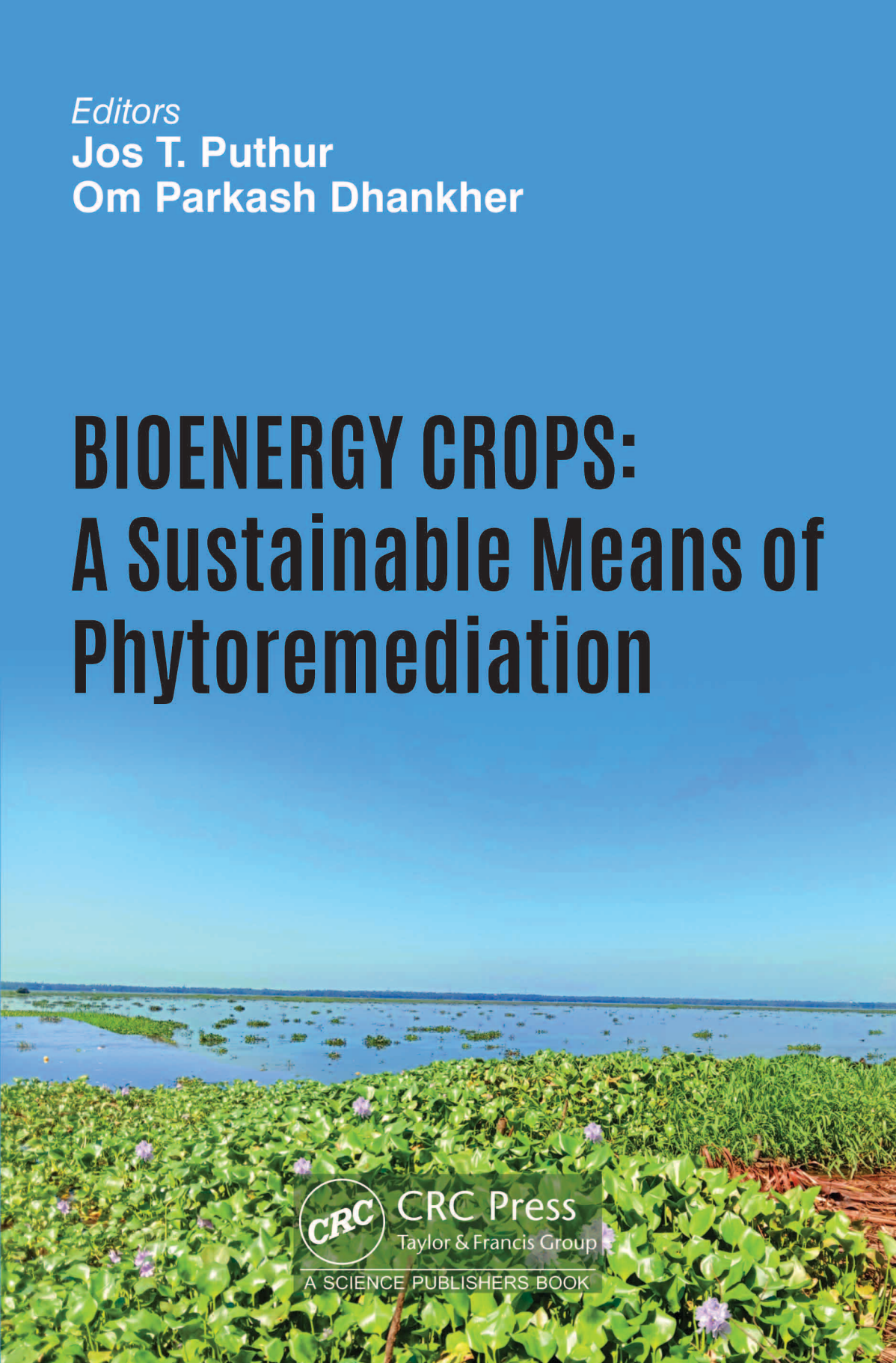
Editors
Jos T. Puthur
Om Parkash Dhankher

BIOENERGY CROPS: A Sustainable Means of Phytoremediation



CRC Press
Taylor & Francis Group
A SCIENCE PUBLISHERS BOOK

Bioenergy Crops

A Sustainable Means of Phytoremediation

Editors

Jos T. Puthur

Plant Physiology and Biochemistry Division
Department of Botany, University of Calicut
Kerala, India

Om Parkash Dhankher

Stockbridge School of Agriculture
University of Massachusetts
Amherst, U.S.A.

CRC Press
Taylor & Francis Group
Boca Raton London New York

CRC Press is an imprint of the
Taylor & Francis Group, an **informa** business

A SCIENCE PUBLISHERS BOOK

Cover credits: Image provided by Dr. Edappayil Janeeshma, Department of Botany, University of Calicut, Kerala, India. It has not been taken from any copyrighted source.

First edition published 2022
by CRC Press
6000 Broken Sound Parkway NW, Suite 300, Boca Raton, FL 33487-2742

and by CRC Press
2 Park Square, Milton Park, Abingdon, Oxon, OX14 4RN

CRC Press is an imprint of Taylor & Francis Group, LLC

ISBN: 978-0-367-48913-7 (hbk)
ISBN: 978-1-032-26033-4 (pbk)
ISBN: 978-1-003-04352-2 (ebk)

DOI: 10.1201/9781003043522

Typeset in Times New Roman
by Innovative Processors

Preface

Accumulation of heavy metals and organic xenobiotics has emerged as a big threat to living organisms. Extensive application of agrochemicals, mismanagement of organic wastes, industrial waste depositions, mining, and smelting are the different anthropogenic actions causing the accumulation of these toxic compounds in the environment. "Phytoremediation" was introduced as a strategy to remove or detoxify these compounds by the utilization of plants. However, growing hyperaccumulators in contaminated lands is a time-consuming and costly process. This calls for the application of bioenergy crops in the field of phytoremediation. Bioenergy crops are non-food crops cultivated for the production of biofuels, which generally needs low-cost for maintenance. The selection of plant candidates, which can play the dual role of phytoremediation and bioenergy production, is a task, and current researchers are investigating to identify apt plant candidates, which can make this process eco-friendly as well as economically viable. The main motive of writing this book was to address these issues. The present book includes 14 chapters dealing with different aspects of bioenergy production and phytoremediation that helps to update the current status of research in this field.

Organic pollutants and heavy metals induce different metabolic changes in plants that aid in tolerating the toxic effect of these contaminants. Different plants have different strategies to overcome the oxidative stress induced by the contaminants. It is essential to understand the mechanisms operational in plants, algae, and microorganisms with respect to the tolerance of heavy metals and organic pollutants. Chapter 1 of the book is a comprehensive approach towards phytoremediation and bioenergy production. It discusses the importance of bioenergy production and phytoremediation. Chapters 2 and 3 deal with the sources and impacts of organic and inorganic contaminants. Moreover, chapter 3 explains how microorganisms can enhance the tolerance level of plants by modifying the metabolic pathways as well as chelate the metal ions. Chapters 4 and 5 suggest important bioenergy plant candidates with phytoremediation potential, including *Jatropha curcas, Ricinus communis*, and *Eichhornia crassipes.* Algae can be considered as a good source of biofuel and fertilizer with heavy metal accumulation potential, and this is discussed in chapter 6. Wastewater treatment is another crisis faced by us, and utilization of the potentials of algae is one of the best strategies to overcome this. Chapter 7 explains the importance of aquatic plants with phytoremediation potential. The importance of constructed wetlands is detailed in chapter 8. Chapter 9 discusses the processes behind the conversion of waste materials to bioenergy, where the microbial fuel cells and anaerobic digestion are explained. The major actions taken by the

governments of different countries for land reclamation are discussed in Chapter 10. The importance of the development of new industries for land clearing is explained in the same chapter. Along with the benefits, it is significant to discuss the challenges in utilizing bioenergy crops for phytoremediation, and this topic is dealt in Chapter 11. Chapters 12, 13, and 14 focus on the case studies, and explain the phytoextraction potential of willow plants, hydrocarbon generation, and bioelectricity production.

The book, therefore, comprises a unique combination of chapters on various aspects and will provide a comprehensive view of the utilization of bioenergy crops in phytoremediation. This book will guide the graduate, post-graduate and doctoral students as well as researchers to know the latest updates in the field of phytoremediation. Moreover, it gives a clear idea of utilizing the knowledge to develop different industries and job opportunities in the same field.

It gives immense pleasure to place this book in the hands of the scientific community working in the area of phytoremediation. The book could not been published without the substantial contribution of innovative ideas from enthusiastic researchers and the support of the publishers. Special thanks also due to Dr. Edappayil Janeeshma, Department of Botany, University of Calicut, who put a lot of labor in the timely publication of this book. The support rendered by other research scholars in Plant Physiology Division, Department of Botany, University of Calicut is also gratefully acknowledged.

Dr. Jos T. Puthur
Dr. Om Parkash Dhankher

Contents

CHAPTER
10

Reclamation and Phytoremediation of Heavy Metal Contaminated Land

E. Janeeshma[1], Akhila Sen[1], K.P. Raj Aswathi[1], Riya Johnson[1], Om P. Dhankher[2] and Jos T. Puthur[1]*

[1] Plant Physiology and Biochemistry Division, Department of Botany, University of Calicut, C.U. Campus P.O., Kerala – 673635, India
[2] Agriculture Biotechnology, Stockbridge School of Agriculture, University of Massachusetts, Amherst (U.S.A.)

10.1 Introduction

Heavy metals are elements having high density, atomic weight and number. Mercury (Hg), copper (Cu), cadmium (Cd), zinc (Zn), chromium (Cr), nickel (Ni), arsenic (As) and lead (Pb) are the common heavy metals originating from both natural or anthropogenic sources and causes pollution at a greater extent (Singh et al. 2011, Sarath and Pothur 2020). Heavy metals present in the soil for a long time are a major hazard to the environment (Suman et al. 2018). Land and water pollution due to heavy metal contamination is a significant risk at the global level. All the countries face this situation, but the intensity may vary depending on the area and severity of affecting pollution.

Major disasters like the Exxon Valdez oil spill, Minimata disease and radioactive release due to the Chernobyl accident are pointing out the necessity of preventing the contamination of the environment due to effluents from such sources (Kumar et al. 2011). To overcome heavy metal contamination, techniques that can entirely eliminate the pollutants, or convert them into biodegradable substances have a great importance in maintaining a sustainable environment. This method can be achieved through phytoremediation (Saxena et al. 2019). Phytoremediation includes eradication of elemental pollutants or reducing their bioavailability in the soil using plants. Phytoremediation is an economically feasible and eco-friendly method that can enhance soil fertility through increased release of various organic substances (Ali et al. 2013).

Phytoremediation is also known as the "Green Revolution" in the area of innovative clear-out technologies. According to EPA's Comprehensive Environmental

Corresponding author: jtputhur@yahoo.com

Response Compensation Liability Information System (CERCLIS), using phytoremediation technique, almost 30,000 waste sites contaminated due to battery manufacturers, electroplating, metal finishing, and mining companies were cleaned in US. As compared with USA and Canada, the application of phytotechnology is limited in other countries. Research on phytoremediation technology is flourishing in Europe even if there is a shortage of enough funding (Sharma and Pandey 2014). In such countries, focusing on pollution control through plant resources by forming private companies has become a trend (Lelie et al. 2001). In South Africa, "Ecological Engineering and Phytoremediation Research Programme" was introduced in 1995 by AngloGold Ashanti (then Anglo American Gold Division) and the School of Animal, Plant and Environmental Sciences (APES) of the University of the Witwatersrand, Johannesburg (Wits University). AngloGold Ashanti reduced the negative impact of company's tailings storage facilities (TSFs) by planting half a million number of trees over the last decade using phyto (plant) technology. There are several attempts put forward to prevent/reduce heavy metal contamination. Initiatives like Global Innovation Solution SRL (Romania**),** BIOVALA (Lithuania**),** MLM group, Biofuel NET, SUEZ group, Pond tech, Biofuel NET, BioRemed AB (Sweden), BioPlanta (Germany), Phytorem (France), Clean Biotec S.L.L (Spain**)**, and Waterloo Environmental Biotechnology Inc (Canada) are focusing on delivering cost effective solutions for soil and water pollutions and thus intends to ensure environmental sustainability. These industrial sectors play a major role in the contaminated sites through phyto/bio remediation techniques.

For effective phytoremediation, active involvement and collaboration of native people, farmers, technology suppliers and advisers, remediation experts, regulatory agencies, financial sponsors, NGOs and other voluntary organizations plays a critical role (Hauptvogl et al. 2019). However, due to the lack of practical knowledge, still there are uncertainties in the public view about phytoremediation and, hence, there is limited acceptance among people. To overcome this, the government has to make strong awareness and enough investments to encourage the clean-up initiative among the public and private sectors. For this purpose, a combination of diverse methods like genetic engineering, microbe-assisted and chelate-assisted methods could be more effective in the future.

10.2 Current Scenario

In Western Europe, it was reported that 1,400,000 sites were polluted with heavy metals (McGrath et al. 2001). As per EPA report up to May 2004, the United States possesses almost greater than 40,000 contaminated areas. Furthermore, 600,000 brownfields in the USA are contaminated by heavy metals and require reclamation, due to which 1,00,000 ha of cropland, 55,000 ha of pasture and 50,000 ha of forest have been lost (Sharma and Pandey 2014).

Developing countries like India, China, Pakistan and Bangladesh are also facing soil and water pollution due to the effluent discharge from industrial units. In China, one-sixth of total arable lands are exposed to heavy metal contamination, as well as more than 40% were destroyed because of erosion and desertification (Tang et al. 2013). Industrialization results in the increased content of Ni, Zn, Fe, Cd, Cr, Cu and

Pb in surface sediments of Xiamen, China (Zhang et al. 2007). Recent reports prove that in China, industrial activities resulted in the increased heavy metal pollution of soil. As per the data of Bulletin on National Survey of Soil Contamination, almost 4 million hectares of arable lands were polluted due to Cu, Pb, Ni, As, Cd, DDT (dichloro-diphenyl-trichloroethane), Hg, and PAHs (polycyclic aromatic hydrocarbons) contamination (Su 2014).

A study conducted in Pakistan proved that the coastal sediment is severely contaminated due to Cd, Fe, Pb, Cu, Cr, Co, Zn and Ni (Siddiqui and Saher 2021). In another study conducted, it was proved that increasing industrial activities result in severe ecological concern in Pakistan due to soil and water pollution. Heavy metals such as Cr, Co, Mn, Ni, Cd, Fe, Pb and Zn have resulted in soil and groundwater contamination (Afzal et al. 2014). Similarly, Khan et al. (2010) studied the heavy metals contamination from rock sites in vegetables and soil in Gilgit, Northern Pakistan. Their study detected higher content of heavy metals such as Pb, Zn, Cu, and Ni in vegetables like *Brassica oleracea*, *Mintha sylvestris*, *B. campestris* and *Malva neglecta*. In India, irrigation using wastewater results in the increased heavy metal contamination of soil resulting in the poor quality of crop production. A study by Sharma et al. (2009) proved that wastewater irrigation resulted in heavy metal content such as Ni, Cd, and Pb in the cultivated vegetables collected from production and market sites of a tropical urban area of India. In a study conducted by Patel et al. (2018), majority part of the river Swarnamukhi, India is contaminated with Pb, Cr, Zn, and Cu, which are from various anthropogenic sources.

10.3 Importance of Industrial Developments in Metal Contamination

Rapid industrialization and concomitant increase in the number of toxic metals and metalloids has become a matter of immense concern. Sequestration of the hazardous heavy metals through the phytoremediation potential of plants reduces the risk of exposure of soil flora and fauna to a vast range of toxic materials (Ali et al. 2013, Janeeshma and Puthur 2020). A thorough theoretical and practical knowledge regarding the use of plants for mitigating the hazardous contaminants from the polluted sites will provide futuristic promise to resolve the problem of contamination (Arthur et al. 2005)

According to the national general survey of soil contamination published by the Ministry of Ecology and Environment and the Ministry of Natural Resources in 2014, 19.4 % of the agricultural land in China exceeded Level II requirements of the soil environmental quality standard. It was reported that there are about 1.7 million heavy metal contaminated sites in central and eastern European countries (Li et al. 2019). In developing countries like India, China and Pakistan, industrial effluents cause serious threats to the natural ecosystem (Sharma and Pandey 2014). Due to the enormous ecological and health risk exerted by these hazardous materials, we need to urgently plan for a green and sustainable solution for the reclamation of contaminated lands. This can be attained through various phytoremediation methods. Phytoremediation has more acceptance due to its eco-friendly and cost-effective nature (Pandey et al. 2016). Numerous plants having this remediation capability

are used for the restoration of the polluted land. The accelerated rate of increase in contamination sites demands the need for large-scale phytoremediation industries.

Exceeded level in the expulsion of industrial effluents and the subsequent increase in the level of toxic materials becomes a severe problem of the era. Phytoremediation techniques have their role in such polluted sites (Luo et al. 2017, Sameena and Puthur 2021). Even though the government is spending a huge part of its economy for the reclamation of contaminated sites, the resulting outcome is not satisfactory. The world requires a cost-effective and eco-sustainable method for the renovation of the polluted areas.

Different countries around the world are taking initiatives to develop a worthy technology for the decontamination of land. Government, academicians and non-profit research groups are hardly utilizing the full potential of phytoremediation (Hauptvogl et al. 2019). To explore phytoremediation on a larger scale, multi-technique phytoremediation is being experimented (Luo et al. 2017). Modern scale phytoremediation utilizes the advantage of genetically modified organisms (GMO). Genetic engineering provides enhanced phytoremediation potential to plants through the augmented expression level of metal-chelating genes (Rai et al. 2020). Transgenic *Beta vulgaris* overexpressing StGCS-GS showed enhanced tolerance to Zn, Cd and Cu (Liu et al. 2015). Similarly, overexpression of *Arabidopsis thaliana* ACR2 gene (AtACR2) in *Nicotiana tabacum* increased the phytoremediation of As (Nahar et al. 2017).

Several plants are used as potential candidates for phytoremediation. *Helianthus annuus* proved to be an effective strategy to reduce the level of uranium (U) in contaminated soil in Jordan (Alsabbagh and Abuqudaira 2017). Likewise, *Brassica juncea* was used as a phytoremediation agent in Pb contaminated site in Trenton, New Jersey (Blaylock et al. 1999). The current trends in phytoremediation exploit the combined application of knowledge from the field of genetics, molecular biology, omics, metabolic engineering, and nanotechnology (Rai et al. 2020).

Governmental and non-governmental organizations are more focusing on the reclamation of contaminated lands. They offers job opportunities in various fields and helps in remediating the polluted land in an eco-sustainable manner. Even though the governments have invested a significant amount in conventional phytoremediation technologies, it is inadequate to clean up the contaminated sites. Furthermore, the maintenance of the decontaminated sites by preventing further exposure requires continuous input of energy and money. Leaving the contaminated space as such leads to the spreading of contaminants, and also prevents the utilization of the land for any other purposes. Creating awareness among the native people living in the contaminated sites is another difficult task faced by experts. Hence, collaborative efforts jointly implemented by government and private sectors can provide a solution for this problem.

Large-scale phytoremediation markets get immense importance in the current scenario of global pollution. At present, the two largest markets for phytoremediation are in the USA and Europe. In addition to the clearing up of the polluted lands, phytoremediation offers opportunities in the field of entrepreneurship and employment; also, it gives opportunities for applied research. Opportunities offered by phytoremediation industries are represented in Fig. 10.1.

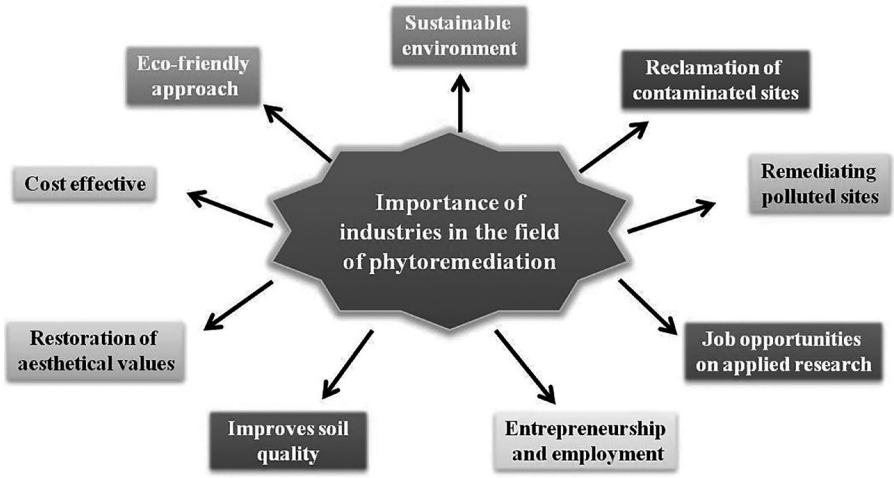


Figure 10.1: Importance and possibilities of industries in phytoremediation sector.

Field projects were successfully conducted in various contaminated sites in Europe. Lead (Pb) and Cd contaminated sites in Czechowice oil refinery in Poland were reclaimed using *B. juncea* by Phytotech, Florida State University, Institute for Ecology of Industrial Areas. Similarly, *Salix viminalis* was used by the Swiss Federal Institute of Technology for the remediation of the Zn and Cd contaminated sites in Switzerland. Implementation of innovative ideas in phytoremediation market sector provides various advantages over conventional techniques. Phytoremediation conducted by various industries for the reclamation of contaminated sites are listed in Table 10.1.

10.4 Modeling Phytoremediating Plant: Role of Public and Private Sectors

Contaminants are a global menace faced by common people of the world. Among them, heavy metal contamination is the major one and it is very important to find a solution to the current problem on an urgent basis. Phytoremediation is holistic, sustainable and cost-effective approach that involves a series of events to decontaminate heavy metals from both land as well as aquatic fields. Various researchers and companies have introduced a large number of plant candidates with phytoremediation potential. Bioenergy crops can be excellent candidates for decontamination of heavy metal contaminated lands as they possess additional advantage of producing renewable energy and hence bioenergy crops is promising to the increased demand of the non-renewable fossil fuels. Various crops such as poplars, willow, *Ricinus communis*, *Jatropha curcas*, *Acacia nilotica*, *Hibiscus cannabinus*, *Cannabis sativa*, *Azadirachta indica*, *Leucaena leucocephala*, *Millettia pinnata*, *Brassica juncea*, *Helianthus annuus* and *panicum vigratum* are successfully introduced into the heavy metal contaminated sites (EPA 1998). Similarly in water bodies, severe heavy metals pollution can be remediated and cleared using different

Table 10.1: Phytoremediation conducted by different organizations

Area contaminated	Xenobiotics	Clearing organization	Plants used	Family	References
US	Uranium	Edenspace System Corporation	*Helianthus annuus* and *Brassica juncea*	Asteraceae Brassicaceae	Singh et al. (2006)
Fort Greely, USA	Strontium	Edenspace System Corporation	*Brassica juncea*	Brassicaceae	Singh et al. (2006)
Switzerland	Zinc and cadmium	Swiss Federal Institute of Technology	*Salix viminalis*	Salicaceae	Singh et al. (2006)
University of Glasgow	Nickel, copper, zinc, cadmium	Sewage disposal site (United Kingdom)	*Salix viminalis*	Salicaceae	Singh et al. (2006)
Bayonne, New Jersey	Lead	Phytotech, Inc.	*Brassica juncea*	Brassicaceae	Watanabe (1997)
Dorchester, Maine	Lead	Edenspace System Corporation	*Brassica juncea*	Brassicaceae	Henry (2000)
U.S.A.	Arsenate	U.S. Army Corp of Engineers Edenspace Systems, Inc.	*Pteris cretica* and *Pteris vittata*	Pteridaceae	Ebbs et al. (2009)
Bayonne, New Jersey	Lead	Phytotech Inc.	*Brassica juncea*	Brassicaceae	Saxena et al. (1999)
Chernobyl	137Cs and 9OSr,	Phytotech Inc.	Helianthus annuus	Asteraceae	Saxena et al. (1999)
Holte, Denmark	Cyanide, BTEX, PAHs, oil	Technical University of Denmark	Salix viminalis and *Populus tremula*	Salicaceae	Schwitzguébe et al. (2002)

plant species such as water hyacinth, azolla, poplar, and duck weed (Liphadzi et al. 2003). In contrast to higher plant species, bioremediation via algae is a novel approach in the field of water management. As green algae are having photosynthetic machinery, they are able to produce higher biomass even under polluted environments. Moreover, being enriched with higher lipid content it can very well act as a source of biofuel production. The selection of plant and algal species having phytoremediation potential and the ability to produce higher biomass is an essential feature to be considered while preparing a water based treatment method. Different industries involved in developing phytoremediating plant candidates are:

10.4.1 Exxon Mobil Corporation

Exxon is a research based American company headquartered in Irving, Texas that works on bioremediation of contaminated hydrocarbons in soil surface. The company has found that treating the soil with microorganisms is a better technique of phytoremediation. Several laboratory studies have been conducted by Exxon for the polycyclic aromatic hydrocarbons' (PAH) biodegradability in contaminated refinery soil via phytoremediation. The incorporation of plants in the contaminated site appears to increase the rate of heavy metal degradation. In addition, when the treatment of soil with different methods is compared, the economic cost of using phytoremediation is less than half of that needed for microbial bioremediation.

10.4.2 Chevron

Chevron is a company indulged in clearing lands using phytoremediation. The company carried out a field research project in Ogden, Utah, to investigate the phytoremediation potential of poplars, to restrict the transport of solute to ground water. Generally, the ground waters are contaminated by diesel and gasoline components and further reaches deep down to eight feet below the surface of soil. Here the roots of plants absorb and forcefully uptake the contaminant by acting as a barrier. Poplars were planted in three rows with a distance of six feet apart and its roots reached the ground water. Thus, poplar was known as a plant for phytoremediation (Liphadgi et al. 2003).

10.4.3 Gas Research Institute (GRI)

Gas Research Institute, situated in Chicago, is involved in treating natural gas. According to statistical data, in United States there are around 260,000 numbers of gas wells and 700 gas processing plants. GRI is an international company concerned with identifying techniques such as phytoremediation, bioventing and land farming for clearing. Some of the well-known projects conducted by GRI include Environmentally Acceptable Project to restrict hydrocarbon mobility movements in soils.

10.4.4 Sierra Environmental Services, Inc.

Sierra Environmental Services is a company which uses plants to remediate the contaminated site in Florida. The project used non-riparian phreatophytes to clear

out the groundwater contaminants of a disposal lagoon area. These non-riparian phreatophytes are commonly called as water loving plants, which develop deep roots to absorb water from the deep down surface. For the study, a number of phreatophytes were evaluated such as alders, ash, aspen, river birch, cottonwoods, mesquite, bald cypress, eucalyptus, greasewood, salt cedar, willows and poplar. These plants restrict the movement of heavy metals into water table and improve the intrinsic bioremediation. This method of bioremediation was considered as an efficient remedy for the contaminated lagoon.

10.4.5 Monsanto

Monsanto is a company that has keen interest in issues of phytoremediation. Monsanto identified various contaminated field sites and investigated the possibility of phytoremediation and its potential effects in contaminated sites. A novel technique developed and introduced by Monsanto was Lasagna TM technology. The new Lasagna TM technology includes a series of events, mainly electroosmosis, which are applied directly in contaminated soils with a remedial approach. This process can also hold an advantage of moving water from ground to plant root zones (Lambert et al. 2000).

10.4.6 Occidental Chemical Corporation

Occidental Chemical Corporation is an agency where Poplar trees are used to decontaminate trichloroethylene (TCE) contaminated groundwater. Several experiments were performed, which indicates that poplars absorb and take up the contaminants from the decontaminated soil. State of Washington provided the permission to Occidental to conduct field trials using applied TCE. Field experiment of two years was conducted to assess the rate of decontamination by hybrid poplars from groundwater. It was also noted that poplars possess the potential of high transpiration through which TCE can be removed by poplar trees (Wood 1997).

10.4.7 Phytotech

Phytotech is commonly involved in phytoremediation technologies by engineering plants to treat water and soil contaminated with heavy metals. The main treatment method used in their technology was phytoextraction. It is a simple, cost effective, sustainable and friendly approach towards removal of heavy metals. Here, plants are grown in contaminated soil and harvested after accumulation of toxic metals in tissue of the plant. The rate of accumulation of heavy metal varies for different plant species and thus cleans up the whole land. Statistical data suggests that from 10-acre site phytoextraction can remove 400 ppm of Pb from the top one foot, which requires 500 tons of biomass and $1/4^{th}$ of the soil was cleaned. Phytotech has undertaken several programs and among them, SITE and rhizofiltration technology are widely known. Under the SITE program, phytoremediation technology was done in the contaminated soil at metal-plating facility in Findlay, Ohio. Several other successful field remediations were carried out in U.S and abroad by this company. Rhizofiltration was done to remove cesium/stromium (Cs/Sr) at Chernobyl and uranium (U) from polluted groundwater in Ashtabula, Ohio. At Chernobyl, sunflowers filtered and

absorbed the radionuclides from small ponds within 10 days. Similarly in Ashtabula site, a nine-month project by Phytotech cleaned up the U containing groundwater.

10.4.8 National Risk Management Research Laboratory (NRMRL)

NRMRL is an environmental protection agency situated in America, with headquarters in Cincinnati, Ohio and divisions in North Carolina, Oklahoma, and New Jersey. The agency is involved in risk management research and specifically solves environmental issues (NRMRL, 2000). They are recognized as leader of scientific expertise, which directly supports the action to reduce contaminations of air, water and land, cleanup of hazardous heavy metals and improve water quality. Their main aim is to prevent and reduce air, water and land pollution and thus to restore ecosystem (EPA 2000).

10.4.9 Remediation Technology Development Forum (RTDF)

The RTDF is a development forum which discusses the collaborative projects and works to be conducted and performed to decontaminate, purify and protect the environment from hazardous waste and heavy metal accumulation. It was started in 1992 with collaboration between two parties, i.e. Monsanto and EPA with an aim to hold hands between government and industry together with developing innovative ideas to overcome contamination problems. The RTDF was introduced to progress the development of more cost-effective, economically feasible approach for the remediation of contaminated sites.

10.4.10 National Exposure Research Laboratory in Athens, Georgia

NERL is a protection agency that looks for benefits and limitations of phytoremediation and phytodegradation. The agency described and investigated different processes involved in phytoremediation such as phytoextraction, phytoaccumulation, rhizofiltration, phytodegradation, and phytovolatilization. The advantage of using plants are that they have aesthetic values, balanced water system, advanced enzymatic machinery, are nutrients rich, and have potential of completely breaking down hazardous contaminants, and are economically feasible. Now research focuses on identifying the pathways and signalling mechanisms of hazardous material degradation by vascular plants and microorganisms. A collaborative work of Athens laboratory and the Army at the Iowa Army Ammunition Plant to phytoremediate heavy metals and radionuclides is under progress.

10.5 Clearing of Contaminated Land

Restoring the contaminated land is very essential for a nation to fulfill the basic needs of the increasing population. The task of clearing contaminated land is being achieved with the help of different firms and government agencies. Governments of different countries always made efforts for the remediation of contaminated land.

But due to different socio-economic crises, the participation of private industries in the field of phytoremediation is the need of the hour.

The generation of industrial waste is the major contribution of mankind to increase the contamination of soil and groundwater. So it is essential to arrange a waste management plan for each such industry. But these industries are also facing difficulties to obtain proper support and infrastructure for cleanup of the contaminated area. Moreover, groundwater contamination is also a growing concern for the human population. Unfortunately, conventional pump-and-treat method is being used for the cleanup of groundwater at 93 percent of contaminated sites (EPA 1996). This is a high cost and low performance method as compared to the other technologies. Thus, it is essential to develop new industries in the field of hazardous material management, phytoremediation, and land rehabilitation.

10.5.1 Government agencies in contaminated land cleanup programs

10.5.1.1 National Research Council (NRC) Canada

The scientific research of the country is chiefly dependent on this institute, started by President John McDougall in 2011. Algal carbon conversion flagship program is one of the best strategies of waste management and bioenergy production introduced by NRC with the involvement of Canadian Natural Resources Limited (Canadian Natural) and Pond Technologies within a budget of $19 million. In this project, 25,000 L photobioreactor was planned to be constructed for the transformation of CO_2 in the environment to the algal biomass. The infrastructure and the photobioreacter is by the support of the Pond Technologies and the algal strains were supplied by the Government.

The Government of Canada introduced a 15-year program, the Federal Contaminated Sites Action Plan (FCSAP), which was executed in 2005 with a budget of $4.54 billion. Due to the demand for environmental sustainability, FCSAP was renewed for another 15 years. The major aim of this program is to analyze the highest priority sites, federal contaminated sites and associated federal financial liabilities, and the formulation of appropriate strategies to avoid environmental and human health risks due to the toxic xenobiotics contaminated sites (FCSAP 2012).

The National Research Council (NRC), associated with Department of Fisheries and Oceans (DFO), worked on other important project, and proved that the microbial assisted biodegradation of oil at 1°C in the high Arctic marine region is possible. Program of Energy Research and Development (PERD) of NRC significantly contributed to the funding of this project. This work mainly focused on the kinetics of microbial actions.

10.5.1.2 EPA (Environmental Protection Agency)

The Environmental Protection Agency of US introduced “Initiatives to Promote Innovative Technology in Waste Management Programs” (EPA 1996) for the establishment of partnerships between government and different industries. The Technology Innovation Office of EPA mainly focuses on the innovation of novel

remediation technologies that increase research on remediation technologies. Different methods to analyze sediment cleanup programs, on-site and off-site methods to assess the intensity of metal transfer to humans, improved models for predicting the biomagnification of xenobiotics to the fishes, and faster and cheaper tools that detect changes in sediment toxicity are the major outcomes of EP soil clearing program. EPA Brownfield programs and Land Revitalization Programs were the milestones in the land clearing programs of the nation. Evaluation of site condition and the hazardous material presented in the soil give primary information regarding the impact of this toxicity on the human population. The evaluation was based on the Hazard Ranking System (HRS) and sites with HRS scores of 28.50 or greater were included in the National Priorities List (NPL). Further remedial investigation and actions will be carried out at these sites.

10.5.1.3 European Commission

The European Commission (EC) was established on 16 January 1958 and this institute implemented laws to protect the environment and proposed strategies to clear contaminated sites (EC 2018). The contaminated land clearing was a major agenda of EC and with the help of European Soil Data Centre (ESDAC) by JRC, the collection of soil data and monitoring of the heavy metal pollution was possible (Tóth et al. 2016).

The research conducted in 2016 on the topic "Progress in the management of contaminated sites in Europe" with the help of National Reference Centers (NRCs) aided in providing extensive knowledge on the rate of clearing contaminated land. According to the report, 650,000 sites were remediated from the 2.5 million contaminated sites and it is a great improvement in the land clearing process of the country. According to the data obtained by EC, the mineral oil and heavy metal toxicity are the crucial issues in the contamination reported sites. Based on the information from 39 countries, the major remediation technique implemented in these land clearing is the "dig-and-dump", an *ex-situ* technique, which implicates the digging and off-site disposal of polluted sediments. But the real concern over this clearing purpose is the budget. Approximately €4.3 billion was utilized for the same and a major portion of the expenditure came from the public budget (EC 2018). It was finally decided that the responsible industries or firms have to clear the land, soil, and water, which had been contaminated by them and for this purpose extensive investments in the field of land clearing is essential.

10.5.1.4 The Ministry of Environment, Forest and Climate Change (MoFE)

The Ministry of Environment, Forest and Climate Change was established in 1985, helping with the execution of India's environmental and forestry policies and programs. The annual budget of MoFE was US$430 million for the year 2020-21. According to the remediation strategies of MoFE, site specific remediation target levels (SSTLs) were calculated for each contaminated site by analyzing the impact of contamination on humans. "Creation of Management Structure for Hazardous Substances" is another program established by the Indian government. The sub-schemes of this program are:

- SAMPATTI - 'Sustainable Management of Pre-owned Asset through Trade Initiatives':
- Capacity building of government agencies/organizations/department/civil society/institute with respect to environmentally sound management of chemicals and wastes.
- Organizing awareness program with various stakeholders for implementation of various wastes and chemicals management rules.
- Innovative technologies for environmentally sound management of chemicals and wastes
- Setting up facilities for the management of biomedical waste (CBMWTF) and treatment, storage and disposal of hazardous waste (TSDF).

"Capacity Building for Industrial Pollution Management (CBIPM) Project" from MoFE supported by World Bank from October 2010 to March 2018 is a historical move in the land clearing programs of India. The contaminated sites of Andhra Pradesh (Kadapa) and West Bengal (Dhapa) were selected for this work. West Bengal State Pollution Control Board is implementing clearing of dumpsite (12.14 hectare) at Dhapa with a budget of Rs. 57.44 Crore. Similarly, the Kadapa (10.38 acre) of Andhra is being cleared by Andhra Pollution Control Board with a project cost of Rs. 30.17 Crore.

10.5.2 Private organizations

The introduction of different private industries and stand-up programs in the field of land cleanup is really essential to overcome the shortage of experts, equipment, money and other recourses. Figure 10.2 represents different phytoremediation agencies.

Figure 10.2: Various agencies in the field of phytoremediation.

10.5.2.1 Pond tech

It is a Canadian company investing in algal bioprocess with a vision to transform algae as the basis of a low carbon economy. Algae-based superfoods like *Spirulina* and *Chlorella*, protein enriched animal feeds, biofuels and cosmetics products are the major pond tech products. This industry will help to reduce the extensive carbon emission from other firms.

10.5.2.2 Biofuel NET

BioFuelNet is another Canadian company established for the mobilization of biofuel research aiding in the utilization of non-food biomass as biofuel feedstock.

10.5.2.3 SUEZ group

It is an American company implemented to remediate polluted soil and water tables and they exploit different phytotechniques in the field. They follow standard LNE NF X 31-620-1-2-3-4 for clearing a contaminated land. They showed excellence in providing human and technical resources, technical and financial feasibility, and conducting laboratory tests and field tests for a better resolution. According to the characteristics of the contaminated sites, SUEZ is proposing different methods of treatments:

In situ remediation including venting, bioventing, sparging, simultaneous treatment of the soil, groundwater and floating materials and the treatment of chlorinated pollution.

Off-site remediation (soil excavation) was done by the transferring of contaminated soil to different certified biocenters for treatment, usage of waste tracking documents, and the optimization and recovery of tonnages on the Neoter® platform (this platform is utilized for various treatments and pretreatments).

10.5.3 MLM group

An American company that aids to remediate brownfield sites with a detailed investigation of the regulatory framework and has the familiarity of working with developers, principal contractors, engineering consultants, regulators, and other stakeholders to achieve appropriate solutions in a short duration. More than the removal of contaminants, this firm provides legal support.

MLM undertakes appropriate investigation and assessment of brownfield sites such as former gasworks, chemical works and other industrial sites which often have complex soil, gas and groundwater contamination conditions. The progressive work involves inception, providing case studies, designing appropriate site investigations and monitoring programs, undertaking risk assessments and developing a robust conceptual site model for remediation. Work may be required to clear planning conditions and enable future development, understand risks and liability for site divestment of the Environmental Protection Act. Whether it involves long-term monitoring or active remediation, the clean-up and management of contaminated sites can be complex and costly. MLM has a reputation for deliverable solutions focussed on end use. One of the projects is:

Haulbowline Island East Tip Phytoremediation Project

Haulbowline Island east tip is a project that involved phytoremediation of the East Tip located in Cork Harbour, a location in Ireland. The contaminants released by the steel works processing industry was deposited on an area of reclaimed foreshore, which became known as the 'East Tip'. This project cleared the area of the East Tip and transformed it into a public recreational amenity**.**

10.5.3.1 Argyll environmental

This company was founded in UK (2002) to find strategies to solve different environmental crisis and contamination issues. The collaboration with UK's top law firms makes this company a more appropriate candidate for clearing contaminated land.

10.5.3.2 Veolia's

New investments are being implemented in India to clear contaminated lands and Veolia's waste management technology is a pioneer in this field. Veolia offers remediation within an industry, large-scale restoration project for municipal governments by different techniques (physical, chemical, biological methods) and also provides the clearing equipment. This industry also implemented different techniques to treat methane, leachate and industrial wastewater.

10.6 Conclusion

Heavy metal contamination is a major threat to human health. Restoration of contaminated regions has a crucial role in attaining the needs of the exponentially growing population. Phytoremediation has great importance in the ecological aspect. It completely removes contaminants in a safe manner. There are several efforts to accomplish this task by governments of different countries. At the same time, industries that focus on phytoremediation are emerging in different countries. However, due to the lack of enough knowledge, still there are uncertainties in the public view about phytoremediation. The introduction of different industries in land reclamation is a good strategy of the nation and it reduces the efforts of the government sector in land restoration.

Acknowledgments

EJ, AS, ARKP and RJ gratefully acknowledge the financial assistance from University Grants Commission (UGC) and Council of Scientific and Industrial Research (CSIR), India through JRF fellowships. JTP acknowledges the financial assistance provided by Kerala State Council for Science, Technology and Environment in the form of KSCSTE Research Grant (KSCSTE/5179/2017-SRSLS). The authors extend their sincere thanks to the Department of Science & Technology (DST), Government of India for granting fund under Fund for Improvement of S&T Infrastructure (FIST) programme (DST-FIST/15-16/28.05.2015).

References

Afzal, M., G. Shabir, S. Iqbal, T. Mustafa, Q.M. Khan and Z.M. Khalid. 2014. Assessment of heavy metal contamination in soil and groundwater at leather industrial area of Kasur, Pakistan. CLEAN – Soil, Air, Water 42(8): 1133-1139.

Ali, H., E. Khan and M.A. Sajad. 2013. Phytoremediation of heavy metals – Concepts and applications. Chemosphere 91(7): 869-881.

Alsabbagh, A.H. and T.M. Abuqudaira. 2017. Phytoremediation of Jordanian uranium-rich soil using sunflower. Water Air Soil Pollut. 228(6): 219.

Arthur, E.L., P.J. Rice, P.J. Rice, T.A. Anderson, S.M. Baladi, K.L. Henderson and J.R. Coats. 2005. Phytoremediation—An overview. Crit. Rev. Plant Sci. 24(2): 109-122.

Blaylock, M.J., M.P. Elless, J.W. Huang and S.M. Dushenkov. 1999. Phytoremediation of lead-contaminated soil at a New Jersey brownfield site. Remed. Jour. 9(3): 93-101.

Ebbs, S., S. Hatfield, V. Nagarajan and M. Blaylock. 2009. A comparison of the dietary arsenic exposures from ingestion of contaminated soil and hyperaccumulating Pteris ferns used in a residential phytoremediation project. Int. J. Phytoremediation 12(1): 121-132.

Environmental Protection Agency of United States (EPA). 1996. National Water Quality Inventory Report to Congress.

Environmental Protection Agency of United States (US EPA). 2001. Citizen's Guide to Phytoremediation.

European Commission (EC). 2018. Annual Report of European Commission.

Hauptvogl, M., M. Kotrla, M. Prčík, Ž. Pauková, M. Kováčik and T. Lošák. 2019. Phytoremediation potential of fast-growing energy plants: Challenges and perspectives – A review. Pol. J. Environ. Stud. 29(1): 505-516.

Henry, J.R. 2000. An overview of the phytoremediation of lead and mercury. NNEMS Report 2000: 3-9.

Janeeshma, E. and J.T. Puthur. 2020. Direct and indirect influence of arbuscular mycorrhizae on enhancing metal tolerance of plants. Arch. Microbiol. 202(1): 1-16.

Khan, S., S. Rehman, A.Z. Khan, M.A. Khan and M.T. Shah. 2010. Soil and vegetables enrichment with heavy metals from geological sources in Gilgit, northern Pakistan. Ecotoxicol. Environ. Saf. 73(7): 1820-1827.

Kumar, A., B.S. Bisht, V.D. Joshi and T. Dhewa. 2011. Review on bioremediation of polluted environment: A management tool. Int. J. Environ. Sci. 1: 1079-1093.

Lambert, M., Leven, B.A. and R.M. Green. 2000. New methods of cleaning up heavy metal in soils and water. Environmental Science and Technology Briefs for Citizens 7(4): 133-163.

Lelie, D.V.D., J.P Schwitzguébel, D.J. Glass, J. Vangronsveld and A. Baker. 2001. Peer reviewed: Assessing phytoremediation's progress in the United States and Europe. Environ. Sci. Technol. 35: 446-452.

Li, T., Y. Liu, S. Lin, Y. Liu and Y. Xie. 2019. Soil pollution management in China: A brief introduction. Sustainability, 11(3): 556.

Liphadzi, M.S., M.B. Kirkham, K.R. Mankin and G.M. Paulsen. 2003. EDTA-assisted heavy-metal uptake by poplar and sunflower grown at a long-term sewage-sludge farm. Plant and Soil, 257(1), 171-182.

Liu, D., Z. An, Z. Mao, L. Ma and Z. Lu. 2015. Enhanced heavy metal tolerance and accumulation by transgenic sugar beets expressing *Streptococcus thermophilus* StGCS-GS in the presence of Cd, Zn and Cu alone or in combination. PLoS One, 10(6): e0128824.

Luo, J., L. Cai, S. Qi, J. Wu and X.S. Gu. 2017. A multi-technique phytoremediation approach to purify metals contaminated soil from e-waste recycling site. J. Environ. Manage. 204: 17-22.

Nahar, N., A. Rahman, N.N. Nawani, S. Ghosh and A. Mandal. 2017. Phytoremediation of arsenic from the contaminated soil using transgenic tobacco plants expressing ACR2 gene of *Arabidopsis thaliana*. J. Plant Physiol. 218: 121-126.

National Risk Management Research Laboratory (US). 2000. Introduction to Phytoremediation.

Pandey, V. C., O. Bajpai, and N. Singh. 2016. Energy crops in sustainable phytoremediation. Renewable Sustainable Energy Rev. 54: 58-73.

Patel, P., N.J. Raju, B.S.R. Reddy, U. Suresh, D.B Sankar and T.V.K. Reddy. 2018. Heavy metal contamination in river water and sediments of the Swarnamukhi River Basin, India: Risk assessment and environmental implications. Environ. Geochem. Health 40(2): 609-623.

Rai, P.K., K.H. Kim, S.S. Lee and J.H. Lee. 2020. Molecular mechanisms in phytoremediation of environmental contaminants and prospects of engineered transgenic plants/microbes. Sci. Total Environ. 705: 135858.

Sameena, P.P. and J.T. Puthur. 2021. Cotyledonary leaves effectively shield the true leaves in *Ricinus communis* L. from copper toxicity. Int. J. Phytoremediation 23: 492-504.

Sarath, N.G. and J.T. Puthur. 2020. Heavy metal pollution assessment in a mangrove ecosystem scheduled as a community reserve. Wet. Ecol. and Manag. 1-12.

Saxena, G., D. Purchase, S.I. Mulla, G.D. Saratale and R.N. Bhargava. 2019. Phytoremediation of heavy metal-contaminated sites: Eco-environmental concerns, field studies, sustainability issues, and future prospects. Rev. Environ. Contam. T. 249: 71-131.

Saxena, P.K., R.S. Krishna, T. Dan, M.R. Perras and N.N. Vettakkorumakankav. 1999. Phytoremediation of heavy metal contaminated and polluted soils. pp. 305-329. *In*: Prasad, M.N.V. and J. Hagemeyer [eds.]. Heavy Metal Stress in Plants – From Molecules to Ecosystems. Springer, Berlin, Heidelberg.

Schwitzguébel, J.P., D. van der Lelie, A. Baker, D.J. Glass and J. Vangronsveld. 2002. Phytoremediation: European and American trends, successes, obstacles and needs. J. Soils and Sediments 2(2): 91-99.

Sharma, P. and S. Pandey. 2014. Status of phytoremediation in world scenario. Int. J. Environ. Bioremediat. Biodegrad. 2(4): 178-191.

Sharma, R.K., M. Agrawal and F.M. Marshall. 2009. Heavy metals in vegetables collected from production and market sites of a tropical urban area of India. Food Chem. Toxicol. 47(3): 583-591.

Siddiqui, A.S. and N.U. Saher. 2021. Distribution profile of heavy metals and associated contamination trend with the sedimentary environment of Pakistan coast bordering the Northern Arabian Sea. Environ. Sci. Pollut. Res. 1-18.

Singh, P., Rana, D. Geeta, S. Asha and K.J Pawan. 2006. Biotechnological approaches to improve phytoremediation efficiency for environment contaminants. pp. 223-258. *In*: Singh, S.N. and R.D. Tripathi [eds.]. Environmental Bioremediation Technologies. Springer Publication, NY.

Singh, R., N. Gautam, A. Mishra and R. Gupta. 2011. Heavy metals and living systems: An overview. Indian J. Pharmacol. 43(3): 246.

Su, C. 2014. A review on heavy metal contamination in the soil worldwide: Situation, impact and remediation techniques. Environ. Skeptics Critics 3(2): 24.

Suman, J., O. Uhlik, J. Viktorova and T. Macek. 2018. Phytoextraction of heavymetals: A promising tool for clean-up of polluted environment. Front. Plant Sci. 9: 1476.

Tang, W., Y. Zhao, C. Wang, B. Shan and J. Cui. 2013. Heavy metal contamination of overlying waters and bed sediments of Haihe Basin in China. Ecotoxicol. Environ. Saf. 98: 317-323.

The Federal Contaminated Sites Action Plan (FCSAP). 2012. Canada, environment and climate change: "action plan for contaminated sites." Program results.

Tóth, G., T. Hermann, G. Szatmári and L. Pásztor. 2016. Maps of heavy metals in the soils of the European Union and proposed priority areas for detailed assessment. Sci. Total Environ. 565: 1054-1062.

Van der Lelie, D., J.P. Schwitzguebel, D.J. Glass, J. Vangronsveld and A.J.M Baker. 2001. Assessing phytoremediation's progress in the United States and Europe. Environ. Sci. Technol. 35: 446A-452A.

Watanabe, M.E. 1997. Phytoremediation on the brink of commercialization. Environ. Sci. Technol. 31(4): 182A-186A.

Wood, P. 1997. Remediation methods for contaminated sites. pp. 47-71. *In*: R. Hester and R. Harrison [eds.]. Contaminated Land and Its Reclamation. The Royal Society of Chemistry, Cambridge.

Zhang, L., X. Ye, H. Feng, Y. Jing, T. Ouyang, X. Yu and W. Chen. 2007. Heavy metal contamination in western Xiamen Bay sediments and its vicinity, China. Mar. Pollu. Bull. 54(7): 974-982.