Review

# Phytoremediation of heavy metals: A green technology

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The environment has been contaminated with organic and inorganic pollutants. Organic pollutants are largely anthropogenic and are introduced to the environment in many ways. Soil contamination with toxic metals, such as Cd, Pb, Cr, Zn, Ni and Cu, as a result of worldwide industrialization has increased noticeably within the past few years. There are some conventional remediation technologies to clean polluted areas, specifically soils contaminated with metals. In spite of being efficient, these methods are expensive, time consuming, and environmentally devastating. Recently, phytoremediation as a cost effective and environmentally friendly technology has been developed by scientists and engineers in which biomass/microorganisms or live plants are used to remediate the polluted areas. It can be categorized into various applications, including phytofiltration, phytostabilization, phytoextraction, and phytodegradation. A brief review of phytoremediation of soils contaminated with heavy metals has been complied to provide an extensive applicability of this green technology.

Key words: Phytoremediation, heavy metals, soil pollution, toxicity.

# INTRODUCTION

Since the beginning of the industrial revolution, heavy metal contamination of the biosphere has increased considerably and became a serious environmental concern. Contamination by heavy metals can be considered as one of the most critical threats to soil and water resources as well as to human health (Yoon et al., 2006). During the past decades, the annual widespread release of heavy metals reached 22000 t (metric ton) for Cd, 939000 t for Cu, 1350000 t for Zn, and 738000 t for Pb (Singh et al., 2003).

Sources of metal contamination include anthropogenic and geological activities. Industrial pollutants, smelting, mining, military activities, fuel production and agricultural chemicals are some of the anthropogenic activities that cause metal contamination (Jadia and Fulekar, 2009). The application of phosphate fertilizers to the agricultural soil has led to increase in Cd, Cu, Zn and As (Zarcinas et al., 2004). Indeed, the increasing demand for agricultural products has led to extensive cultivation in agricultural lands. Applying fertilizers, pesticides and herbicides is necessary to protect the quality and quantities of these products. However, the excessive use of these agrochemicals creates environmental problems, such as accumulation of these chemical substances in the soil and plant uptake (Sahibin et al., 2002). Unlike organic matter, these metals cannot be altered by microorganisms. The toxicity of heavy metals is a very serious issue, because they have a long persistence in the environment. The half-life of these toxic elements is more than 20 years (Ruiz et al., 2009). According to the United States Environmental Action Group (USEAG), this

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environmental problem has threatened the health of more than 10 million people in many countries (Environmental News Service, 2006). Heavy metal pollution has spread throughout the world. 53 elements are classified as heavy metals. Their densities exceed 5 g cm<sup>-3</sup>, and they are known as universal pollutants in industrial areas (Sarma, 2011).

# ENVIRONMENTAL POLLUTION AND SOURCES OF CONTAMINATION

Environmental pollution is the present of chemicals at poisonous levels in land, water and air. Pollution can be defined as an accidental or deliberate contamination of the environment with waste generated by human activities. Our environment has been contaminated with organic and inorganic pollutants, because pollutants are released into the environment through many different ways. Soil, water and air have been contaminated as a result of industrial activities and the unmanageable growth of large cities. Metals such as Cd, Cu, Cr, Ni, Zn and Pb are known to be serious environmental pollutants.

#### Soil contamination by heavy metals

The two different ways that heavy metals enter the environment are from natural and anthropogenic sources. Natural sources of heavy metals contamination usually result from the weathering of mines, which are themselves created anthropogenically (Wei et al., 2008). Heavy metal is defined as any element with metallic characteristics, such as density, conductivity, stability as cations, and an atomic number greater than 20 (Raskin et al., 1994). Heavy metal pollution is a crucial environmental concern throughout the world. It occurs in the soil, in water, in living organisms, and at the bottom of the sediments. Environmental contamination by heavy metals as a result of industrial and mining activities became widespread in the late 19th and early 20th centuries (Benavides et al., 2005). Heavy metals, including Cd, Cu, Cr, Zn, Ni and Pb as critical pollutants, have an adverse effect on the environment, specifically at high concentrations in areas with severe anthropogenic activities (United States Protection Agency, 1997). Although they are natural components of the earth's crust, heavy metals' biochemical equivalence and geochemical cycles have changed noticeably due to human activities (Baccio et al., 2003). These metals are just being transformed from one form to another, because of their inability to degrade naturally. The heavy metals namely Cu, Fe, Zn, Mo and Mn are micronutrients and are considered to be essential to maintaining life in biological systems. However, at higher concentrations, these metals become highly toxic and threaten the health

of animals and humans by influencing the quality of crops, water and atmosphere. The heavy metals Cd, Cu, Ni and Hg create greater phytotoxicity than Zn and Pb (Raskin et al., 1994).

The pollution of soil is a crucial matter that has attracted considerable public attention over the past few decades. A large proportion of land has become hazardous and non-arable for humans and animals, because of extensive pollution. It is unusual to have soils without at least traces of heavy metals, and the levels of these elements become more toxic due to anthropogenic or natural activities that are harmful for living systems (Turan and Esringu, 2007). Organic pollutants are anthropogenic and degrade in the soil compared to heavy metals, which are non-degradable and occur naturally in the environment (Garbisu and Alkorta, 2001). Heavy metals can be developed by industrial activities, volcanic operations and parent material. Generally, depending on the type of element and its location, the concentration of metals in the soil ranges from traces levels to as high as 100000 mg kg<sup>-1</sup> (Blaylock and Huang, 2000).

#### Toxicity of heavy metals in plants

Heavy metals can be poisonous for macro- and microorganisms through direct influence on the biochemical and physiological procedures, reducing growth, deteriorating cell organelles, and preventing photosynthesis. Regarding the transportation of metals from roots to the aerial parts of the plants, some metals (especially Pb) tend to be accumulated in roots more than in aerial parts, because of some barriers that prevent their movement. However, other metals, such as Cd, moves easily in plants (Garbisu and Alkorta, 2001). Generally, all plants are able to accumulate essential elements, such as Cu, Fe, Zn, Ca, K, Mg and Na, from soil solutions for growth and development. However, during this process, plants also accumulate some non-essential elements, such as Cd, As, Cr, Al and Pb that have no biological activity.

#### **REMEDIATION OF HEAVY METALS**

Current conventional methods to remediate heavy metalcontaminated soil and water, such as *ex situ* excavation, landfill of the top contaminated soils (Zhou and Song, 2004), detoxification (Ghosh and Singh, 2005), and physico-chemical remediation, are expensive (Danh et al., 2009), time consuming, labor exhaustive and increase the mobilization of contaminants, and destroy the biotic and structure of the soil. Therefore, these remediation techniques are not technically or financially suitable for large contaminated areas (Baccio et al., 2003). Bioremediation was developed as a technology to degrade pollutants into a low toxic level by using microorganisms. However, the use of this technology to remediate contaminated areas by applying living organism was less successful for extensive metal and organic pollutants. Plants are able to metabolize substances produced in natural ecosystems (Vidali, 2001). Phytoremediation is an approach in which plants are applied to detoxify contaminated areas (Garbisu and Alkorta, 2001; Mangkoedihardjo and Surahmaida, 2008).

# DEFINITION AND GENERAL TYPES OF PHYTOREMEDIATION

Phytoremediation is a promising new technology that uses plants to clean up contaminated areas. It is a low cost, long term, environmentally and aesthetically friendly method of immobilizing/stabilizing, degrading, transferring, removing, or detoxifying contaminants, including metals, pesticides, hydrocarbons, and chlorinated solvents (Susarla et al., 2002; Jadia and Fulekar, 2008; Zhang et al., 2010). Over the past 2 decades, it has become a highly accepted means of detoxifying contaminated water and soil (U.S.EPA, 2001). Historically, phytoremediation has been considered a natural process, first identified and proved more than 300 years ago (Lasat, 2000). The specific plant and wild species that are used in this technique are effective at accumulating increasing amounts of toxic heavy metals (Ghosh and Singh, 2005; Brunet et al., 2008). These plants are known as accumulators. They accumulate heavy metals at higher concentrations (≥ 100 times) above ground than do non-hyperaccumulators growing in the same conditions, without showing any observable symptoms in their tissues (Barceló and Poschenrieder, 2003). Phytoremediation can be applied to detoxify areas with trivial pollution of metal, nutrients, organic matter, or contaminants. Nagaraju and Karimulla (2002) described that some species, including Jatropha curcas (from Euphorbiaceae), Dodonaea viscose (from Sapindaceae), and Cassia auriculata (from Fabaceae), had potential for remediation of soils polluted with different kinds of trace and major elements. Phytoremediation can be classified into different applications, such as phytofiltration or rhizofiltration. phytostabilization, phytovolatilization, phytodegradation (Long et al., 2002), and phytoextraction (Jadia and Fulekar, 2009).

# Phytofiltration or rhizofiltration

Phytofiltration or rhizofiltration is the removal by plant roots of contaminants in waste water, surface water, or extracted ground water (Pivetz, 2001). Abhilashet al. (2009) investigated the potential of *Limnocharis flava* (L.) Buchenau, grown for phytofiltration of Cd in polluted water with low concentrations of Cd in a hydroponic experiment. They spiked 45-day-old seedlings of *L. flava* with different concentrations of Cd (0.5, 1, 2 and 4 mg  $L^{-1}$ ). The concentration of Cd in different parts of the plant was highest in the roots followed by leaves and peduncle. This suggested that *L. flava* was a suitable species for phytofiltration of low concentrations of Cd in water.

### Phytostabilization

Phytostabilization is a simple, cost-effective, and less environmental invasive approach to stabilize and reduce the bioavailability of contaminants by using plants. In fact, this approach uses plant roots to restrict the mobility and bioavailability of contaminants in the soil (Jadia and Fulekar, 2009). Plants can reduce the future adverse effects of pollutants in the environment by keeping them from entering the ground water or spreading in the air. This method is applicable when there is no prompt action to detoxify contaminated areas (for example, if a responsible company only exists for a short time, or if an area is not of high concern on a remediation agenda) (Garbisu and Alkorta, 2001). In this approach, the chemical and biological characteristics of polluted soils are amended by increasing the organic matter content, cation exchange capacity (CEC), nutrient level, and biological actions (Alvarenga et al., 2008). In phytostabilization, plants are responsible for reducing the percolation of water within the soil matrix, which may create a hazardous leachate, inhibiting direct contact with polluted soil by acting as barrier, and interfering with soil erosion, which results in the spread of toxic metals to the other sites (Raskin and Ensley, 2000). Phytostabilization is a suitable technique to remediate Cd. Cu. As, Zn and Cr. Alvarenga et al. (2009) investigated the effect of three organic residues, sewage sludge, municipal solid waste compost, and garden waste compost, on the phytostabilization of an extremely acidic metal-contaminated soil. The plant species used in this experiment was perennial ryegrass (Loliumperenne L.). The organic residues were used at 25, 50 and 100 Mg ha<sup>-1</sup> (dry weight basis). These reagents immobilized and decreased the mobile fraction of Cu, Pb and Zn. It was inferred that ryegrass had the potential to be used in phytostabilization for mine-polluted soil and municipal solid waste compost, and to a lesser extent, sewage sludge, used at 50 Mg ha<sup>-1</sup>, and that it is efficient in the *in* situ immobilization of metals, developing the chemical properties of the soil, and greatly enhancing the plant biomass.

# Phytovolatilization

Phytovolatilization is the use of green plants to extract volatile contaminants, such as Hg and Se, from polluted soils and to ascend them into the air from their foliage (Karami and Shamsuddin, 2010). Bañuelos (2000)

perceived that some plants were able to transform Se in the form of dimethylselenide and dimethyldiselenide in high-selenium media.

#### **Phytodegradation**

Phytodegradation is the use of plants and microorganisms to uptake, metabolize, and degrade the organic contaminant. In this approach, plant roots are used in association with microorganisms to detoxify soil contaminated with organic compounds (Garbisu and Alkorta, 2001). It is also known as phytotransformation. Some plants are able to decontaminate soil, sludge, sediment, and ground and surface water by producing enzymes. This approach involves organic compounds, including herbicides, insecticides, chlorinated solvents, and inorganic contaminants (Pivetz, 2001).

#### **Phytoextraction**

Phytoextration is a phytoremediation technique that uses plants to remove heavy metals, such as Cd, from water, soil, and sediments (Yanai et al., 2006; Van Nevel et al., 2007). It is an ideal method for removing pollutants from soil without adversely affecting the soil's properties. Furthermore, in this approach, metals accumulated in harvestable parts of the plant can be simply restored from the ash that is produced after drying, ashing, and composting these harvestable parts (Garbisu and Alkorta, 2001). Phytoextraction has also been called phytomining or biomining (Pivetz, 2001). This technology is a more advanced form of phytoremediation, in which high-biomass crops grown in the contaminated soil are used to bioharvest and recover heavy metals. It can be applied in mineral industry to commercially produce metals by cropping (Sheoran et al., 2009).

The ability of plants to transport and uptake heavy metals from the soil into their above-ground shoots and the harvestable parts of their underground roots is the key to successful phytoextraction (Garbisu and Alkorta, 2001; Chen et al., 2003). Robinson et al. (2006) stated that a few field experiments and commercial exercises have been done in the past decade to investigate successful phytoextraction. Moreover, for phytoextraction to be considered successful, the contaminated areas need to be detoxified to a level specified by environmental rules and for a lower cost than conventional techniques (Kos and Le tan, 2003). Nascimento and Xing (2006) expressed that phytoextraction may be considered as a commercial technology in the future.

Several literatures have described the potential of various species for the phytoextraction of heavy metals contaminated areas (Grispen et al., 2006; Daghan et al., 2008; Neugschwandtner et al., 2008; Zadeh et al., 2008; Liu et al., 2010; Nwaichi and Onyeike, 2010). Mangkoedihardjo and Surahmaida (2008) examined the potential of *J. curcas* L. for decontamination of Cd- and

Pb-contaminated soil. The garden soil was artificially contaminated by  $Pb(NO_3)_2$  and  $Cd(NO_3)_2$ . Plants were treated with different levels of these elements in a separate and mixed compound for a period of one month. The result showed that the primary concentration (50 mg kg<sup>-1</sup>) of these two elements had no harmful effects on the plants. The researchers found that J. curcas L. has a potential for phytoremediation of Cd and Pb in contaminated areas. Ang et al. (2003) studied the removal of Cd, Pb, As and Hg from slime tailings at Forest Research Institute, Malaysia. Various timber plants, including Hopea odorata, Acacia mangium, Swietenia macrophylla, and Intsia palembanica, were planted in slime tailing to determine their potential for bioaccumulation of Cd, Hg, Pb and As. The results of this study suggested that H. odorata and I. palembanica had the potential for Cd removal in a short period of time compared with others, whereas A. mangium was suitable for removal of As. Jiang et al. (2004) determined the growth performance and ability for Cu phytoextraction of Elsholtzia splendens. In a greenhouse study. CuSO<sub>4</sub>.5H<sub>2</sub>O was applied in various concentrations such as 100, 200, 400, 600, 800, 1000 and 1200 mg kg<sup>-1</sup>. The plant species showed a high ability to tolerate Cu toxicity and performed its usual growth when exposed to Cu up to 80 mg kg<sup>-1</sup> of available Cu. Li et al. (2009) studied the phytoextraction potential of carambola (Averrhoa carambola) as a tree species with high biomass. After 170 days growing on low Cd-contaminated soil, this species produced more biomass of shoots (18.6 t ha<sup>-1</sup>) and accumulated 213 g Cd per hectare. The researchers suggested that carambola is a suitable choice for low Cdcontaminated soils. The phytoextraction potential of a hybrid poplar (Populus deltoids × Populus nigra) in two purple and alluvial soils contaminated with Cd was evaluated by Wu et al. (2009). It was observed that the accumulation of Cd in plant parts increased with the increase of this element in the two soils. The accumulation of Cd in plant roots was higher than in shoots and then in leaves in purple soil, but the reverse was true in alluvial soil.

Murakami et al. (2007) also examined the ability of soybeans (*Glycine max* L. Merr., cv. Enrei and Suzuyutaka), maize (*Zea mays* L., cv. Gold Dent), and rice (*Oryza sativa* L., cv. Nipponbare and Milyang 23) for phytoextraction of Cd-polluted areas. The species were planted on one andosol and two fluvisols contaminated with low concentrations of Cd (0.83 to 4.29 mg Cd kg<sup>-1</sup>) for 60 days. The results indicated that the accumulation of Cd in shoots of Milyang 23 rice was 1 to 15% of the total Cd in the soil. It was inferred that these species had the potential to remediate paddy soil with low Cd contents.

#### Selection of hyper-accumulator of plants

Successful phytoremediation requires recognition of

suitable plant species to accumulate metals in toxic levels as well as creating high biomass (Clemens et al., 2002; Odoemelam and Ukpe, 2008). Generally, the ideal plants for phytoextraction should have high capacity to accumulate toxic levels of metals in their aerial parts (shoots), high growth rates, and tolerance to high salinity and high pH. Moreover, these plants must produce high dry biomass, simply grown and completely harvestable, and must uptake and translocate metals to aerial parts efficiently (Alkorta et al., 2004; Sarma, 2011). Overall, it is recommended to use the native plant species that grow locally near the site. These species are less competitive under local conditions and will reduce the metal concentration to an acceptable level for normal plant growth (Rajakaruna et al., 2006).

# Advantages of phytoremediation

Phytoremediation is a low-cost and effective strategy to clean up contaminated soils without requiring high-cost tools and expert human resources (Environmental protection agency, 2000; Ghosh and Singh, 2005). As a green technology, it is applicable for different kinds of organic and inorganic pollutants and provides aesthetic benefits to the environment by using trees and creating green areas, which is socially and psychologically beneficial for all (Ghosh and Singh, 2005; Lewis, 2006). This green technology is suitable for large areas in which other approaches would be expensive and ineffective (Vidali, 2001; Prasad and Freitas, 2003). In addition, as a practical approach to decontaminating soil and water, residues can be reused with minimal harm to the environment (Schnoor, 2002). Furthermore, the expansion of contaminants to air and water is reduced by preventing leaching and soil erosion that may result from wind and water activity (Pivetz, 2001; Ghosh and Singh, 2005).

# Disadvantages of phytoremediation

Time is the most serious limitation of phytoremediation, because this approach may require several years for effective remediation (Vidali, 2001; Rajakaruna et al., 2006). Moreover, preserving the vegetation in extensively contaminated areas is complicated (Vidali, 2001), and human health could also be threatened by entering the pollutant into the food chain through animals feeding on the contaminated plants (Pivetz, 2001). This technology is not impressive when just a small part of the contaminant is bio-available for plants in the soil (Rajakaruna et al., 2006). Beside that, it is limited to the low or mildly contaminated areas enclosed by the plant root district (Ghosh and Singh, 2005).

# CRITERIA FOR METAL ACCUMULATION IN PLANTS

All plant species have the ability to uptake metals;

however, some can accumulate greater amounts of metals (100 times more than the average plant in the same condition without showing any adverse effect). The woody or herbaceous plants that accumulate and tolerate heavy metals in an amount greater than the toxic levels in their tissue are known as hyperaccumulators (Baker et al., 2000; Barceló and Poschenrieder, 2003; Zhou and Song, 2004). In recent years, the use of hyperaccumulators for remediation of contaminated sites due to their capacity to take up heavy metals from polluted soil and accumulate them in their shoots has been receiving a great deal of attention from researchers (Sun et al., 2007, 2009). The main criteria for hyperaccumulators are; (i) accumulating capability, (ii) tolerance capability, (iii) removal efficiency (RE) based on plant biomass, (iv) bio-concentration factor (BCF) and (v) transfer factor (TF).

# Accumulating capability

Accumulating capability is the natural capacity of plants to accumulate metals in their above-ground parts (the threshold concentration) in amounts greater than 100 mg kg<sup>-1</sup> for Cd (Zhou and Song, 2004), 1000 mg kg<sup>-1</sup> for Cu, Cr, Pb, and Co, 10 mg kg<sup>-1</sup> for Hg (Baker et al., 2000) and 10000 mg kg<sup>-1</sup> dry weight of shoots for Ni and Zn (Lasat, 2002).

# Tolerance capability

Tolerance capability is the ability of plants to grow in heavy metal-contaminated sites and to have considerable tolerance to heavy metals without showing any reverse effects, such as chlorosis, necrosis, whitishbrown color, or reduction in the above-ground biomass (or at least not a significant reduction) (Sun et al., 2009).

# **Removal efficiency**

Removal efficiency based on plant biomass is the total concentrations of metals and dry biomass of plants to the total loaded metals in the growth media (Soleimani et al., 2010).

# BCF

BCF index is the ratio of heavy metal concentration in plant roots to that in the soil (Yoon et al., 2006). Cluis (2004) reported that the BCF for hyperaccumulators is > 1, and in some cases can increase up to 100.

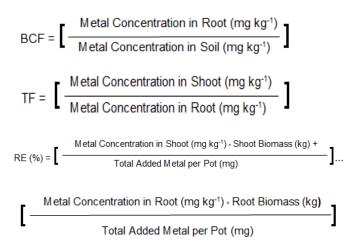
# ΤF

TF is the capability of plants to take up heavy metals in

 Table 1. Some hyperaccumulator species of metals.

Species	Metal	Reference
Clerodendrum infortunatum	Cu	Rajakaruna and Böhm (2002)
Croton bonplandianus	Cu	Rajakaruna and Böhm (2002)
Thordisa villosa	Cu	Rajakaruna and Böhm (2002)
Pityrogramma calomelanos	As	Dembitsky and Rezanka (2003)
Pistia stratiotes	Zn, Pb, Ni, Hg, Cu, Cd, Ag, and Cr	Odjegba and Fasidi (2004)
Alyssum lesbiacum	Ni	Cluis (2004)
Helicotylenchus indicus	Pb	Sekara et al. (2005)
Bidens pilosa	Cd	Sun et al. (2009)
Thlaspi caerluescens	Cd, Zn, and Pb	Cluis (2004) and Banasova et al. (2008)
Lonicera japonica	Cd	Liu et al. (2009)
Solanum nigrum L.	Cd	Sun et al. (2008)
Sedum alferedii	Cd	Sun et al. (2007)
Brassica junceae	Ni and Cr	Saraswat and Rai (2009)

their roots and to translocate them from the roots to their above-ground parts (shoots). Therefore, it is the ratio of heavy metal concentration in aerial parts of the plant to that in its roots (Mattina et al., 2003; Liu et al., 2010). This specific criterion for hyperaccumulators should reach > 1 to indicate that the concentration of heavy metals above ground is greater than that below ground (roots). Therefore, it can be concluded that this criteria is more crucial in phytoextraction, where harvesting the aerial parts of the plant is the most important objective (Wei and Zhou, 2004; Karami and Shamsuddin, 2010). Baker and Whiting (2002) reported that excluders can be identified by a TF < 1, whereas accumulators are characterized by a TF > 1. BCF, TF and RE are calculated by the following equations:



McGrath and Zhao (2003) reported that BCFs and **TF**s are > 1 in hyperaccumulators. More than 400 species from 45 families all over the world have been classified as hyperaccumulators (Sun et al., 2009). Sarma (2011) reported the latest number of metal hyperaccumulators. According to his report, more than 500 plant species consisting of 101 families are classified as metal hyperaccumulators, including Euphorbiaceae, Violaceae, Poaceae, Lamiaceae, Flacourtiaceace, Cunouniaceae, Asateraceae, Brassicaceae, Caryophyllace, and Cyperaceae. Zhou and Song (2004) reported that the hyperaccumulation of Cd and As occurs rarely in the plant families. They found that because hyperaccumulators produce low shoot biomass with long periods of maturity and long growing seasons, there are only a few plants with high metal accumulation ability and high biomass. However, Baker et al. (2000) found many species that can be classified as hyperaccumulators based on their capacity to tolerate toxic concentrations of metals, such as Cd, Cu, As, Co, Mn, Zn, Ni, Pb and Se (Table 1).

#### CONCLUSION

Heavy metals are one of the most critical threats to the soil and water resources, as well as to human health. These metals are released into the environment through mining, smelting of metal ores, industrial emissions, and the application of pesticides, herbicides and fertilizers. Metals, such as Cd, Cu, Pb, Zn, and metalloids (e.g. As), are considered to be metallic pollutants. Conventional remediation technologies are expensive, time consuming and environmentally divesting. Therefore, it is inevitable to use a low cost and environmentally friendly technology to remediate polluted soils with heavy metals, specifically in developing countries. Phytoremediation of metals is the most effective plant-based method to remove pollutants from contaminated areas. This green technology can be applied to remediate the polluted soils without creating any destructive effect of soil structure. Some specific plants, such as herbs and woody species, have been proven to have noticeable potential to absorb toxic metals. These plants are known as hyperaccumulators. Researchers are trying to find new plant species that are suitable to be used in removing heavy

metals from contaminated soils.

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