REVIEW ARTICLE

Phytoremediation of Metals and Metalloids from Industrial Wastewater

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Abstract

Heavy metal and metalloid pollution are growing concern around the world. Toxic heavy metals (HMs) such as cadmium (Cd), chromium (Cr), mercury (Hg), arsenic (As), lead (Pb), and zinc (Zn) are a major environmental issue which is generated from anthropogenic activities. Metals and metalloids are a class of elements that fall between metals and non-metals in respect of physico-chemical characteristics. The absorption of such toxic metals in farmlands raises concerns about food safety as well as decreases in plant growth and productivity and yield of crops. Several metalloids are recognized to be required or quasi-essential for plant growth and development, such as boron, selenium, and silicon. Various ions may be beneficial to plant growth and development when present in low concentrations, but when present in large concentrations, they frequently have harmful impacts. Understanding the molecular mechanisms involved in metalloid absorption by plant roots, subsequent transport to various tissues, and inter/intra-cellular redistribution is crucial in this regard. There have also been discoveries of different transporters and membrane channels involved in these processes. It has also touched on the absorption, distribution, and storage of metalloids in plants, as well as the molecular mechanisms that underpin their response. Traditional wastewater treatment technologies are typically expensive, time-consuming, dangerous to the environment, and inefficient. The phytoremediation of metals and metalloids have been examined in depth in this review. Furthermore, we have discussed earlier theories and arguments about the role and consequences of metalloids in plants using current information to provide interesting insights. Researchers focus on techniques that used enhance the accuracy of phytostabilization and phytoextraction, such as genetically engineered, microbiota and chelate-assisted strategies. The above overview also highlights the limitations and future perspectives of sustainable phytoremediation.

Keywords: Green technology, Health hazards, Metals removal, Phytoextraction, Sustainable development.

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Highlights

- The use of phytoremediation technology to clean up polluted area with HMs and metalloids is addressed.
- We described conventional phytoremediation strategies as well as the molecular mechanisms in phytoremediation.
- Phytoremediation is an advanced tool for restoring polluted sites to their natural state.

Introduction

Rapid urbanization and industrialization have wreaked havoc on global environmental matrix throughout the last century. Pollution caused by anthropogenic activities such as mining, smelting, fossil fuel combustion, fertilizer use, industries and sewage has had an irreversible harmful impact on all kinds of life on earth, including humans (Clemens, 2006; Cristaldi *et al.*, 2017; Sharma *et al.*, 2021a; 2021b; 2021c; Sharma and Kumar, 2021). Such contaminants, which come in the form of solid, liquid, and gaseous wastes and enter the food chain through a variety of routes and have become a major source of rising health concerns around the world (Muthusaravanan *et al.*, 2018). Soil degradation processes such as erosion, salinization, and HMs contamination have all harmed soil health (da Conceiçao Gomes *et al.*, 2016). If the density of an element is greater than 5 g/cm^3, it is designated as a HMs. Cu, Pb, Zn, Hg, As, and Cd are among the transition elements that belong to HMs (Laghlimi *et al.*, 2015). This massive discharge accumulates HMs in agricultural soils and water resources, posing a health concern to humans due to the possibility of their entering the food chain (Sarwar *et al.*, 2017; Sharma *et al.*, 2021d). Because of the unrestrained production of metallic waste, as well as its unchanging properties, persistence, and biomagnifications, HMs contamination of soil has now become a worldwide threat. This was previously shown that roughly 10 million individuals worldwide suffer from health problems because of HMs contamination in soil (Shakoor *et al.*, 2013). According to studies, more than 15% of the country's cropland and agricultural land has become useless owing to HMs contamination, greatly exceeding the limit of environmental quality regulations for soil. Soil contamination has afflicted several European countries, including Germany, Spain, Italy, Denmark, France, Slovakia, and many others. Around 600,000 ha of brownfield sites in America were found to be contaminated by HMs in 2012, giving this type of contamination a global

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reputation (Mahar *et al.*, 2016). Massive efforts have been undertaken in the last two decades to create a variety of soil-cleaning systems based on physical, chemical, or biological technologies, which are further split into two categories: on-site or off-site (Lim *et al.*, 2014). The traditional physico-chemical treatments include soil excavation and transfer to land-filling, washing, acid extraction, and immobilization of HMs using chemicals such as limestone and ethylene diamine tetra-acetic acid (EDTA) to limit their dissemination in the ecosystem (Clemens, 2006). Vapor extraction, thermal desorption, and ion exchange are some of the latest and forthcoming approaches, followed by the disposal of waste items in landfills. Despite the availability of several conventional and contemporary technologies, financial and technological challenges have made HMs soil rehabilitation a time-consuming operation. Labor-intensive procedures, generation of secondary HMs pollution during migration, reduction of soil fertility, destruction of natural soil microfauna, generation of voluminous hazardous sludge, and high operational costs are all major drawbacks of these approaches, limiting their widespread use in developing nations (Ali *et al.*, 2013). Tsao, (2003) estimates that the yearly cost of global remediation efforts is between $25 and $50 billion US dollars, with about $6-8 billion US dollars spent in the United States only. It has been deemed one of the most suitable methods available (da Conceição Gomes *et al.*, 2016). Biodegradation, bio-stimulation, bio-venting, bio-leaching, bio-filtration, bio-augmentation, and phytoremediation are some of the strategies used in this approach (Muthusaravanan *et al.*, 2018). Phytoremediation, also known as Phyto-cleaning and Phyto-correction, is a plant-based approach that restores damaged land and water resources by utilizing plants' natural abilities, such as selective uptake, translocation, accumulation, and breakdown of toxins. By utilizing naturally existing or genetically designed plants, this relatively new technique has shown significant potential and is being considered a green alternative solution to the global problem of HMs contamination (Leguizamo *et al.*, 2017). This review paper provides a background, ideas, and current prospects in phytoremediation of HMs and metalloids in depth.

Uptake of Metalloids by Plants

Metalloids were elements of nature found in the earth's crust that share qualities with both metals and non-metals. Metalloids are widely distributed in the environment, along with a mixture of inorganic and organic substances, as well as other biochemicals (Kroukamp, Wondimu, & Forbes, 2016). Metalloids can be found in particularly high quantities in some soils because of indiscriminate industrial exploitation of these elements, resulting in ecosystem degradation, negative effects on plant growth, and potential risks to people due to the entry into the food supply chain (Anjum *et al.*, 2014; Maksymiec, 2007; Singh *et al.*, 2011). Metalloid absorption is an important physiological process that has a big impact on plant development. Both active and passive pathways are known to drive plant absorption and subsequent transport (Rejomon *et al.*, 2010; Valvanidis & Vlachogianni, 2010).

For the cellular uptake of metalloids from the soil and subsequent transfer to aerial tissues, the plant uses both active and passive transport pathways (Kroukamp *et al.*, 2016). Several lines of evidence point to integral membrane proteins being involved in the uptake and/or exclusion of metalloids from cells. The difference in solute concentration, which drives transport via these membrane-spanning proteins from high to low concentration, which transport against the concentration gradient, can drive transport via these membrane-spanning proteins (Zangi & Filella, 2012). Adenosine triphosphate (ATP) is employed as an energy source in inactive transport, and it is immediately absorbed by major active transporters or other ion-pumping proteins carrying Na^+ or H^+, resulting in an electrochemical potential difference on both sides of the cell membrane (Zangi & Filella, 2012). The force for transport is provided by the difference in electrochemical potential, and this type is known as secondary active transport, which is commonly used in the movement of ions (Zangi & Filella, 2012).

Plants for Phytoremediation

The potential of plant species to tolerate, accumulate, stabilize, and decompose the contaminant of interest, such as HMs and metalloids, is used to choose plant species for phytoremediation (Sharma *et al.*, 2021e). Over the last few decades, over 500 plant species have been recognized as having the ability to accumulate extremely high quantities of HMs in their aerial portions. Through phytomining and phytoextraction, these plants, known as hyperaccumulators, are being intensively utilized for HMs remediation. Hyperaccumulators can accumulate up to 500 times higher quantities of HMs in different plant sections than what is found in the soil. Plants are the most popular hyperaccumulating species because of their inherent characteristics of rapid growth, high HMs accumulation capability, and adaptability to a variety of soil types (Cappa and Pilon-Smits, 2014). Fast-growing woody plants outperform hyperaccumulating herbaceous plants in terms of removing HMs from contaminated soils (Luo *et al.*, 2016). Several investigations have advised that mixed vegetation employment of herbs, shrubs, and trees in combination, be used for long-term clean-up projects in which specialist species play a role at different stages (Laghlimi *et al.*, 2015). Various Phytoremediation strategies are shown in Fig. 1 and metal (loid) phytoremediator plants are shown in Table. 1

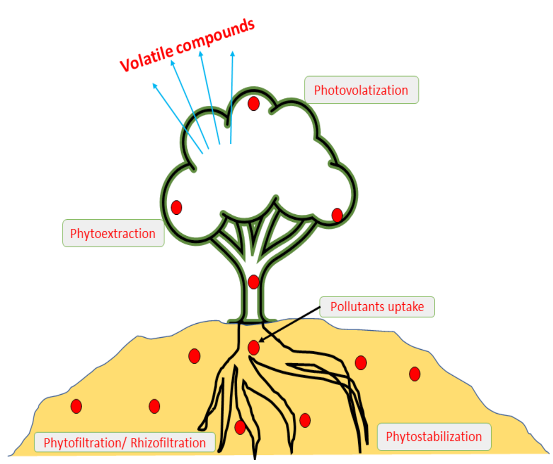

Fig. 1: Phytoremediation strategies in plants.

Transporter of Metalloids

Metalloid transport is regulated in plants by active or passive transport systems (Pommerrenig *et al.*, 2015; Jahn & Bienert, 2011; Filella, 2012). Numerous transporter protein families control the active and passive transport mechanisms that efficiently regulate the absorption, transport, and extrusion of many metalloids (Deshmukh *et al.*, 2020; Miwa & Fujiwara, 2010). Earlier, it was thought that uncharged metalloid transmembrane transport was mediated by passive diffusion across the lipid bilayer rather than proteins. Aquaporins and active transporters, among other membrane proteins involved in metalloid uptake, have been found (Bhat *et al.*, 2019).

Insights and Innovation Solutions for Phytoremediation

Phytoremediation Assisted by Microbes

Plant growth-promoting bacteria (PGPB) that can colonize the rhizospheric zone and boost plant growth and mineral nutrition are being used in bioremediation (Sharma *et al.*, 2021f; Sharma, 2021a; 2021b). Some microorganisms can break down or transform dangerous substances into less damaging versions (Ullah *et al.*, 2015). Various PGPB were shown to improve plant phytoremediation capacity by allowing HMs to be taken up by the roots. These microbes are important in HMs clean-up because they produce chemicals including siderophores and organic acids, which increase HMs bioavailability by lowering soil pH (Chen *et al.*, 2017). Some bacteria were found to secrete polymeric substances such as polysaccharides and glomalin, which help to stabilize HMs (Rajkumar *et al.*, 2015). Several plant growth promoting rhizobacteria (PGPR) plays an important role in phytoremediation processes in a variety of ways, including (a) increasing plant detoxification rates, (b) increasing enzyme root secretion, which leads to faster pollutant breakdown, and (c) altering soil pH (Lemtiri *et al.*, 2016). As a result, various bacterium strains have been discovered to boost plant HMs resistance.

Table 1: Phytoremediation: a long-term environmental strategy for removal of HMs.

Heavy metals & metalloids	*Plants*	*References*
Zn	*Atriplex halimus*	Lutts *et al.*, 2004
As	*Brassica Juncea*	Ko *et al.*, 2008
Ni	*Beeyacoddiirkh*	Robinson *et al.*, 1997
Cd	*Boehmerianivea*	Pan *et al.*, 2019
Cr	*Genipa americana*	Santana *et al.*, 2019
Cu	*Lactuca sativa*	Shams *et al.*, 2019
Co	*Haumaniastrum robertii*	Kabeya *et al.*, 2018
Cu/Pb	*Helianthus annuus*	Forte and Mutiti, 2017
Cu/Zn	*Hydrocotyle ranunculoides*	Demarco *et al.*, 2018
Cd	*Lagerstroemia indica*	Wang *et al.*, 2016
Cd	*Solanum nigrum*	Wei *et al.*, 2013
Cd/Cu	*Suaedafruticosa*	Bankaji *et al.*, 2015
Hg	*Spartina sp.*	Tian *et al.*, 2004
Cu/Ni	*Dalbergia sissoo*	Kalam *et al.*, 2019

Phytoremediation Assisted by Earthworms

The primary category of soil macroinvertebrates is earthworms, also known as "ecosystem engineers." They are essential for organic matter decomposition, nitrogen cycling, and soil improvement (Sharma *et al.*, 2020). Earthworms help to lower the pH of soil by secreting organic acids like fulvic and humic acids through their gut microflora, which improves nutrition and HMs bioavailability in the rhizosphere (Lemtiri *et al.*, 2016; Wang *et al.*, 2020). Wang *et al.*, 2020, for example, found that including earthworms in the growth medium improves the phytoremediation capacity for Cd in Solanum nigrum. *Pontoscolex corethrurus* can reduce Cr and Ni tolerance (Bongoua-Devisme *et al.*, 2019). In sandy soil contaminated with Cu, *Rhizoglomus clarum* integration enhances the phytoextraction capability of *Canavalia ensiformis* plants (Santana *et al.*, 2019). The combination of *Brassica juncea* plants and the earthworm *Eisenia fetida* considerably improves Cd detoxification effectiveness (Kaur *et al.*, 2018). The ability of *Avenastrigosa schreb* plants to extract Cd, Cr, and Pb increases when *Ensenia andrei* vermicompost is added to HMs-contaminated soil (Hoehne *et al.*, 2016).

Arbuscular Mycorrhizal Fungi Assisted Phytoremediation

Arbuscular mycorrhizal fungi (AMF) are symbiotic fungi that form a symbiotic relationship with root host plants to increase

Table 2: Gens and plants involved in the Transgenic Phytoremediation.

Bacteria	*Enzymes expressed*	*Plant*	*Genes*	*Useful effects*	*References*
Caenorhabditis elegans	Phytochelatin synthase	*Nicotiana tabacum*	AtPCS1 and CePCS	Improved As accumulation	Wojas *et al.*, 2010
Ceratophyllum demersum		*Arabidopsis thaliana*	CdPCS1	Improved As&Cd accumulation	Shukla *et al.*, 2013
Saccharomyces cerevisiae	Metallothionein transporter	*Nicotiana tabacum*	ScMTII gene	Improved Cd and Zn accumulation	Daghan *et al.*, 2013
Streptococcus thermophilus	γ-Glutamylcysteine synthetase and glutathione synthetase	*Beta vulgaris*	StGCS-GS	Improved Cd Cu and Zn tolerance	Liu *et al.*, 2015
Escherichia coli	γ-glutamylcysteine synthetase	*Poplar*	ECS genes	Improved Cd flux and detoxification	He *et al.*, 2015
Saccharomyces cerevisiae	Glutathione synthase and phytochelatin synthase	*Arabidopsis thaliana*	gsh1 and AtPCS1	Improved Cd and As tolerance	Guo *et al.*, 2008
Pseudomonas fluorescens	iron-regulated transporter	*Sedum alfredii*	SaNramp1	Improved Zn uptake	Wang *et al.*, 2019

phosphorus phytoavailability (Zhang *et al.*, 2015). AMF used two strategies to decontaminate HMs: (a) immobilization of HMs through the production of chelating agents and adsorption to fungal cell walls, and (b) phytoextraction of HMs through improved plant growth and increased HMs uptake in the rhizosphere through changing the chemical composition of root exudate and/or lowering soil pH (Cabral *et al.*, 2015). The inoculation of *Cassia italica* by AMF, greatly improved Cd tolerance by limiting the metal's transfer to aerial regions (Hashem *et al*., 2016). *Festuca arundinacea* plants and *Glomus mosseae* fungi have a symbiotic relationship that improves Ni translocation as well as the expression of ATP-binding cassette (ABC) transporter and metallothionein genes (Shabani *et al.*, 2018). In *Zea mays* plants cultivated in soil contaminated with Sr and Cd, AMF inoculation dramatically improves growth, and HMs uptake (Chang *et al.*, 2018). According to Armendariz *et al.*, 2019 *Glycine max* plants infected with *Bradyrhizobium japonicum* E109 and *Azospirillum brasilense* Az39 had improved as stress responses. The capacity of the endophytic fungus *Piriformospora indica* to reduce Cd toxicity by enhancing the physiological status of *Helianthus annuus* L. seedlings (Shahabivand *et al.*, 2017). Similarly, Rahman *et al.*, 2020 recently revealed that exogenous inoculation of *Artemisia annua* with *Piriformospora indica* can give resistance to As stress.

Genetically Modified Approaches

Transgenic plants are plants that have been genetically changed by DNA editing and genome transformation to incorporate additional genes that do not present naturally in the species to improve HMs uptake and translocation (Rai *et al.*, 2020). Engineered transgenic techniques are now widely regarded as the most important area of biotechnology research for enhancing phytoremediation. Overexpression of genes was used to alleviate the stress caused by HMs and to boost plants' phytoremediation capacities (Liu *et al.*, 2020). To circumvent some of the limitations of phytoremediation, hyper-accumulator plants can also be modified by genetic approaches/molecular mechanisms. As a result, current advances in biotechnology through gene expression have been extensively researched to improve phytoremediation procedures. Tolerance plant species were given genes from bacteria, fungi, or plants involved in the sequestration and breakdown of HMs. As a result, two approaches have been pursued: (a) overexpression of genes involved in HMs hyperaccumulation, and (b) introduction of genes from other organisms such as bacteria, fungus, or plants. The primary goal of this transgenic strategy is to obtain plants with a high capacity to tolerate, accumulate, or break down HMs (Gomes *et al.*, 2016). This method may also result in plants with desirable agronomic characteristics, such as high green biomass and a deep root system, as well as rapid development under a variety of pedo-climatic settings (Rai *et al.*, 2020). Transgenic phytoremediation has been shown in Table. 2.

Conclusions and Perspectives

HMs and metalloid concentrations in the environment have improved because of anthropogenic activity and natural erosion. Metalloids are absorbed through passive routes, such as simple diffusion or assisted diffusion, or active routes, which need energy. The influx of HMs and minerals from the soil to various plant organs, as well as the efflux of hazardous chemicals created inside the cell, are both dependent on transport pathways. For uptake and efflux, different metalloids require distinct membrane proteins, which differ from genus to genus. Because arsenic is extremely poisonous to plants, it is vital to prevent its absorption. Phytoremediation research is truly interdisciplinary, requiring knowledge of soil chemistry, plant biology, ecosystems, and soil microbiology, as well as environmental engineering. Physical and chemical methods for cleaning up and restoring heavy metal-contaminated soils have significant drawbacks, including high costs, irreversible changes in soil properties, destruction of native soil microorganisms, and the creation of secondary pollution issues. Phytoremediation is an environmentally friendly and economically and environmentally capable solar-powered technology that has widespread public support. Recent advancements and successes in such molecular studies will greatly aid in understanding the mechanism and improve the effectiveness of phytoremediation. Phytoremediation is expected to become a commercially viable technology for remediation and phytomining of HMs and metalloids in the future.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal that could have appeared to influence the work reported in this paper.

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