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Review Paper

Phytoremediation A Green Approach To Heavy Metal Removal: A Review

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ABSTRACT

Metal contamination is a substantial environmental challenge caused by the introduction of heavy metal ions into the environment. Since heavy metals are long lasting, they build up in the environment and ultimately pollute the food chain. This pollution compromises both environmental and human health. Heavy metal contamination in soil and water is a significant environmental issue, originating from both natural and anthropogenic sources. Essential heavy metals are necessary for the proper functioning of the human body, but their excess can be harmful. In contrast, non-essential heavy metals are toxic even at very low concentrations. The process of removing heavy metals from polluted soils is very tough, particularly when it comes on a large-scale basis. Phytoremediation is an evolving approach that uses various plants to remove, degrade, stabilize, or trap contaminants in soil and water. It is an economical and nature-friendly technique, providing a suitable alternative to chemical and physical methods for eliminating heavy metal contaminants from soil. Hyperaccumulator plants are remarkable plant species that can absorb and store very high amounts of certain heavy metals like cadmium, nickel, and zinc in their tissues. *Thlaspi caerulescens*, *Alyssum lesbiacum*, *Sesbania drummondii*, *Pteris longifolia*, *Pteris vittata* are few plants used in the phytoremediation of heavy metals.

1. Introduction

Metal contamination is a substantial environmental challenge caused by the introduction of heavy metal ions into the environment. Human activities like mining, farming, waste disposal, sewage treatment industrial processes, power generation played significant role in the rising levels of metal pollution in soil, water, and air [1-4]. Heavy metals have a half-life exceeding twenty years, making them highly resilient in the environment [5-7]. Elements with densities greater than 5 g/cm³ are classified as heavy metals and are widely regarded as global pollutants [8]. Since heavy metals are long lasting, they build up in the environment and ultimately pollute the food chain. This pollution compromises both environmental and human health. Heavy metals can build up in the tissues of organisms, a process referred to as bioaccumulation. As these metals move up the food chain, their concentration tends to rise, a phenomenon known as biomagnification [9]. Some heavy metals are known to cause cancer, genetic mutations, birth defects, and interfere with hormone regulation, while others can result in neurological and behavioral problems, especially in children. [10]. Heavy metals are prevalent pollutants in the soil, such as arsenic (As), cadmium (Cd), chromium (Cr), mercury (Hg), lead (Pb), copper (Cu), zinc (Zn), and nickel (Ni) [11].

These elements show cytotoxic, genotoxic, and mutagenic effects on plants. They can be classified into: essential micronutrients for plants (Cu, Fe, Mn, Mo, Ni, and Zn), and non-essential or toxic elements, which are harmful to plants even in small quantities (As, Cd, Co, Cr, Hg, Pb, Sb, Cr) [12-31]. Although Ni is an essential micronutrient and a crucial part of enzymes involved in the nitrogen cycle, excessive levels in the soil can disrupt plant physiology and biochemical processes [32]. Plants exposed to As even at very low concentration, can cause many harmful morphological physiological, and biochemical changes. The recent research on Arsenic in the soil-plant system indicates that As toxicity to plants varies with its speciation in plants (e.g., arsenite, As(III); arsenate, As(V)), with the type of plant species, and with other soil factors controlling As accumulation in plants [33]. Toxicity of Cr(VI) leads to lipid peroxidation in plants, resulting in significant damage to cell membranes, including the breakdown of photosynthetic pigments [34].

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2. Sources of heavy metal pollution

Heavy metal contamination in soil and water is a significant environmental issue, originating from both natural and anthropogenic sources. Natural sources such as volcanoes, mining, and metal smelting and refining disseminate heavy metals like arsenic, cadmium, and mercury, lead, into the environment. Volcanic eruptions release hazardous metals into the atmosphere, which later deposited onto the soil and water. In the same way, operations like mining and smelting contribute to the release of metals such as copper, lead, and mercury into the ecosystem [35]. The discharge of sewage and untreated effluent from industrial and domestic sources aggravate the problem, introducing many types of toxic metals, including cadmium and chromium, into both soil and water [36-39]. Industrial discharge, primarily from manufacturing and refining processes, is another major source of heavy metal contamination, often leading to the accumulation of arsenic, lead, and mercury in both mediums [37][40]. Moreover, the use of agricultural chemicals, such as pesticides and fertilizers, releases substantial quantities of heavy like zinc and copper into the soil, which can then leach into water bodies, affecting water quality [41]. Bacterial activities, especially in wetlands and contaminated areas, can contribute to the buildup of toxic mercury compounds like monomethyl mercury, which accumulate in both soil and water, further deteriorating water quality. Vehicle emissions and fossil fuel combustion, Incomplete fossil fuel burning in power plants, production of electronic goods and their disposal, Military operations and their associated activities, is another significant contributor to heavy metal contamination, releasing metals like lead and mercury into the environment [35][42]. Other sources include the production and use of cosmetics and chemical fertilizers, which can introduce metals like chromium and nickel into the soil [43-44].

3. Health risks associated with heavy metal exposure

Essential heavy metals are necessary for the proper functioning of the human body, but their excess can be harmful. In contrast, non-essential heavy metals are toxic even at very low concentrations [45].

- Manganese (Mn) is responsible for neurological complications such as Alzheimer's and Parkinson's disease, Apoptotic cell death and alteration of homeostasis [46-47].
- Arsenic (As) cause neurotoxicity like cognitive impairment, neuro developmental changes, neurodegenerative diseases for e.g., Alzheimer's and Parkinson's disease. It is carcinogen leading to epigenetic alterations, DNA damage. Arsenic is also responsible for hyperkeratosis, hyperpigmentation, Bowen's disease, and skin cancer, abnormalities, neural tube defects, impaired sperm production, endometrial cancer, and pregnancy complications and DNA alteration, chromosomal abnormalities, micronuclei production, and mutation [48-51].
- Cadmium (Cd) triggers neurodegenerative defects, including amyotrophic lateral sclerosis, and multiple sclerosis. Renal failure, glucosuria, aminoaciduria, and kidney damage. Liver and kidney cancer, hypertension, atherosclerosis, and heart disease, infertility and ovulation disturbances, DNA damage and mutation are other harmful impact of Cd toxicity [52-56].
- Lead (Pb) is reported as causative metal for Cognitive impairment, neurological disturbances, and learning disabilities, Proximal tubular dysfunction, Fanconi-like syndrome, and kidney failure, Carcinogenic for Immuno suppression, increased allergies, and autoimmunity, Arteriosclerosis, hypertension, and atherosclerosis. Contact dermatitis and systemic contact dermatitis. Its poisoning causes problems in children such as impaired development, reduced intelligence, loss of short-term memory, learning disabilities and coordination problems; causes renal failure; increased risk for development of cardiovascular disease [57-60].
- Copper (Cu) causes neurotoxicity like neuro developmental issues, Wilson's disease, schizophrenia-like behavior. Liver damage due to copper accumulation [61-62].
- Zinc (Zn) Zn toxicity is responsible for adverse effects on neurodevelopment and potential for increased cancer risk at high levels. Over dosage can cause dizziness and fatigue [63-65].
- Mercury (Hg) is very toxic. It causes Neurological disturbances, developmental issues in children. Kidney damage and dysfunction. Liver damage and failure. Cancer, Increased atherosclerosis and heart disease, Dermatitis and skin lesions. Anxiety, autoimmune diseases, depression, difficulty with balance, drowsiness, fatigue, hair loss, insomnia, irritability, memory loss, recurrent infections, restlessness, vision disturbances, tremors, temper outbursts, ulcers and damage to brain, kidney and lungs [66-70].
- Thallium (Tl) cause Brain and peripheral nerve damage, edema, and necrosis, Kidney damage and delayed excretion [71-72].
- Nickel (Ni) toxicity known to cause Allergic dermatitis known as nickel itch; Its inhalation can cause cancer of the lungs, nose, and sinuses; cancers of the throat and stomach have also been attributed to its inhalation; hematotoxic, immunotoxic, neurotoxic, genotoxic, reproductive toxic, pulmonary toxic, nephrotoxic, and hepatotoxic. It is also responsible for hair loss [73-74].
- Chromium (Cr) toxicity cause liver damage, steatosis, necrosis, and impaired mitochondrial bioenergetics, DNA strand breakage, chromosomal abnormalities, and carcinogenicity., Contact dermatitis and allergic reactions Inhibition of immune cell function, hypersensitivity reactions [75-77].
- Cobalt (Co) toxicity cause Reversible systolic cardiac depression, cardiomyopathy [78].

4. Methods involving removal of heavy metal pollution

Soil is consisting of a mixture of organic and inorganic solid constituents, water, and several gases in distinct proportions. The mineral components of soil widely depend on the parent material and the climatic conditions under which it was formed. As a result, soils can show significant variation in their physical, chemical, and biological traits. The movement of soil water is affected by physical factors such as soil texture and structure. Soil moisture plays an important role in

controlling solute movement, salt solubility, chemical reactions, and microbiological activities. Ultimately, it affects the accessibility of metal ions. The process of removing heavy metals from polluted soils is very tough, particularly when it comes on a large-scale basis. The advancement of technologies for eliminating metals from the environment has been a focus for many years, with various approaches developed to mitigate or reclaim heavy metal-polluted soils and waters, including those at landfill and dumping sites.[79]

Table 1 Heavy metal removal Techniques

Methods	Remediation Approaches
Physical method	Heat treatment, Electromediated ion, Soil replacement, Vitrification
Chemical method	Precipitation, Ion exchange, Chemical extraction and oxidation, Soil amendment, Chemical leaching, Nano remediation
Biological method	Bioleaching, Biological stabilization, Animal remediation, Composting, Phytoremediation, Microbial bioremediation, Biofilm based remediation, Integrated biosystem remediation, Genetic engineering
Physiochemical method	Soil washing, chemically activated adsorption, Ultrasonic leaching
Physiological method	Bio electrokinetic remediation, Sediment microbial fuel cell, Immobilized Biosorption

5. Phytoremediation: A Green and Eco-friendly approach

Phytoremediation is an evolving approach that uses various plants to remove, degrade, stabilize, or trap contaminants in soil and water [80]. It is an economical and nature-friendly technique, providing a suitable alternative to chemical and physical methods for eliminating heavy metal contaminants from soil [81]. The term phytoremediation coined in 1991 suggested by Chaney (1983). which means (Phyto = plant and remediation = correct evil). It is popular technique due to its affordable cost, high efficiency, environmentally sustainability, applicability on-site, and powered by solar energy remediation [82-83]. Physical or chemical methods such as excavation, precipitation, heat treatment, chemical leaching, which involve further use chemicals to treat the heavy metals in the soil again load it with the harmful chemicals. These methods are still costly and depend on the pollutant and soil characteristics [84]. Plants generally handle the contaminants without affecting surface soil. This ensures the preservation of its productivity and nutrient content. They may improve soil fertility with inputs of organic matter [85]. Phytoremediation utilizes many mechanisms including degradation (rhizodegradation, phytodegradation), accumulation (phytoextraction, rhizofiltration), dissipation (phytovolatilization), and immobilization (hydraulic control and phytostabilization) to degrade, remove, or immobilize the pollutants [86].

6. Phytoremediation mechanism

1. Phytoextraction

Phytoextraction is the process through which plants absorb heavy metals from the soil or water through their roots, and then transport and store them to above-ground biomass, primarily in shoots, for accumulation [87]. This is beneficial because the plant biomass can be harvested, effectively removing contaminants from the environment. This technique is primarily used for inorganic contaminants [88]. Hyperaccumulators, requires high shoot biomass and efficient translocation of metals from roots to shoots are often chosen for this technique [89]. This is beneficial because the plant biomass can be harvested, effectively removing contaminants from the environment. Vamerali et al., 2010, studied the crops such as maize and barley for phytoextraction to prevent contamination of the food chain [90]. Ornamental plants like *Trifolium repens* have been reported for improving the phytoextraction process of Cd, Ni, and Cu [91]. The process of phytoextraction is affected by factors like soil properties, metal speciation, and the plant species used [92]. Crops for phytoextraction should not be used for human or animal consumption due to the risk of food chain contamination.

2. Phytostabilization

Phytostabilization is a process that uses plants to stabilize contaminants in the soil, which reducing their mobility and bioavailability. Thus, it prevents them from migrating to groundwater or entering the food chain [93]. Plants confine heavy metals in their roots through the formation of either complexation, precipitation, or metal valence reduction, consequently immobilizing the metals in the soil [94]. Phytostabilization does not completely remove contaminants but prevents their movement, contaminants still remain in the soil [95]. This technique is good for reducing the bioavailability of metals like Cu, Zn, and Cd, typically applied in areas with contaminated soils or mining waste [96].

3. Rhizofiltration

Rhizofiltration is a process in which plant roots are utilized to absorb contaminants, mainly from wastewater, consequently reducing their concentration. In this mechanism pollutants are to be taken up by the plant roots, where they are either absorbed into the root tissues or precipitate within the rhizosphere, makes their mobility slow [97]. Species such as *Zea mays* (corn) shows a high potential for mercury (Hg) uptake [98]. Plant species like *Phragmites australis* and *Kyllinga nemoralis* have been tested for their efficiency in extracting heavy metals from wastewater, reported rhizofiltration particularly effective for this purpose [99].

4. Phytovolatilization

Phytovolatilization is a process where plants absorb heavy metals, convert them into volatile forms, and release them into the atmosphere [97]. The contaminants are taken up by the plant roots, transformed into volatile compounds such as mercury (Hg) to Hg₀ or selenium (Se) to dimethyl diselenide, and subsequently released through the leaves [100]. This

technique is particularly useful for removing volatile contaminants like Hg, Se, and arsenic[101]. However, this mechanism can transfer pollutants to the atmosphere, where they can potentially be redeposited. One of the studies have shown that plants such as *Pteris vittata* are capable of metabolizing arsenic into volatile forms, contributing to its removal from the environment [102].

5. Phytodegradation

This technique is basically used for organic pollutants like bioremediation of pesticides, herbicides, and other synthetic chemicals rather than heavy metals. Phytodegradation refers to the degradation of organic pollutants by plants, with the help of specific enzymes. Plants metabolize and detoxify organic pollutants through their enzymatic activities, such as the use of dehalogenase and oxygenase enzymes[103].

6. Phytodesalination

Phytodesalination is a technique used to remove salts from saline soils, which could eventually support normal plant growth [104]. Halophytic plants are used to remove excess salts from saline soils, which can help to reclaim land for agriculture[105]. Halophytic plants accumulate and translocate salts like sodium chloride (NaCl) from soil into their biomass[106].

6. Hyperaccumulator Plants

Hyperaccumulator plants are remarkable plant species that can absorb and store very high amounts of certain heavy metals like cadmium, nickel, and zinc in their tissues. These plants have special abilities to handle these metals, such as storing them safely in vacuoles (small storage compartments in the cells), which prevents the metals from harming the plant. This allows the plants to grow and reproduce in polluted areas without getting damaged by the metals. Many of these plants can store more than 1000 parts per million (ppm) of metals.

Table 2: List of plants with metal accumulating tendencies

Metal	Plant Species	References
Cadmium (Cd)	<i>Thlaspi caerulescens</i>	[107]
	<i>Nicotiana tabacum</i>	[108]
	<i>Xanthium strumarium</i>	[109]
	<i>Eichhorniacrassipes</i>	[110]
	<i>Salixsps</i>	[111]
Zinc (Zn)	<i>Thlaspi caerulescens</i>	[107]
	<i>P. australis</i>	[112]
	<i>E. canadensis</i>	[113]
	<i>Typha angustifolia</i>	[114]
Nickel (Ni)	<i>Thlaspi caerulescens</i>	[97]
	<i>Alyssum serpyllifolium</i>	[115]
	<i>Berkhey acoddii</i>	[116]
	<i>Alyssum lesbiacum</i>	[117]
	<i>Alyssum bertolonii</i>	[117]
	<i>Isatis pinnatifolia</i>	[118]
Lead (Pb)	<i>Sesbania drummondii</i>	[119]
	<i>Mesembryanthemum criniforum</i>	[120]
	<i>Brassica juncea</i>	[120]
	<i>Xanthiumstrumarium</i>	[120]
Chromium (Cr)	<i>Pterisvittata</i>	[121]
Arsenic (As)	<i>Pteris vittata</i>	[121]
	<i>Pteris cretica</i>	[122]
	<i>Pteris longifolia</i>	[122]
Copper (Cu)	<i>Eleocharis acicularis</i>	[123]

7. Advantages of Phytoremediation

Large-scale studies have shown that phytoremediation is a cheaper than other metal removal techniques. Research has consistently found that the cost of phytoremediation is much lower compared to traditional remediation methods. Mulbry et. al reported that phytoremediation was more cost-effective than traditional methods for treating dairy effluent[124]. Similarly, Cunningham et al. found that phytoremediation costs between \$2,500 and \$15,000 per hectare, whereas treatments using microorganisms ranged from \$20,000 to \$60,000 per hectare, with in-situ microbial treatments costing between \$7,500 and \$20,000 per hectare for petroleum hydrocarbon removal [125]. Phytoremediation can effectively eliminate the harmful impacts of heavy metals from various environments, such as soil, water, and air. Thus, phytoremediation presents a cost-effective, feasible alternative to conventional environmental remediation methods.

8. Limitations of Phytoremediation

Phytoremediation is a cutting-edge solution for dealing with heavy metal contamination, although there are some restrictions.

1. Phytoremediation is a time taking technique.
2. Most studies in this domain are carried out in controlled environment and over limited areas, making it unclear how effective phytoremediation would be when applied on a larger scale.
3. Phytoremediation requires hyperaccumulators that grow quickly and produce large biomass; however, most hyperaccumulators are slow-growing and have lower biomass, which limits their effectiveness for large-scale applications.
4. This method is suitable for only low contaminated environment because it is not possible for plant to survive in high metal concentrations.
5. Animals and other living beings could be harmed if they eat plants that have high levels of pollutants, as it may cause poisoning. So, these plants need proper monitoring, and should be treated properly before disposal into the environment.

9. Conclusion

Phytoremediation offers a promising, eco-friendly approach for addressing heavy metal contamination in the environment, providing a sustainable alternative to traditional remediation methods. It utilizes plants' natural abilities to remove, degrade, stabilize, or trap pollutants in soil, water, and air. Although it has several advantages, including cost-effectiveness, environmental sustainability, and applicability on-site, the technique is not without limitations. These include the time-consuming nature of the process, its effectiveness mainly in low-contaminated environments, and the need for hyperaccumulator plants with rapid growth and large biomass. Additionally, potential risks to animals and humans from consuming contaminated plants highlight the importance of proper monitoring and management. Despite these challenges, continued research and development of phytoremediation techniques can enhance their effectiveness for large-scale applications and make them a viable solution for mitigating heavy metal pollution.

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