synthesis, characterization applications of iron oxide nanoparticles for antialgal and wastewater bioremediation using three brown algae. Int J Phytoremediation:1–15

El-Sheikh AH, Al-Degs YS, Al-As' ad RM, Sweileh JA (2011) Effect of oxidation and geometrical dimensions of carbon nanotubes on Hg (II) sorption and preconcentration from real waters. Desalination 270(1–3):214–220

Esrafili L, Firuzabadi FD, Morsali A, Hu ML (2021) Reuse of predesigned dual-functional metal organic frameworks (DF-MOFs) after heavy metal removal. J Hazard Mater 403:123696

Ferraz MA, Lourençlo JCN (2000) The influence of organic matter content of contaminated soils on the leaching rate of heavy metals. Environ Prog 19(1):53–58

Furgal KM, Meyer RL, Bester K (2015) Removing selected steroid hormones, biocides and pharmaceuticals from water by means of biogenic manganese oxide nanoparticles in situ at ppb levels. Chemosphere 136:321–326

Gao L, He Q, Xing J, Ge Z (2020) Removal of doxorubicin by magnetic copper phosphate nanoflowers for individual urine source separation. Chemosphere 238:124690

Goh PS, Ismail AF (2018) A review on inorganic membranes for desalination and wastewater treatment. Desalination 434:60–80

Grossl PR, Sparks DL, Ainsworth CC (1994) Rapid kinetics of Cu (II) adsorption/desorption on goethite. Environ Sci Technol 28(8):1422–1429

Gupta VK, Moradi O, Tyagi I, Agarwal S, Sadegh H, Shahryari-Ghoshekandi R, Makhlouf ASH, Goodarzi M, Garshasbi A (2016) Study on the removal of heavy metal ions from industry waste by carbon nanotubes: effect of the surface modification: a review. Crit Rev Environ Sci Technol 46(2):93–118

Hall S, Tang R, Baeyens J, Dewil R (2009) Removing polycyclic aromatic hydrocarbons from water by adsorption on silicagel. Polycycl Aromat Compd 29(3):160–183

Haneef T, Ul Mustafa MR, Rasool K, Ho YC, Mohamed Kutty SR (2020) Removal of polycyclic aromatic hydrocarbons in a heterogeneous Fenton like oxidation system using nanoscale zero-valent iron as a catalyst. Water 12(9):2430

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

Hosseini SS, Bringas E, Tan NR, Ortiz I, Ghahramani M, Shahmirzadi MAA (2016) Recent progress in development of high performance polymeric membranes and materials for metal plating wastewater treatment: a review. J Water Process Eng 9:78–110

Hu D, Lian Z, Xian H, Jiang R, Wang N, Weng Y, Peng X, Wang S, Ouyang XK (2020) Adsorption of Pb (II) from aqueous solution by polyacrylic acid grafted magnetic chitosan nanocomposite. Int J Biol Macromol 154:1537–1547

Huang SH, Chen DH (2009) Rapid removal of heavy metal cations and anions from aqueous solutions by an amino-functionalized magnetic nano-adsorbent. J Hazard Mater 163(1):174–179

Huang CC, Lo SL, Lien HL (2012) Zero-valent copper nanoparticles for effective dechlorination of dichloromethane using sodium borohydride as a reductant. Chem Eng J 203:95–100

Ihsanullah, Al-Khaldi FA, Abu-Sharkh B, Abulkibash AM, Qureshi MI, Laoui T, Atieh MA (2016) Effect of acid modification on adsorption of hexavalent chromium (Cr (VI)) from aqueous solution by activated carbon and carbon nanotubes. Desalin Water Treat 57(16):7232–7244

International Association of Hydrogeologists (2020) Groundwater—more about the hidden resource. https://iah.org/education/general-public/groundwater-hidden-resource. Accessed 17 Sept 2021

Iqbal J, Shah MH (2013) Health risk assessment of metals in surface water from freshwater source lakes, Pakistan. Hum Ecol Risk Assess Int J 19(6):1530–1543

Iravani S, Varma RS (2020) Bacteria in heavy metal remediation and nanoparticle biosynthesis. ACS Sustain Chem Eng 8(14):5395–5409

Jahan S, Strezov V (2017) Water quality assessment of Australian ports using water quality evaluation indices. PLoS One 12(12):e0189284

Jeong BH, Hoek EM, Yan Y, Subramani A, Huang X, Hurwitz G, Ghosh AK, Jawor A (2007) Interfacial polymerization of thin film nanocomposites: a new concept for reverse osmosis membranes. J Membr Sci 294(1–2):1–7

Jiao Z, Meng Y, He C, Yin X, Wang X, Wei Y (2021) One-pot synthesis of silicon-based zirconium phosphate for the enhanced adsorption of Sr (II) from the contaminated wastewater. Microporous Mesoporous Mater 318:111016

Joseph L, Jun BM, Flora JR, Park CM, Yoon Y (2019) Removal of heavy metals from water sources in the developing world using low-cost materials: a review. Chemosphere 229:142–159

Kalfa OM, Yalçınkaya Ö, Türker AR (2009) Synthesis of nano B2O3/TiO2 composite material as a new solid phase extractor and its application to preconcentration and separation of cadmium. J Hazard Mater 166(1):455–461

Kamat PV, Huehn R, Nicolaescu R (2002) A "sense and shoot" approach for photocatalytic degradation of organic contaminants in water. J Phys Chem B 106(4):788–794

Kapahi M, Sachdeva S (2019) Bioremediation options for heavy metal pollution. J Health Pollut 9(24)

Khezri B, Pumera M (2019) Metal–organic frameworks based nano/micro/millimeter-sized self-propelled autonomous machines. Adv Mater 31(14):1806530

Khoso WA, Haleem N, Baig MA, Jamal Y (2021) Synthesis, characterization and heavy metal removal efficiency of nickel ferrite nanoparticles (NFN's). Sci Rep 11(1):1–10

Kim S, Chen L, Johnson JK, Marand E (2007) Polysulfone and functionalized carbon nanotube mixed matrix membranes for gas separation: theory and experiment. J Membr Sci 294(1–2):147–158

Kim ES, Hwang G, El-Din MG, Liu Y (2012) Development of nanosilver and multi-walled carbon nanotubes thin-film nanocomposite membrane for enhanced water treatment. J Membr Sci 394:37–48

Klaus-Joerger T, Joerger R, Olsson E, Granqvist CG (2001) Bacteria as workers in the living factory: metal-accumulating bacteria and their potential for materials science. Trends Biotechnol 19(1):15–20

Kumar ASK, Kakan SS, Rajesh N (2013) A novel amine impregnated graphene oxide adsorbent for the removal of hexavalent chromium. Chem Eng J 230:328–337

Kumar V, Sharma A, Minakshi, Bhardwaj R, Thukral AK (2018) Temporal distribution, source apportionment, and pollution assessment of metals in the sediments of Beas river, India. Hum Ecol Risk Assess Int J 24(8):2162–2181

Kumar V, Sharma A, Kumar R, Bhardwaj R, Kumar Thukral A, Rodrigo-Comino J (2020) Assessment of heavy-metal pollution in three different Indian water bodies by combination of multivariate analysis and water pollution indices. Hum Ecol Risk Assess Int J 26(1):1–16

Lam B, Déon S, Morin-Crini N, Crini G, Fievet P (2018) Polymer-enhanced ultrafiltration for heavy metal removal: influence of chitosan and carboxymethyl cellulose on filtration performances. J Clean Prod 171:927–933

Laurén DJ, McDonald DG (1987) Acclimation to copper by rainbow trout, Salmo gairdneri: physiology. Can J Fish Aquat Sci 44(1):99–104

Lengke M, Southam G (2006) Bioaccumulation of gold by sulfate-reducing bacteria cultured in the presence of gold (I)-thiosulfate complex. Geochim Cosmochim Acta 70(14):3646–3661

Lengke MF, Ravel B, Fleet ME, Wanger G, Gordon RA, Southam G (2006) Mechanisms of gold bioaccumulation by filamentous cyanobacteria from gold (III)− chloride complex. Environ Sci Technol 40(20):6304–6309

Letnik I, Avrahami R, Rokem JS, Greiner A, Zussman E, Greenblatt C (2015) Living composites of electrospun yeast cells for bioremediation and ethanol production. Biomacromolecules 16(10):3322–3328

Li YH, Ding J, Luan Z, Di Z, Zhu Y, Xu C, Wu D, Wei B (2003) Competitive adsorption of Pb2+, Cu2+ and Cd2+ ions from aqueous solutions by multiwalled carbon nanotubes. Carbon 41(14):2787–2792

Li YH, Di Z, Ding J, Wu D, Luan Z, Zhu Y (2005) Adsorption thermodynamic, kinetic and desorption studies of Pb2+ on carbon nanotubes. Water Res 39(4):605–609

Li Q, Mahendra S, Lyon DY, Brunet L, Liga MV, Li D, Alvarez PJ (2008) Antimicrobial nanomaterials for water disinfection and microbial control: potential applications and implications. Water Res 42(18):4591–4602

Li B, Liu T, Wang Y, Wang Z (2012) ZnO/graphene-oxide nanocomposite with remarkably enhanced visible-light-driven photocatalytic performance. J Colloid Interface Sci 377(1):114–121

Liang C, Zhan C, Zeng F, Xu D, Wang Y, Zhao W, Zhang J, Guo J, Feng H, Ma X (2018) Bilayer tubular micromotors for simultaneous environmental monitoring and remediation. ACS Appl Mater Interfaces 10(41):35099–35107

Lind ML, Ghosh AK, Jawor A, Huang X, Hou W, Yang Y, Hoek EM (2009) Influence of zeolite crystal size on zeolite-polyamide thin film nanocomposite membranes. Langmuir 25(17):10139–10145

Liu H, Tang X, Liu Q (2014) A novel point-of-use water treatment method by antimicrobial nanosilver textile material. J Water Health 12(4):670–677

Lu C, Chiu H (2006) Adsorption of zinc (II) from water with purified carbon nanotubes. Chem Eng Sci 61(4):1138–1145

Lu C, Liu C (2006) Removal of nickel (II) from aqueous solution by carbon nanotubes. J Chem Technol Biotechnol 81(12):1932–1940

Luo X, Zeng J, Liu S, Zhang L (2015) An effective and recyclable adsorbent for the removal of heavy metal ions from aqueous system: magnetic chitosan/cellulose microspheres. Bioresour Technol 194:403–406

Maher A, Sadeghi M, Moheb A (2014) Heavy metal elimination from drinking water using nanofiltration membrane technology and process optimization using response surface methodology. Desalination 352:166–173

Maric T, Mayorga-Martinez CC, Khezri B, Nasir MZM, Chia X, Pumera M (2018) Nanorobots constructed from nanoclay: using nature to create self-propelled autonomous nanomachines. Adv Funct Mater 28(40):1802762

Maric T, Mayorga-Martinez CC, Nasir MZM, Pumera M (2019) Platinum–halloysite nanoclay nanojets as sensitive and selective mobile nanosensors for mercury detection. Adv Mater Technol 4(2):1800502

Maric T, Nasir MZM, Rosli NF, Budanović M, Webster RD, Cho NJ, Pumera M (2020) Microrobots derived from variety plant pollen grains for efficient environmental clean up and as an anti-cancer drug carrier. Adv Funct Mater 30(19):2000112

Martins M, Mourato C, Sanches S, Noronha JP, Crespo MB, Pereira IA (2017) Biogenic platinum and palladium nanoparticles as new catalysts for the removal of pharmaceutical compounds. Water Res 108:160–168

Mitchell VG (2006) Applying integrated urban water management concepts: a review of Australian experience. Environ Manag 37(5):589–605

Moghaddam K (2010) An introduction to microbial metal nanoparticle preparation method. J Young Investig 19(1):1–17

Mortvedt JJ (1996) Heavy metal contaminants in inorganic and organic fertilizers. In: Fertilizers and environment. Springer, Dordrecht, pp 5–11

Mushtaq F (2019) Clean energy activated micro-and nanocatalysts towards environmental remediation (Doctoral dissertation, ETH Zurich)

Mustapha MU, Halimoon N (2015) Microorganisms and biosorption of heavy metals in the environment: a review paper. J Microb Biochem Technol 7(5):253–256

National Nanotechnology Initiative: The Initiative and Its Implementation Plan; NSTC/NSET report, March 2001, Washington, DC. www.nano.gov/nsetrpts.htm. Accessed 12 Oct 2021

Nies DH (1999) Microbial heavy-metal resistance. Appl Microbiol Biotechnol 51(6):730–750

Palimi MJ, Rostami M, Mahdavian M, Ramezanzadeh B (2014) Surface modification of Fe2O3 nanoparticles with 3-aminopropyltrimethoxysilane (APTMS): an attempt to investigate surface treatment on surface chemistry and mechanical properties of polyurethane/Fe2O3 nanocomposites. Appl Surf Sci 320:60–72

Panov AG, Larsen RG, Totah NI, Larsen SC, Grassian VH (2000) Photooxidation of toluene and p-xylene in cation-exchanged zeolites X, Y, ZSM-5, and Beta: the role of zeolite physicochemical properties in product yield and selectivity. J Phys Chem B 104(24):5706–5714

Pantsar-Kallio M, Reinikainen SP, Oksanen M (2001) Interactions of soil components and their effects on speciation of chromium in soils. Anal Chim Acta 439(1):9–17

Pascoe D, Beattie JH (1979) Resistance to cadmium by pretreated rainbow trout alevins. J Fish Biol 14(3):303–308

Ponder SM, Darab JG, Mallouk TE (2000) Remediation of Cr (VI) and Pb (II) aqueous solutions using supported, nanoscale zero-valent iron. Environ Sci Technol 34(12):2564–2569

Potnis AA, Raghavan PS, Rajaram H (2021) Overview on cyanobacterial exopolysaccharides and biofilms: role in bioremediation. Rev Environ Sci Biotechnol 20:781–794

Qadir M, Wichelns D, Raschid-Sally L, McCornick PG, Drechsel P, Bahri A, Minhas PS (2010) The challenges of wastewater irrigation in developing countries. Agric Water Manag 97(4):561–568

Qiu YR, Mao LJ (2013) Removal of heavy metal ions from aqueous solution by ultrafiltration assisted with copolymer of maleic acid and acrylic acid. Desalination 329:78–85

Ranandeh Kalankesh L, Alikhasi S, Mansuri F, Malakootian M (2015) Removal of chromium from industrial wastewater using silicon nanoparticle. J Water Wastewater 26(1):27–36

Remacle J (1990) The cell wall and metal binding. In: Biosorption of heavy metals. CRC press, Boca Ranton, pp 83–92

Ren X, Chen C, Nagatsu M, Wang X (2011) Carbon nanotubes as adsorbents in environmental pollution management: a review. Chem Eng J 170(2–3):395–410

Ren X, Li J, Tan X, Wang X (2013) Comparative study of graphene oxide, activated carbon and carbon nanotubes as adsorbents for copper decontamination. Dalton Trans 42(15):5266–5274

Renou S, Givaudan JG, Poulain S, Dirassouyan F, Moulin P (2008) Landfill leachate treatment: review and opportunity. J Hazard Mater 150(3):468–493

Richter BD, Blount ME, Bottorff C, Brooks HE, Demmerle A, Gardner BL, Herrmann H, Kremer M, Kuehn TJ, Kulow E, Lewis L (2018) Assessing the sustainability of urban water supply systems. J Am Water Works Ass 110(2):40–47

Romera E, González F, Ballester A, Blázquez ML, Munoz JA (2007) Comparative study of biosorption of heavy metals using different types of algae. Bioresour Technol 98(17):3344–3353

Roy K, Sarkar CK, Ghosh CK (2015) Photocatalytic activity of biogenic silver nanoparticles synthesized using yeast (Saccharomyces cerevisiae) extract. Appl Nanosci 5(8):953–959

Rupakheti D, Tripathee L, Kang S, Sharma CM, Paudyal R, Sillanpää M (2017) Assessment of water quality and health risks for toxic trace elements in urban Phewa and remote Gosainkunda lakes, Nepal. Human Ecol Risk Assess 23(5):959–973

Saha P, Paul B (2019) Assessment of heavy metal toxicity related with human health risk in the surface water of an industrialized area by a novel technique. Hum Ecol Risk Assess Int J 25(4):966–987

Saha B, Das S, Saikia J, Das G (2011) Preferential and enhanced adsorption of different dyes on iron oxide nanoparticles: a comparative study. J Phys Chem C 115(16):8024–8033

Saikia J, Saha B, Das G (2011) Efficient removal of chromate and arsenate from individual and mixed system by malachite nanoparticles. J Hazard Mater 186(1):575–582

Saikia J, Sikdar Y, Saha B, Das G (2013) Malachite nanoparticle: a potent surface for the adsorption of xanthene dyes. J Environ Chem Eng 1(4):1166–1173

Samonin VV, Nikonova VY, Podvyaznikov ML (2008) Sorption properties of fullerene-modified activated carbon with respect to metal ions. Prot Met 44(2):190–192

Schwertmann U, Taylor RM (1979) Natural and synthetic poorly crystallized lepidocrocite. Clay Miner 14(4):285–293

SenthilKumar P, Ramalingam S, Sathyaselvabala V, Kirupha SD, Sivanesan S (2011) Removal of copper (II) ions from aqueous solution by adsorption using cashew nut shell. Desalination 266(1–3):63–71

Sharma PR, Chattopadhyay A, Sharma SK, Geng L, Amiralian N, Martin D, Hsiao BS (2018) Nanocellulose from spinifex as an effective adsorbent to remove cadmium (II) from water. ACS Sustain Chem Eng 6(3):3279–3290

Sherbet GV (1978) The biophysical characterisation of the cell surface. Academic Press, London/New York

Shivalkar S, Gautam PK, Chaudhary S, Samanta SK, Sahoo AK (2021) Recent development of autonomously driven micro/nanobots for efficient treatment of polluted water. J Environ Manag 281:111750

Simmons P, Tobin JM, Singleton I (1995) Considerations on the use of commercially available yeast biomass for the treatment of metal-containing effluents. J Ind Microbiol Biotechnol 14(3–4):240–246

Singh J, Kumar V, Kim KH, Rawat M (2019) Biogenic synthesis of copper oxide nanoparticles using plant extract and its prodigious potential for photocatalytic degradation of dyes. Environ Res 177:108569

Smith SC, Rodrigues DF (2015) Carbon-based nanomaterials for removal of chemical and biological contaminants from water: a review of mechanisms and applications. Carbon 91:122–143

Sturala J, Hermanová S, Artigues L, Sofer Z, Pumera M (2019) Thiographene synthesized from fluorographene via xanthogenate with immobilized enzymes for environmental remediation. Nanoscale 11(22):10695–10701

Tang Y, Liang S, Yu S, Gao N, Zhang J, Guo H, Wang Y (2012) Enhanced adsorption of humic acid on amine functionalized magnetic mesoporous composite microspheres. Colloids Surf A Physicochem Eng Asp 406:61–67

Tungittiplakorn W, Lion LW, Cohen C, Kim JY (2004) Engineered polymeric nanoparticles for soil remediation. Environ Sci Technol 38(5):1605–1610

Tungittiplakorn W, Cohen C, Lion LW (2005) Engineered polymeric nanoparticles for bioremediation of hydrophobic contaminants. Environ Sci Technol 39(5):1354–1358

Wang J, Chen C (2006) Biosorption of heavy metals by Saccharomyces cerevisiae: a review. Biotechnol Adv 24(5):427–451

Wang X, Cai W, Lin Y, Wang G, Liang C (2010) Mass production of micro/nanostructured porous ZnO plates and their strong structurally enhanced and selective adsorption performance for environmental remediation. J Mater Chem 20(39):8582–8590

Wu B, Zhao DY, Jia HY, Zhang Y, Zhang XX, Cheng SP (2009) Preliminary risk assessment of trace metal pollution in surface water from Yangtze River in Nanjing Section, China. Bull Environ Contam Toxicol 82(4):405–409

Yin J, Deng B (2015) Polymer-matrix nanocomposite membranes for water treatment. J Membr Sci 479:256–275

Zhang WX, Wang CB, Lien HL (1998) Treatment of chlorinated organic contaminants with nanoscale bimetallic particles. Catal Today 40(4):387–395

Zhao G, Sanchez S, Schmidt OG, Pumera M (2013) Poisoning of bubble propelled catalytic micromotors: the chemical environment matters. Nanoscale 5(7):2909–2914

Zhou Q, Yang N, Li Y, Ren B, Ding X, Bian H, Yao X (2020) Total concentrations and sources of heavy metal pollution in global river and lake water bodies from 1972 to 2017. Global Ecol Conserv 22:e00925

Zhu WP, Sun SP, Gao J, Fu FJ, Chung TS (2014) Dual-layer polybenzimidazole/polyethersulfone (PBI/PES) nanofiltration (NF) hollow fiber membranes for heavy metals removal from wastewater. J Membr Sci 456:117–127

Zhu WP, Gao J, Sun SP, Zhang S, Chung TS (2015) Poly (amidoamine) dendrimer (PAMAM) grafted on thin film composite (TFC) nanofiltration (NF) hollow fiber membranes for heavy metal removal. J Membr Sci 487:117–126

Zinicovscaia I, Duca G, Cepoi L, Chiriac T, Rudi L, Mitina T, Frontasyeva MV, Pavlov S, Gundorina SF (2015) Biotechnology of metal removal from industrial wastewater: zinc case study. Clean–Soil Air Water 43(1):112–117

Chapter 27
Phytoremediation and Management of Environmental Contaminants: Conclusion and Future Perspectives

Ritu Gill, M. Naeem, A. A. Ansari, and Sarvajeet Singh Gill

Abstract Contamination of the environment (soil and water) due to rapid urbanization, industrialization practices, luxurious use of agrochemicals (chemical fertilizers and pesticides), heavy metals, and metalloids poses a serious threat to the environment and human health. The present volume exclusively deals with phytoremediation practices and management of environmental contaminants, where, studies in 26 chapters on various aspects of bioremediation practices (phytoremediation, phytostabilization, rhizodegradation, nano-phytoremediation, and microbial consortium) for the removal/management of heavy metals, trace metals, metalloids, and other contaminants have been included and discussed.

Keywords Phytoremediation · Phytostabilization · Rhizodegradation · Nano-phytoremediation · Microbial consortium · Metals and metalloids

Twenty-first century's major challenges like rapidly changing global climatic conditions, ever-increasing global population, war or war-like situations, rapid urbanization, industrialization, luxurious use of agrochemicals (chemical fertilizers and pesticides), release of industrial effluents in water bodies, decreasing water table, reduced agriculturally suitable land area and microflora, array of abiotic (salinity, drought, flooding, metals and metalloids, low and high-temperature pose) and biotic stress factors (virus, bacteria, fungi, nematodes) stresses pose a serious threat to food security and human health (Cherniwchan 2012; Wu et al. 2016; Saleem et al. 2020; Zaheer et al. 2020; Kamran et al. 2021; Corami 2021; Naeem et al. 2022;

R. Gill · S. S. Gill (✉)
Centre for Biotechnology, Maharshi Dayanand University, Rohtak, Haryana, India
e-mail: ssgill14@mdurohtak.ac.in

M. Naeem
Plant Physiology Section, Department of Botany, Aligarh Muslim University,
Aligarh, UP, India

A. A. Ansari
Department of Biology, Faculty of Science, University of Tabuk, Tabuk, Saudi Arabia

L. Newman et al. (eds.), *Phytoremediation*, https://doi.org/10.1007/978-3-031-17988-4_27

Kafle et al. 2022). The global population is expected to increase by 8.5 billion by 2030 and 9.7 billion by the year 2050, and 10.4 billion in 2100 as per the UN reports on the global population (Fig. 27.1, UNDESAPD 2022) which will demand more and safe food. Therefore, feeding the global population of 9.7 billion in 2050 would require a rapid increase in overall food production by some 70 percent in a sustainable manner (Ranganathan et al. 2018). UN Food and Agriculture Organization (2022) warned that 90 percent of Earth's topsoil at risk by 2050 due to anthropogenic and natural activities. Natural and anthropogenic activities in a very rapid pace allowed the exposure of heavy metals and metalloids [Cd, Cr, Cu, As, Pb, Zn, Ni, Fe, Mn etc], radionuclides (naturally-occurring radioactive materials (U, Th, Ra, Rn, Pb, Po) as well as technologically enhanced naturally-occurring radioactive materials) [volcanic activities, erosion, weathering, nuclear accidents (^{133}Xe, ^{131}I, ^{134}Cs, ^{137}Cs, and ^{90}Sr), nuclear weapon testing, leakage of nuclear wastes, medical and agriculture testing facilities with isotopes like ^{131}I & ^{14}C], organic contaminants [aromatic compounds, hydrocarbons, substituted hydrocarbons, phenols, organochlorines, pesticides], agrochemicals [chemical fertilizers, plant-protection agents, and plant growth promoting hormones] (Fig. 27.2) and oil spills [complex mixture of hydrocarbon and organic compounds including benzene and poly aromatic hydrocarbons] to the global environment (He et al. 2015; Prakash et al. 2013; Afzal et al. 2014; Liu et al. 2017; Jagetiya et al. 2014; Yan et al. 2020; Malik et al. 2017; Naeem et al. 2022; Ron and Rosenberg 2014; Kafle et al. 2022). Therefore, there is an urgent need to decontaminate the agriculturally viable land to ensure food security and human health. FAO UN emphasized on soil health with the notion that "healthy soils are a pre-requisite in achieving the UN Sustainable Development Goals (SDGs)" (FAO 2022a, b; https://www.fao.org/global-soil-partnership/about/gsp-action-framework-2022-2030/en/).

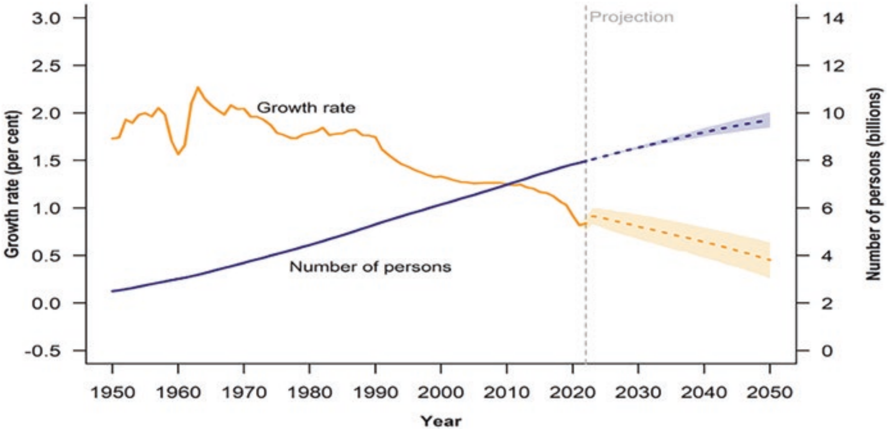


Fig. 27.1 Global population size and annual growth rate: estimates, 1950–2022, and medium scenario with 95 percent prediction intervals, 2022–2050

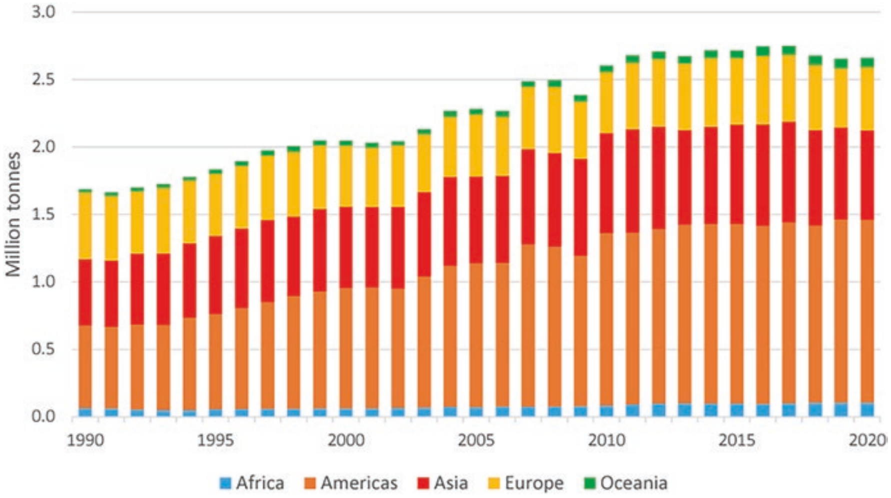


Fig. 27.2 Total pesticides use by region (FAO 2022a, b)

Among many techniques for the cleanup of the environment (Soil, water & air), phytoremediation (phytodegradation, phytoextraction, phytostabilization or phyto-immobilization, phytovolatilization, rhizodegradation, and rhizofiltration) of organic and inorganic contaminants is one of the cost-effective, sustainable and environment friendly technologies which utilizes the services of plants and associated microorganisms in the rhizosphere.

In the domain of phytoremediation, the efficiency of this technique depends on the capability of plant species and rhizospheric diversity of associated micro-organisms used for the cleanup of soil contaminated with heavy metals and metalloids, radionuclides, organic contaminants, agrochemicals, and oil spills. Plants and associated micro-organisms have the unique capability to remediate the contaminated soil without affecting the quality of the topsoil. Specifically, isolation, identification, and association of plant growth-promoting bacteria with tolerant plant species can add to the capability of plant species being used for phytoremediation. Therefore, in addition to the existing hyper-accumulating tolerant plant species and micro-organisms, there is an urgent need to explore more plant species and micro-organisms to assist and pace the process of phytoremediation.

Various plant species (*Aeolanthus biformifolius*, *Arabidopsis halleri*, *Astragalus bisulcatus*, *Austrodanthonia caespitosa*, *Azolla caroliniana*, *Berkheya coddii*, *Biscutella laevigata*, *Brassica Spp*, *Cajanus cajan*, *Callitriche brutia*, *Callitriche lusitanica*, *Callitriche stagnalis*, *Dicranopteris linearis*, *Eichhornia crassipes*, *Fontinalis antipyretica*, *Haumaniastrum robertii*, *Helianthus annus*, *Impatiens glandulifera*, *Ipomea balsamina*, *Lemna minor*, *Mirabilis jalapa*, *Noccaea caerulescens, Noccaea rotondifolia subsp. cepaeifolia*, *Prosopis juliflora*, *Pteris vittata*, *Pycnandra acuminate*, *Ranunculus trichophyllus*, *Sedum alfredii*, *Sorghum sudanense*, *Tegetes patula*, *Thlaspi caerulescens*, *Typha angustifolia*, *Vetiveria* *zizanoides*, *Vigna unguiculata*, *Virotia neurophylla*, and *Zea mays*) have been identified for phytoremediation (Ansari et al. 2015a, b, 2016a, b, 2017, 2018). Pyrosequencing of the rhizosphere of hyperaccumulating plants also provided significant evidence of the importance of micro-organisms in plant assisted phytoremediation of contaminated sites.

Exploration of tolerant plants with phytoremediation potential and associated microorganisms can further add to the remediation potential. Furthermore, selected plants and microorganisms can also be engineered genetically for efficiency enhancement. Nanotechnological advancements are also being employed to enhance the efficiency of phytoremediation with the use of nano-formulations.

Acknowledgments Work on plant abiotic stress tolerance in SSG laboratory was partially supported by University Grants Commission (UGC), Department of Science and Technology (DST), Council of Scientific & Industrial Research (CSIR), Govt. of India. SSG and RG also acknowledge partial support from DBT-BUILDER grant. We acknowledge the use of figures (1 & 2) from UNDESAPD, 2022 and FAO, 2022a, b.

References

Afzal M, Khan QM, Sessitsch A (2014) Endophytic bacteria: prospects and applications for the phytoremediation of organic pollutants. Chemosphere 117:232–242

Ansari AA, Gill SS, Gill R, Lanza GR, Newman L (eds) (2015a) Phytoremediation Management of Environmental Contaminants, vol 1. Springer, Cham, ISBN 978-3-319-10394-5, XV, 348. https://doi.org/10.1007/978-3-319-10395-2

Ansari AA, Gill SS, Gill R, Lanza GR, Newman L (eds) (2015b) Phytoremediation Management of Environmental Contaminants, vol 2. Springer, Cham, ISBN 978-3-319-10968-8, XV, 366. https://doi.org/10.1007/978-3-319-10969-5

Ansari AA, Gill SS, Gill R, Lanza GR, Newman L (eds) (2016a) Phytoremediation Management of Environmental Contaminants, vol 3. Springer, Cham, ISBN 978-3-319-40146-1, XV, 576. https://doi.org/10.1007/978-3-319-40148-5

Ansari AA, Gill SS, Gill R, Lanza GR, Newman L (eds) (2016b) Phytoremediation Management of Environmental Contaminants, vol 4. Springer, Cham, ISBN 978-3-319-41810-0, XV, 409. https://doi.org/10.1007/978-3-319-41811-7

Ansari AA, Gill SS, Gill R, Lanza GR, Newman L (eds) (2017) Phytoremediation Management of Environmental Contaminants, vol 5. Springer, Cham, ISBN 978-3-319-52379-8, XIV, 514. https://doi.org/10.1007/978-3-319-52381-1

Ansari AA, Gill SS, Gill R, Lanza GR, Newman L (eds) (2018) Phytoremediation Management of Environmental Contaminants, vol 6. Springer, Cham, ISBN 978-3-319-99650-9, XV, 476. https://doi.org/10.1007/978-3-319-99651-6

Cherniwchan J (2012) Economic growth, industrialization, and the environment. Resour Energy Econ 34:442–467

Corami A (2021) Phytoremediation impacts on water productivity. Water Productivity J 1(2):13–22

FAO (2022a) FAOSTAT: pesticide use. FAO, Rome. http://www.fao.org/faostat/en/#data/

FAO (2022b) Global soil partnership 2012–2022 – sustainable soil management in action. FAO, Rome. https://www.fao.org/documents/card/en/c/cc0921en

He Z, Shentu J, Yang X, Baligar VC, Zhang T, Stoffella PJ (2015) Heavy metal contamination of soils: sources, indicators and assessment. J Environ Indicat 9:17–18. https://www.fao.org/global-soil-partnership/about/gsp-action-framework-2022-2030/en/

Jagetiya B, Sharma A, Soni A, Khatik UK (2014) Phytoremediation of radionuclides: a report on the state of the art D.K. In: Gupta CW (ed) Radionuclide contamination and remediation through plants. Springer, Cham, pp 1–31

Kafle A, Timilsina A, Gautam A, Adhikari K, Bhattarai A, Arya N (2022) Phytoremediation: mechanisms, plant selection and enhancement by natural and synthetic agents. Environ Adv 8:100203. https://doi.org/10.1016/j.envadv.2022.100203

Kamran M, Danish M, Saleem MH, Malik Z, Parveen A, Abbasi GH, Jamil M, Ali S, Afzal S, Riaz M (2021) Application of abscisic acid and 6-benzylaminopurine modulated morpho-physiological and antioxidative defense responses of tomato (*Solanum lycopersicum* L.) by minimizing cobalt uptake. Chemosphere 263:128169

Liu J, Xin X, Zhou Q (2017) Phytoremediation of contaminated soils using ornamental plants. Environ Rev 26(1):43–54. https://doi.org/10.1139/er-2017-0022

Malik Z, Ahmad M, Abassi GH, Dawood M, Hussain A, Jamil M (2017) Agrochemicals and soil microbes: interaction for soil health Xenobiotics in the soil environment. Springer, pp 139–152

Naeem M, Jimenez Bremont JF, Ansari AA, Gill SS (eds) (2022) Agrochemicals in soil and environment: impacts and remediation. Springer, Singapore, ISBN: 978-981-16-9309-0; 978-981-16-9310-6, p. XXVI, 612. https://doi.org/10.1007/978-981-16-9310-6

Prakash D, Gabani P, Chandel AK, Ronen Z, Singh OV (2013) Bioremediation: a genuine technology to remediate radionuclides from the environment. Microb Biotechnol 6:349–360

Ranganathan J, Waite R, Searchinger T, Hanson C (2018) How to sustainably feed 10 billion people by 2050, in 21 charts. https://www.wri.org/insights/how-sustainably-feed-10-billion-people-2050-21-charts

Ron EZ, Rosenberg E (2014) Enhanced bioremediation of oil spills in the sea. Curr Opin Biotechnol 27:191–194

Saleem MH, Ali S, Rehman M, Rana MS, Rizwan M, Kamran M, Imran M, Riaz M, Soliman MH, Elkelish A (2020) Influence of phosphorus on copper phytoextraction via modulating cellular organelles in two jute (*Corchorus capsularis* L.) varieties grown in a copper mining soil of Hubei Province, China. Chemosphere 248:126032

United Nations Department of Economic and Social Affairs, Population Division (2022). World population prospects 2022: summary of results. UN DESA/POP/2022/TR/NO. 3

Wu Q, Zhou H, Tam NF, Tian Y, Tan Y, Zhou S, Li Q, Chen Y, Leung JY (2016) Contamination, toxicity and speciation of heavy metals in an industrialized urban river: implications for the dispersal of heavy metals. Mar Pollut Bull 104:153–161

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

Zaheer IE, Ali S, Saleem MH, Imran M, Alnusairi GS, Alharbi BM, Riaz M, Abbas Z, Rizwan M, Soliman MH (2020) Role of iron–lysine on morpho-physiological traits and combating chromium toxicity in rapeseed (*Brassica napus* L.) plants irrigated with different levels of tannery wastewater. Plant Physiol Biochem 155:70–84

Index

L. Newman et al. (eds.), *Phytoremediation*,
https://doi.org/10.1007/978-3-031-17988-4