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# Phytoremediation Approaches for Heavy Metal Pollution: A Review

### **Review Article**

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#### Abstract

Soil pollution due to heavy metals derived from anthropogenic activities is a major global concern. Detrimental effects of heavy metals on the environment and human health are now well understood. A major challenge is removal and reduction of heavy metal contamination. Of all the remediation techniques available for metal-contaminated soil, phytoremediation is the most cost-effective, environmentally friendly, and practical approach. Phytoremediation includes the removal, relocation, or reduction of contaminants using plants that hyperaccumulate these contaminants. On the basis of the mode of action, phytoremediation is subdivided into subclasses such as phytostabilization, phytofiltration, phytovolatilization, and phytoextraction. In this review, we discuss the need for phytoremediation and its approaches with a special context to the heavy metals.

Keywords: Heavy metals; Hyperaccumulation; Phytoextraction; Phytofiltration; Phytostabilization; Phytovolatization

#### Introduction

Detrimental effects of heavy metals on the environment are evident. Soil contaminated with heavy metals is often deprived of nutrients and microbial diversity, and the high concentration of heavy metals cause the plants to accumulate these metals or affect the growth and development of plants [1,2]. The disposal of these metals into the soil aggravates soil health problems [3]. Furthermore, these metals when present in different concentrations can be scarce, optimum, or phytotoxic to the plants [4]. Therefore, removal of the heavy metals from the environment by using remediation techniques is critical.

In environmental science, remediation is a method for reducing or removing the pollutants by acting on the source of contamination to protect the environment and humans from the harmful effects of the contaminants. Returning the contaminated soil to its natural state is not always possible but necessary. Remediation activities should always be economical and optimized, and the outcome should be balanced amid the benefits, risks, expenditure, and feasibility. Therefore, any acceptable remediation measures can be aptly planned by understanding the source and nature of contamination, the site, and remediation technologies to be adopted.

Various techniques are available for remediation. The simplest method is to remove the uppermost layer of the contaminated soil by digging and landfilling or capping the contaminated site. However, this method has disadvantages and risks. There is always a possibility that the contaminant can leak out during excavation, handling, transporting, and capping, which might contaminate the ground water. In addition, this method is very expensive and laborious. Different techniques are available for the remediation of metal-contaminated soil, namely chemical, physical, and biological techniques [5]. The chemical method involves the use of harsh chemicals for chemical wash, such as leaching of heavy metals using chelating agents [6]. Therefore, researchers developed the bioremediation technique,

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a process by which organic wastes are biologically degraded under controlled conditions to an innocuous state or to levels below the concentration limits established by regulatory authorities [7].

Chemical and physical remediation techniques are costly. According to Glass et al., the cost of land filling for a contaminated site and chemical recycling of contaminants varies between 100 and 500 US\$/ton, and the cost for electrokinetic monitoring is approximately 20–200 US\$/ton, whereas the cost involved in phytoextraction is 5-40 US\$/ton. Therefore, phytoextraction is an effective low-cost technique for the enhanced remediation of metal-contaminated soil [8]. Phytoremediation provides sustainable measures for the remediation of metal-contaminated soil.

## Phytoremediation approaches and hyperaccumulation of metals in plants

Phytoremediation is defined as the use of plants to remove, transfer, and degrade contaminants in soil, sediment, and water [9]. Phytoremediation uses living organisms, particularly plants and microorganisms, to reduce, eliminate, transform, and detoxify benign products present in soil, sediments, water, and air. Phytoremediation technology, a bioremediation method, uses plants as filters for accumulating, immobilizing, and transforming contaminants to a less harmful form [3].

The term "phytoremediation" is formed by combining the

Greek word "phyto" meaning plant and the Latin word "remedium" meaning to restore or clean.

Phytoremediation includes various remediation techniques that involve many treatment strategies leading to contaminant degradation, removal (through accumulation or dissipation), or immobilization [10].

These remediation techniques may use genetically engineered or naturally occurring plants for removing contaminants from the surrounding environment [11,12]. Utsunamyia and Chaney reintroduced and developed the method of using hyperaccumulating plants for extracting metals from contaminated soil [13,14]. Baker et al. reportedly conducted the first field trial on zinc (Zn) and cadmium (Cd) phytoextraction [15].

#### Types of phytoremediation

Based on contaminants, field conditions, clean-up level required, and plant type, phytoremediation methods can be used i.e., phytostabilization/phytoimmobilization for reducing mobility of contaminant or phytovolatization/phytoextraction for removal of the contaminant [16].

Phytoremediation approaches involve different plant-based technologies with different modes of action and mechanism. Figure 1 displays the schematic representation of the phytoremediation mechanism. Some of the widely used phytoremediation approaches



are as follows:

- Phytostabilization is the immobilization or precipitation of contaminants from soil, groundwater, and mine tailings by plants, thus decreasing their availability.
- 2. Phytofiltration uses plant roots and other parts to adsorb or absorb contaminants from the aqueous environment.
- 3. Phytovolatilization uses plants that can evapotranspirate contaminants, such as selenium (Se), mercury (Hg), and volatile hydrocarbons, from soil and groundwater.
- 4. Phytoextraction is the uptake and concentration of metals from contaminated soil or water directly into the plant tissue and their subsequent removal from the plants.
- 5. Phytodegradation includes the microbial degradation of metals in rhizosphere soil and groundwater.
- 6. Phytotransformation is the plant uptake of contaminants from water and their conversion into organic compounds, which are less toxic or nontoxic.
- 7. Vegetative cap uses plants with a unique property of evaportranspiration, thus preventing the leaching of contaminants.

#### i. Phytostabilization

Phytostabilization involves the use of plants to eliminate the bioavailability of toxic metals in soil [17]. Contaminants in soil are immobilized by certain hyperaccumulating plants through absorption and accumulation by roots, adsorption onto roots or precipitation within the root zone, and physical stabilization of soil.

Green vegetation is very helpful in controlling soil erosion as plant roots effectively bind the soil. Furthermore, the roots of vegetation facilitate holding a considerable amount of rain water that returns to the atmosphere through transpiration. The roots reduce the amount of heavy metals entering the water table and other water bodies [18]. To re-establish vegetation at sites where flora have disappeared or been destroyed due to the presence of high metal concentrations, metaltolerant plant species can be planted, thereby reducing the effective migration of contaminants through soil leaching, groundwater contamination, wind, and transportation of the exposed surface soil [18,19]. Some plants developed metal tolerance during evolution while others may have this ability inherently [20].

Plants selected for phytostabilization preferably should be tolerant to concerned contaminats, hold them in their roots and should resist heavy metal accumulation in their above-ground exposed parts to prevent the entry of heavy metals into the food web [10,21]. Metal accumulation in plants is measured and expressed in terms of the bio-concentration factor (BF) or accumulation factor (AF) and translocation factor (TF) or shoot:root (S:R) ratio [22].

Bioconcentration factor (BF)	Total element concentration in the shoot tissue
or accumulation factor (AF)	Total element concentration in mine tailings

 $\frac{\text{Translocation factor (TF)}}{\text{or shoot:root (S:R) ratio}} = \frac{\text{Total element concentration in the shoot tissue}}{\text{Total element concentration in the root tissue}}$ 

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In a recent study, Agrostis castellana having root bioaccumulation indices >2 and transfer factor < 1 was reported to be a suitable plant for the phytostabilization of abandoned mine sites in Spain, which are heavily polluted with heavy metals, such as Zn, copper (Cu), lead (Pb), Cd, and arsenic (As). However, due to substantial heavy metal accumulation in the above-ground exposed parts of the plant even at the low transfer factor obserevd, close monitoring and no hunting or grazing in areas under restoration was recommended to prevent the entry of toxic metals into the food chain [24]. Another study assessed the growth potential of 36 plants belonging to 17 species on a contaminated site and reported that plants with a high bioconcentration factor and a low translocation factor have the ability of phytostabilization [25]. Of all the plants studied, Phyla nodiflora was the most efficient in accumulating Cu and Zn in its shoots, and thus was appropriate for phytoextraction, whereas Gentiana pennelliana was most suitable for phytostabilization of sites contaminated with Pb, Cu, and Zn [25].

To improve the physical and biological characteristics of contaminated soil, natural and synthetic supplements were added during phytostabilization processes. Thus, phytostabilization is termed as "aided phytostabilization" or "chemophytostabilization." Changing the pH, increasing organic matter content by adding compost, adding essential growth nutrients, increasing water holding capacity, and reducing heavy metal bioavailability facilitate phytostabilization.

Five times reduction was observed in Pb and Zn concentrations in aerial parts and in the roots of Lolium italicum and Festuca arundinacea, whose growth was greatly improved by the added compost [26]. Decreased phytotoxicity index was recorded after adding compost, cyclonic ashes, and steel shots to an industrial contaminated sandy soil [27]. Complexing agents, such as citric acid and ethylenediaminetetraacetic acid (EDTA), were shown to influence the phytostabilization capacity [28]. Addition of a synthetic (Calcinit + urea + PK14% + calcium carbonate) or organic (cow slurry) compost had a positive response on soil properties, growth, and remediation potential of L. perenne but decreased root-toshoot translocation factors compared with the control plants [29]. In an aided phytostabilization approach, the soil of an ore dustcontaminated site in northern Sweden was amended with alkaline fly ashes and peat for reducing the mobility of trace elements and was vegetated with a mixture consisting of 6 grass and 13 herb species. The results showed that the proposed approach significantly increased microbial biomass and respiration, decreased microbial stress, and increased key soil enzyme activities [30]. In addition, plant growth-promoting bacteria (PGPB) improved the revegetation of two native species, quailbush and buffalo grass, of mine tailings, minimizing the requirement for compost amendment; however, the results were plant-specific [31]. In a phytostabilization study of mine soil in France, a mixture of legume species, such as Anthyllis vulneraria, and nonlegume species increased the biomass of the other species, and consequently increased the biomass production of the plant community [32].

Care should be taken so that phytostabilized metals remain in the soil ecosystem. Because of the change in soil conditions and the

degradation of organic matter, a possibility always exists of partial and gradual release and leaching, resulting in the dispersion of phytostabilized metals to surrounding areas through soil erosion [21]. Therefore, long-term monitoring or "follow-up" programs are required in phytostabilization processes to monitor heavy metal mobilization, bioavailability, toxicity, and ecological impact [21].

#### ii. Phytofiltration

Phytofiltration involves the use of plants for removing pollutants from contaminated surface waters or wastewaters, thus cleaning various aquatic environments. When plant roots, seedlings, or excised plant shoots are used in phytofiltration to adsorb or absorb contaminants from the aqueous environment, it is termed as rhizofiltration, blastofiltration, and caulofiltration, respectively [33,34]. According to Gardea-Torresdey et al., mechanisms involved in biosorption include chemisorption, complexation, ion exchange, micro precipitation, hydroxide condensation onto the biosurface, and surface adsorption [35]. Young plants of *Berkheya coddii* growing in pots on ultramafic soil enriched with Cd, nickel (Ni), Zn, or Pb substantially accumulated a considerable amount of these metals, whereas excised shoots in solutions containing the same heavy metals accumulated a high amount of these metals in the leaves [34].

In rhizofiltration, terrestrial, rather than aquatic, plants are used because terrestrial plants form extensive fibrous root systems covered with root hairs, and therefore have more surface area than the others [10]. Preferably, a plant used for rhizofiltration must accumulate and tolerate high concentrations of metals and should be easy to handle, have low maintenance cost, and produce minimal secondary waste requiring disposal. Furthermore, the plants must produce a considerable root biomass or have a large root surface area [36].

Various aquatic plants have the potential to remove heavy metals from water, for example, Eichhornia crassipes [37], Hydrocotyle umbellata L. [38], and Lemna minor L. [39]; however, these plants have limited capacity for rhizofiltration because of their small, slow-growing roots [40]. The high water content in aquatic plants adds to the problem of drying, composting, and incineration. Despite limitations, E. crassipes (water hyacinth) was effective in removing trace elements from waste streams [37]. Furthermore, Micranthemum umbrosum is an effective phytofiltrator of As and moderate accumulator of Cd without any phytotoxic effect [41]. The aquatic plants Callitriche stagnalis S., Potamogeton natans L., and P. pectinatus L. tested in uranium phytofiltration experiments reduced uranium concentrations in water from 500 to 72.3 µg/L, emphasizing the efficiency of the selected plants in removing uranium from water [42]. The bryophyte Fontinalis antipyretica and Callitrichaceae members accumulate uranium with preferential partitioning in rhizomes/roots, emerging as promising candidates for the development of phytofiltration [43].

Phytofiltration studies have been conducted on As accumulation by aquatic plants. A study of 18 representative aquatic plant species, such as species *Ranunculus trichophyllus*, *R. peltatus* subsp. *saniculifolius*, *L. minor*, and *Azolla caroliniana*, and the leaves of *Juncus effusus*, reported that these species have a very high potential for As phytofiltration when they are introduced into constructed treatment wetlands or natural water bodies [44].

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Terrestrial plants, such as sunflower, Indian mustard, tobacco, rye, spinach, and corn, were studied for their ability to remove Pb from effluents, with sunflower exhibiting the greatest ability [45]. The roots of Indian mustard (*Brassica juncea* Czern.) are effective in removing Cd, chromium (Cr), Cu, Ni, Pb, and Zn [39], whereas sunflower (*Helianthus annus* L.) removes Pb [39], U [46], <sup>137</sup>Cs, and <sup>90</sup>Sr [47] from hydroponic solutions. Cassava (*Manihot sculenta* Cranz) waste biomass was effective in removing two divalent metal ions Cd (II) and Zn (II) from aqueous solutions [48].

Sharp dock (*Polygonum amphibium*), duckweed (*L. minor*), water hyacinth (*E. crassipes*), water dropwort (*Oenathe javanica*), and calamus (*Lepironia articulata*) are suitable for phytoremediation of polluted water, because sharp dock accumulates N and P in its shoots, water hyacinth and duckweed are Cd hyperaccumulators, water dropwort is a Hg hyperaccumulator, and calamus is a Pb hyperaccumulator [49].

#### iii. Phytovolatilization

Phytovolatilization involves the use of plants that uptake metals from soil, biologically convert them in a volatile form, and then release them into the atmosphere by volatilization. Some metal contaminants, such as As, Hg, and Se, exist naturally in the gaseous form in the environment.

Phytovolatilization can be used for organic pollutants and heavy metals. Furthermore, it has a limitation that it does not eliminate the pollutant completely; it only transfers it from one form (soil) to another (atmosphere) from where the pollutant can redeposit. Therefore, phytovolatilization is the most controversial phytoremediation technology [33]. Whether the volatilization of these elements into the atmosphere is safe or harmful remains unknown [50]. Se phytovolatilization has received the most attention to date; the release of volatile Se compounds from higher plants was first reported by Lewis et al., who demonstrated that both Se nonaccumulator and accumulator species volatilize Se [51]. Brassicaceae members can release 40 gm Se ha<sup>-1</sup> day <sup>-1</sup> as various gaseous compounds [52].

B. juncea is effective in removing up to 95% Hg from contaminated solutions through volatilization and plant accumulation (phytofiltration) [53]. Most Hg volatilization occurs from the roots, which may have unforeseen environmental effects [53]. Hg uptake and evaporation are achieved by some bacteria. Researchers are attempting to develop a transgenic plant by transferring the required genes using rDNA technology for environmental restoration. Methylmercury is a strong neurotoxic agent, which is biosynthesized in Hg-contaminated soil. Bacterial genes, such as merA (for mercuric reductase) and merB (for organomercurial lyase), were transformed into Arabidopsis thaliana to produce genetically engineered plants capable of detoxifying organic Hg. Furthermore, these genes, which are necessary for plants to detoxify organic Hg by converting it to volatile and less toxic elemental Hg, were expressed in the newly transformed plants [54]. Bacterial genes, such as those for Hg reductase, have already been successfully transferred into Brassica, tobacco, and yellow poplar trees [55].

#### iv. Phytoextraction

Phytoextraction, the most commonly recognized

phytoremediation technology, is also known as phytoaccumulation, phytoabsorption, or phytosequestration. It involves the use of plants that absorb metals from soil and translocate them to harvestable shoots where they accumulate.

Phytoextraction, a specific clean-up technology, cannot be confused with phytoremediation, which is a concept [33]. Several plants that may belong to distantly related families, but have the common ability to grow on metalliferous soil and accumulate extremely higher levels of heavy metals in the aerial organs than other plants, without deleterious effects from phytotoxins, are termed as "hyperaccumulator" [56]. These hyperaccumulator plants form the basis of phytoextraction. Baker and Brooks reported that hyperaccumulators should have a metal accumulation value exceeding the threshold value of the shoot metal concentration of 1% (Zn and Mn), 0.1% [Ni, cobalt (Co), Cr, Cu, Pb, and aluminium (Al)], 0.01% (Cd and Se), or 0.001% (Hg) of the dry weight shoot biomass [15].

Based on its methodology, phytoextraction is generally grouped into two categories. The first method called continuous phytoextraction involves the use of hyperaccumulating plants, whereas the second method called chelate-induced phytoextraction involves the use of high-biomass crop plants and chelating agents [10,21].

In continuous phytoextraction, metal-accumulating plants are seeded or transplanted into metal-contaminated soil and are cultivated using established agricultural practices. The roots of growing plants absorb metal elements from the soil and translocate them to the aerial shoots where they accumulate. According to a previous study, approximately 450 angiosperm species belonging to the families Asteraceae, Brassicaceae, Caryophyllaceae, Cyperaceae, Cunouniaceae, Fabaceae, Flacourtiaceae, Lamiaceae, Poaceaee, Violaceae, and Euphobiaceae [10] have been identified as heavy metal (As, Cd, Co, Cu, Mn, Ni, Pb, Sb, Se, Tl, and Zn) hyperaccumulators to date, accounting for less than 0.2% of all known species [56].

Researchers are continuously searching to find new hyperaccumulators in nature, which remain unidentified, and new reports on these plants continue to accrue [57]. Few hyperaccumulators (only five species to date) are available for Cd, which is one of the most toxic heavy metals [56]. A study recently discovered a new Cd hyperaccumulator plant *Youngia erythrocarpa*, a farmland weed [57]. Ni is hyperaccumulated by most taxa (more than 75%), and approximately 25% of the discovered hyperaccumulators belong to the family Brassicaceae, and particularly to *Thlaspi* and *Alyssum* [56].

Planting and harvesting of hyperaccumulators must be repeated for reducing the contamination at a particular site. Furthermore, the time required depends on the target metal, plant selected, and its efficacy; the duration of the process can vary from 1 to 20 years [58,59]. The success of phytoextraction depends on the ability to produce high biomass yields and to accumulate high quantities of environmentally critical metals in the shoot tissue [33,58,60]. For example, Ebbs et al. reported that *B. juncea* to be more effective in removing Zn and Cd from soil than *Thlaspi caerulescens* (a known hyperaccumulator of Zn), although *T. caerulescens* accumulated 10 and 2.5 times more Cd and Zn concentration, respectively, in its shoot than *B. juncea* [61]. *B. juncea* exhibited this property because it produces 10 times more shoot biomass than *T. caerulescens*. In addition to the high biomass production capability, the plant must have high tolerance to the targeted metal(s) and be efficient in translocating them from roots to the harvestable aerial parts of the plant [59]. Recently, the role of symbiotic bacterial species in facilitating plant growth in poor soil with metal accumulation was observed. A novel species of *Rhizobium metallidurans* sp. nov., a symbiotic heavy metal-resistant bacterium, was isolated from a Zn-hyperaccumulating *A. vulneraria* legume [62]. When these bacteria were inoculated in *A. vulneraria*, Zn concentration in the shoots increased up to 36% [63].

Chelate-induced phytoextraction is used when metals do not exist in the available form in the soil for sufficient plant uptake; adding chelates or acidifying agents to the metals facilitates their liberation in the soil solution, thus improving the metal accumulation capacity and uptake speed of nonhyperaccumulating plants [64]. In the past decades, the use of persistent aminopolycarboxylic acids (APCAs), such as EDTA, biodegradable APCAs, ethylene diamine disuccinate (EDDS), and nitrilo triacetic acid as an alternative to EDTA, and low-molecular-weight organic acids (LMWOA) have been used in various phytoextraction experiments [64]. The degree of chelate-induced extraction depends on several factors, such as the geochemical fractions of metal in soil, and type and concentration of chelating agents used [65]. The added chelating agents, however, are toxic to the plants and have a negative effect on soil microbial growth during the chelate-induced phytoextraction process [66]. There is always a potential risk of leaching of metals to groundwater and the presence of nondegradable metal-chelating agent complexes in contaminated soil for a long period [67,68]. EDTA, a strong chelating agent possessing strong complex-forming ability, has been most extensively studied; however, the interest is now shifted on the usage of biodegradable chelating agents, such as EDDS, a biodegradable isomer of EDTA [65]. EDDS, a naturally occurring substance in soil, is easily decomposed into less detrimental byproducts. EDDS is less harmful to the environment, can readily solubilize metals from soil, and is highly efficient in inducing metal accumulation in Brachiaria decumbens shoots [69,65].

#### v. Phytodegradation and phytotransformation

Phytodegradation also known as phytotransformation involves the breakdown of contaminants taken up by plants through metabolic processes within the plant or the breakdown of contaminants externally to the plant through the effect of compounds produced by the plants [70]. It also includes plant-assisted microbial degradation of the contaminants in the rhizosphere region [3,71]. Phytodegradation of organic compounds by plants is reported by many workers [72,73]. Caçador and Duarte, reported phytoconversion of Cr (VI) toxic form to the less toxic Cr (III) by halophytes [74]. Various bacterial and fungal microorganisms can facilitate transformation of toxic metals to their less toxic states. *Pseudomonas maltophilia* strain, isolated from soil at a toxic waste site in Oak Ridge, Tennessee, was reported to catalyze the transformation and precipitation various toxic metal cations and oxyanions [75]. Citric and oxalic acid producing Aspergillus niger, was reported to transform insoluble inorganic metal compounds ZnO,  $Zn_3(PO_4)_2$  and  $Co_3(PO_4)_2$  to their respective organic insoluble metal oxalates [76].

Pteridophytes as metal hyperaccumulators

Pteris vittata, also known as brake fern, is a perennial, evergreen fern native to China and was the first discovered As hyperaccumulator as well as the first fern hyperaccumulator [77]. Furthermore, this fern possesses a remarkable ability for As hyperaccumulation (up to 22,600 mg As kg<sup>-1</sup> in its fronds) [77], which is markedly greater than most plant species (<10 mg As kg<sup>-1</sup>) [78]. Although at a reduced rate, P. vittata is effective in As uptake in the presence of other metals (Ni, Zn, Pb, and Cd); however, its ability to take up other metals is limited [79]. Approximately a dozen of ferns belonging to Pteris and few from others, such as Pityrogramma calomelanos, were reported as As hyperaccumulators; however, not all members of Pteris are As hyperaccumulators [80]. Plasma membranes of the root cells of P. vittata have a higher density of phosphate/arsenate transporters than the nonhyperaccumulator P. tremula, which may be a result of constitutive gene overexpression [81]. As hyperaccumulation by fern depends on the high affinity of the phosphate/arsenate transport systems to arsenate [82] and the plant's capability to increase As bioavailability in the rhizosphere by reducing pH through the root exudation of high amounts of dissolved organic carbon [83]. The decrease in pH increases the amount of water-soluble As that can be readily taken up by the roots [83,84].

#### **Conclusion and Future Prospective**

Phytoremediation techniques are suitable tools for the effective heavy metal remediation of soil, water, and sediments. Special care should be taken while selecting a suitable approach depending on the health attributes of the contamination site, target contaminant, and efficacy of the plant selected. Various biomonitoring tools are available for assessing the effectiveness of heavy metal phytoremediation processes. In the future, additional studies are required to understand the mechanism of action of the plants. Despite few disadvantages of phytoremediation technologies, it is an efficient method for environmental cleaning. With the advancement in the field of genetic recombination technology, genetically engineered plants can be instrumental in the phytoremediation approaches for making environment clean. Future studies should be focused on the combined use of more than one phytoremediation approach for the successful remediation of the polluted area under field conditions.

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