



Phytoremediation: a green technology

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Abstract

The technology of phytoremediation is cost effective and ecologically friendly in which plant utilizes its natural abilities to restore environment. In nature there are a number of plants existing with innate mechanisms for removing heavy metals from soil, air and water as a survival strategy. Among several subsets of phytoremediation, the widely studied strategies are (a) phytoextraction (b) phytofiltration (c) phytovolatilization and (d) phytostabilization. Application of organic / inorganic chelants in soil directly affects the solubility of heavy metals and consequently increases their accumulation in plants that enhances phytoextraction. In the present review current knowledge about the phytoremediation and its techniques are discussed.

Keywords: phytoremediation; phytoextraction; phytofiltration; phytovolatilization; phytostabilization

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1. Introduction

On earth the standard of life is judged by the overall quality of life which is explained by the growth supporting systems required for the existence and survival of human being and as well as provision of physical substances for socio-economic progress (Erakhrumen, 2007). It is evident that anthropogenic sources are responsible for pollution and environmental degradation in order to exploit nature for means of livelihood. All components of the biosphere are facing threats of pollution by a variety of organic / inorganic pollution because of manmade activities that alter the normal biogeochemical cycle (Prasad and Freitas, 2003).

Current cleaning technology like physical removal of polluted soil from a site and dumping

at somewhere else is too costly and destructive to environment (Meagher, 2000). Nowadays, an emerging promising approach is Phytoremediation Technology. It is an innovative field of science and technology for cleaning up contaminated soil, water and air (Salt et al., 1998; Meagher, 2000, Pulford and Watson, 2003). This technology is an alternative or complimentary one that could be applied along with or instead of mechanical congenital cleaning methodologies which mostly require high capital input, labor and intensive energy. It is an in-situ process that utilizes the inbuilt characteristics of plants for environmental remediation. Certain plants have endogenous, genetic biochemical and physiological qualities to combat against the soil, water and air pollution (Cunningham and Berti, 1993; Raskin et al., 1994; Meagher, 2000). Higher plants possess remarkable capabilities for the degradation of many obstinate xenobiotics and act as sink for dreadful chemical pollutions and therefore also called as "green livers". Phytoremediation could also be defined as the

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utilization of green plants for extraction, sequestration and / or detoxification of the pollutants and / or rendering them harmless.

The generic term 'phytoremediation' consists of the Greek prefix phyto (plant) attached to the Latin root remedium (to correct or remove an evil) (Cunningham *et al.*, 1996). It is also often referred as Bioremediation, Botanical-Remediation and Green Remediation (Chaney *et al.*, 1997). This eco-friendly technology is derived by solar energy based on the idea of cleaning nature by the help of nature (UNEP, 2002). The idea of such natural remedy is very old and source cannot be traced; however, a number of wonderful scientific discoveries in different research fields have led to develop this promising eco-based technology (Raskin *et al.*; 1997). Development in this area is only due to the collaboration and cooperation in the interdisciplinary research fields like plant bio chemistry, molecular biology, soil chemistry, agronomy, environmental engineering and at the same time support at state and federal level. Principles of phytoremediation for environmental cleanup, began in the late 1970s or early 80s. It was first implemented and reported as an environmental cleanup technology for agricultural contaminations from last copy such as pesticides and excess plant nutrients like nitrates, ammonia and phosphate (Briggs *et al.*, 1982). This "green" technology has potential to remove toxic metals (As, Cd, Cu, Hg, Pb and Zn)

including radionuclide (Sr, Cs and U) from soil, water and air. Most of the organic pollutants including (PAHs) such as benzoapyrene, nitro aromatics such as trinitrotoluene (TNT), and linear halogenated hydrocarbons such as trichloroethylene (TCE) are very much toxic, teratogenic and even carcinogenic, which are possible important targets of phytoremediation (Cunningham *et al.*, 1996). This review is restricted and focused on the phytoremediation of heavy metal pollution.

2. Phytoremediation of heavy metals

Pollution and its threats are dramatically increased with the industrial revolution due to which world is facing majority of the environmental problems (Ensley, 2000). Different sources of manmade metal pollution are electroplating, smelting, gas exhaust, fuel and energy production, fertilizers, sewerage sludge and other industrial manufacturing (Raskin *et al.*, 1994; Cunningham *et al.*, 1997; Blaylock and Huang, 2000; Prasad and Freitas, 2003). These sources are further elaborated at Table (1). Metal contamination in soil and water is peril to environment and human health which requires an effective and affordable technological solution. Among various conventional heavy metal remedial technologies for cleaning the environment are in situ vitrification, incineration, excavation and land fill, soil washing, soil flushing,

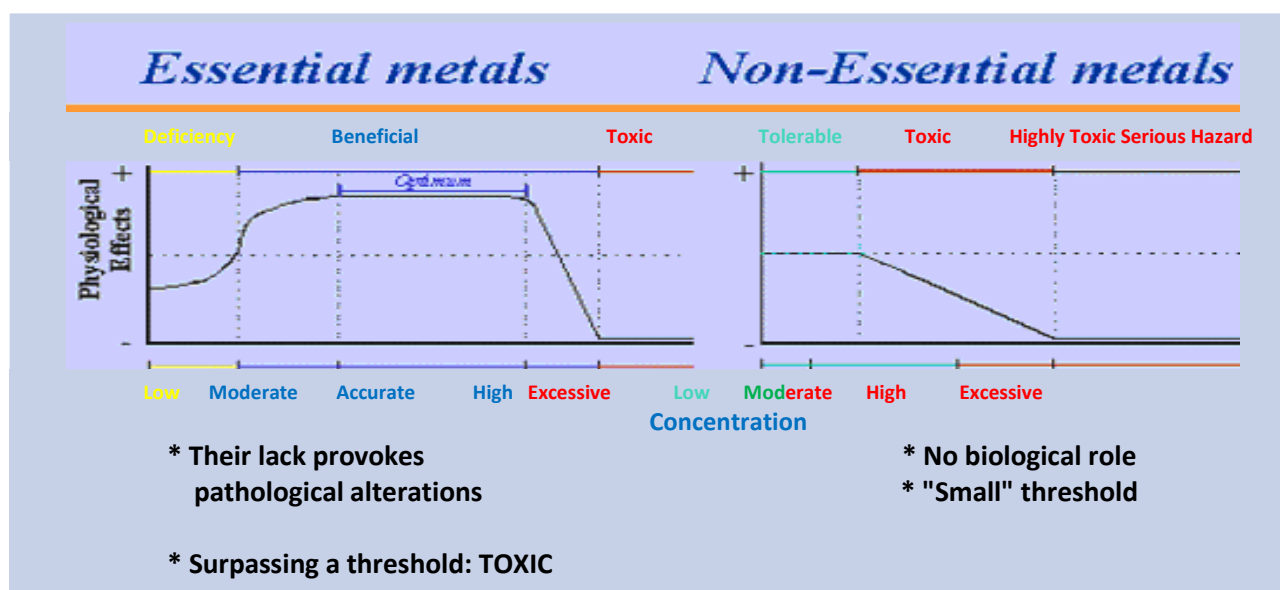


Fig. 1. Conceptual response strategies of metal concentrations in plant tops in relation to increasing total metal concentrations in soil (after: Jadia and Fluekar, 2009)

solidification, stabilization and electrokinetics systems (MADEP, 1993). These remedial methodologies are expensive, require high energy input, damage soil structure and decrease soil productivity. Presently, excavation and burial of the soil at a hazardous waste site is being adopted as a remedial process for the rehabilitation of toxic metal contaminated site at an average cost of \$ 1000000 per acre (Ensley, 2000). Phytoremediation on other hand due to its cost effective means for restoration of hundreds and thousands of contaminated sites polluted by anthropogenic sources draws great attraction and excitement (Salt et al., 1995; Cunningham et al., 1996).

3. Techniques of Phytoremediation

For removal of different hazardous compounds from contaminated soil and water, plant potentials have been exploited that resulted in several technological subsets (Fig. II). Schwitzguebel (2000) has defined the following techniques of phytoremediation:

- Phytoextraction: the use of pollutant-accumulating plants to remove pollutants like metal organics from soil by concentrating them in harvestable plant parts,
- Phytotransformation: the degradation of complex organic to simple molecules or the incorporation of these molecules into plants

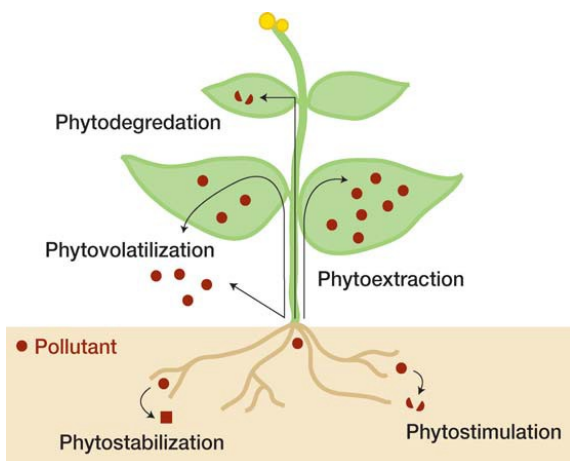


Fig. II. Possible fates of pollutants during phytoremediation: the pollutant (represented by red circles) can be stabilized or degraded in the rhizosphere, sequestered or degraded inside the plant tissue, or volatilized (Pilon-Smith, 2005).

tissues,

- Phytostimulation: plant-assisted bioremediation or the stimulation of microbial and fungal degradation by release of exudates / enzymes into the root zone (rhizosphere),
- Phytovolatilization: the use of plants to volatilize pollutants or metabolites,
- Phytodegradation: enzymatic breakdown of organic pollutants such as trichloroethylene (TCE) and herbicides, both internally and externally and through secreted plant enzymes,
- Phytorhizofiltration: the use of plant roots to ab/adsorb pollutants, mainly metals, but also organic pollutants, from water and aqueous waste streams,
- Pump and tree (Dendroremediation): the use of trees to evaporate water and thus to extract pollutants from the soil,
- Phytostabilization: the use of plants to reduce the mobility and bioavailability of pollutants in the environment, thus preventing their migration to groundwater or their entry into the food chain, and
- Hydraulic Control: the control of the water and the soil field capacity by plant canopies.

In this review, four major sub-sets, namely, Phytoextraction, Phytostabilization, Phytovolatilization and Phyto/Rhizofiltration will be further discussed. An overview on types of this technology is presented in Table (3).

I. Phytoextraction

Phytoextraction represents the largest economic opportunities for phytoremediation (Raskin et al., 1997). It is also called as phytoaccumulation. It is considered as the best approach for removing and isolating the contamination from soil while keeping its structure and fertility intact (EPA, 2000). In metal polluted soil hyper accumulating plants are seeded/ transplanted and are cultivated under established agriculture methodologies. Metals present in soil are absorbed by the plants and then translocated to the above ground shoots for accumulations. When maximum plant growth and metal accumulation are achieved, plants from above ground levels are harvested that

results permanent removal of metals from the site. The removed heavy metals can be recycled from the contaminated plant biomass (Brook et al., 1998). Phytoextraction is fit for the rehabilitation of large areas low to moderate levels of contaminated land at shallow depths (Kumar et al., 1995; Blaylock and Huang, 2000). Possible plants for this technology must be tolerant of the focused metal or metals and be efficient in translocation to the harvestable portion of the plant. In addition, the plant should possess the ability to grow in difficult edaphic conditions like salinity, soil pH, soil structure and water content, to produce dense root system, element selectivity, ease of care and establishment and resistance to disease and insect problems. On the other hand, limitations in the selection of hyper accumulators are shallow root system, slow growth, small biomass production and final disposal (Brooks, 1994). Plant growing naturally in mineralized soil are able to concentrate huge amount of essentials and nonessential metals in their foliage, are basically the cause of inspiration and development of phytoextraction (Baker and Brooks, 1989). In hyperaccumulator species the extent of heavy metals like Zinc, Nickel and Copper accumulation often reaches to 1-5%. It is also thought that cause of the evaluation of this uniform phenomena could be the prevention against the herbivory and disease (Boyd et al., 1994). Various factors are responsible in success of phytoextraction as an environmental cleanup technology. These include level of soil pollution, bioavailability and plant ability to intercept, absorb and concentrate metals in harvestable parts (Ernst, 1996).

However, phytoextraction depends on the interaction among soil, metal and plant. This complex interaction in nature is controlled by the climatic conditions and genetic makeup for site specific phytoremediation. Among different approaches of phytoextraction two basic strategies are finally developed.

A. Chelate Assisted Phytoextraction or induced phytoextraction in which EDTA, HEDTA and EDDNA as an artificial chelant is added for increasing the mobility and uptake of metal contaminants.

B. Continuous Phytoextraction in which plants natural characteristics are exploited for remediation (Salt et al., 1995). Plants secrete phytosideophores (chelating agents) like mugenic and aveinc acids to enhance the bioavailability of soil bond heavy metals.

II. Phytostabilization

It is also termed as Phytorestoration. In this remedial technique, plant stabilizes wastes and prevents exposure pathway through wind and water erosion, enables hydraulic control that restricts the vertical migration of pollutants into ground water, and immobilizes the pollutants physically and chemically by root sorption and chemical fixation with different soil amendments. Selected plant for this technique should be poor translocators for metal contamination towards aerial parts likely to be consumed by humans or animals, easy to establish, quick to grow, having well developed canopies and root systems, and tolerant to metal pollution and other climatic and site stresses that could limit plant growth.

The research of Smith and Bradshaw (1992) led to the development of two cultivars of *Agrosists tenuis Sibth* and one of *Festuca rubra L* which are now commercially available for the Phytostabilization of Pb, Zn, Cu contaminated soils.

III. Phytovolatilization

Toxic metals such as Se, As and Hg may exist as gaseous species in environment. Recently it is discovered that plants that absorb elemental form of metals from soil, could convert them biologically into gaseous species inside the plant, i.e., biomethylated to form volatile molecules and finally release them to the atmosphere. The mentioned process is controversial of all techniques due to its dubious nature that whether release of these volatilized elements in atmosphere is safe. The disadvantage is the volatilized element could be recycled by precipitation and then redeposit back into ecosystem (Henry, 2000). According to Brooks et al. (1998), the release of volatile Se compounds from higher plants was first reported by Lewis et

al. (1999) whereas Terry et al. (1992) reported that members of the Brassicaceae are capable of releasing up to $40\text{g Se ha}^{-1}\text{day}^{-1}$ as various gaseous compounds. Volatile Se compounds, such as dimethylselenide, are 1/600 to 1/500 as toxic as inorganic forms of Se found in the soil (Desouza et al., 2000). After genetic modification of *Arabidopsis thaliana* L. and *Nicotiana tabacum* L. with bacterial organomercurial lyase (Mer B) and mercuric reductase (Mer A) genes (Heaton et al., 1998; Rugh et al., 1998) plants have developed abilities to absorb elemental Hg(II) and methyl mercury (Mer Hg) from the soil and release volatile Hg (0) from leaves to atmosphere. This technology does not require much management after plant seeding. In addition, it has advantage of minimum site disturbance, low erosion rate and there is no need for disposal of hazardous plant material (Heaton et al., 1998).

IV. Phytofiltration

In phytofiltration plant roots (rhizofiltration) or seedlings (blastofiltration) are grown in aerated water from where they participate and concentrate toxic metals from contaminated effluents (Raskin et al., 1997). The techniques involve growing plants hydroponically and transplanting into metal polluted water from where plants absorb and concentrate the metals in their roots and shoots (Dushenkov et al., 1995; Salt et al., 1995; Flathman and Lanza, 1998). Ideal characteristics in plants for rhizofiltration are fast growing roots with capability for removing toxic metals from solution over extended period of time. After saturation with the metal contamination which forms precipitation over root surface, whole plants or roots are harvested for disposal. This precipitation is caused by the root exudates and changes in rhizospheres pH, (Flathman and Lanza, 1998). Blastofiltration represents the second generation of plant based water treatment technology. According to data blastofiltration is more efficient than rhizofiltration for some metals. Due to the dramatic increase in surface to volume ratio after germination, seedlings tend to adsorb large quantities of toxic metal ions (Raskin et al., 1997). Additionally, in aerated water with very little microbial contamination,

the seedling of *B. juncea* grew very rapidly, resulting development of very large surface area in 4-5 days (Salt et al., 1997).

The mechanisms of phytofiltration are not necessarily similar for different metals. Precipitation and exchangeable sorption are involved in the case of Pb. Biological processes are more important for Cd and Pb which are responsible for the slower components of metal removal, its deposition translocation to the shoots from the solution and intracellular uptake to the vacuole (Salt et al., 1997 ; Raskin et al., 1997).

4. Chelant assisted phytoextraction

The term 'chelate' denotes a complex between metal and a chelating agent and not the chelating agent itself (Nowack and Van Briesen, 2005). A shorter word for chelating agent is 'chelant' or 'chelator'. It is therefore, suggested for using the term 'chelant-enhanced phytoextraction'. Other terms such as 'chelant-induced' and 'chelant-assisted' phytoextraction can be used as synonyms to chelant-enhanced phytoextraction. 'Chelate' should be used whenever a metal-chelating agent complex is meant, e.g., when talking about a specific complex in soil physical, chemical and biological properties. A large number but only a fraction of metals are readily available / bioavailability for transporting to the roots (Lasat, 2002). To resolve this problem, chemically enhanced phytoextraction has been developed (Huang et al., 1997). This approach utilizes high biomass crops that are induced to absorb large quantity of metals whereas metals mobility is enhanced by the treatment of different chemicals. Research into the interaction of plants with chelating agents started in the 1950s with a view to alleviating deficiencies in the essential nutrient metals Fe, Mn, Cu and Zn. Initial results also showed that chelants such as EDTA enhanced plant uptake of Pb and Hg (Hale and Wallace, 1970). Jorgensen (1993) and Huang and Cunningham (1996) showed that addition of chelating agents

to soils increased Pb accumulation by crop plants to such an extent that they might be used for cleanup plants of Pb-contaminated soils. Enhanced uptake was not only observed in nutrient solution and pot experiments but also in the field (Liphadzi et al., 2003). Mainly, there are three factors that control the transportation of heavy metals from soil to plants. These include the total amount of bioavailable metals / elements (quantity factor), the activity and the ratio of elements present in soil as in ionic form (intensity factor) and the rate of elements transferred from solid to liquid phases to plant roots (reaction kinetics) (Brümmer et al., 1986).

I. Using organic chelants

Selection of suitable chelants for the extraction of heavy metals from a polluted site is the first issue to be considered, whereas the solubilization of heavy metals must be enhanced to increase extraction efficiency which is mainly based on the capacity of organic chelants to form water soluble organic complexes (Martell and Calvin, 1958). By the formation of complex, metals get extracted or desorbed from different components of soil. Several chelants for example Citric acid, EDTA, CDTA, DTPA, EGTA, EDDHA and NTA were studied to find out their ability of mobilizing metals and increasing metal accumulation in various plant species (Huang et al., 1997; Cooper et al., 1999). Different metals were focused like Pb (Blay lock et al., 1997; Huang et al., 1997), U (Huang et al, 1998), ¹³⁷Cs, and Au. The complexation of heavy metals with various chelants in soil is as follows: EDTA and related synthetic chelates > nitrilotriacetic acid (NTA) > citric acid > oxalic acid > acetic acid (Hong and Pintauro, 1996; Krishnamurti et al., 1998; Wenger et al., 1998). In most of the designed experiments Pb is targeted to test the effect of applying organic chelants on the accumulation of heavy metals. The experiments were conducted with chelants of high metals binding capacity (like EDTA

hydroxyethylethylenediaminetriacetic acid [HEDTA], 1,2-cyclohexylenedinitrilotetraacetic acid [CDTA], and diethylenetriaminepentaacetic acid [DTPA]). Many studies found extremely high Pb concentrations in the biomass of several crops (Table 3). Research was conducted at highly Pb polluted soils where addition of high amount of EDTA, CDTA, or HEDTA increased Pb concentration tremendously to as much as 24g Pb Kg⁻¹ dry matter. In smaller extent, artificial chelants also enhance heavy metals concentration other than Pb in the soil solution and in the biomass of several plants. These discoveries paved the way to successful Pb phytoextraction and defining development of methods to remove other toxic metals using suitable chelants. Likewise, EGTA (ethylenebis [oxyethylenetrinitrilo] tetraacetic acid) has been shown to have a high affinity for Cd²⁺, but not for Zn²⁺. EDTA, HEDTA, and DTPA are selective for Zn²⁺. EDTA, citric and oxalic acid increase (> 200-fold) Cr³⁺ uptake and its concentration in plant roots and shoots from a polluted soil. Acto-aminodiacetic acid stimulates Pb bioavailability whereas S-carboxy-methylcysteine is effective for Cu. In treated soil with ammonium thiocyanate, Indian mustard accumulated Au upto 57 mg/ kg. On the other hand, *Iberis intermedia* and *Biscutia lovevigata* accumulated 0.4% and 1.5% thallium on a dry weight basis, respectively. It is reported by Ebbs et al. (1998) and Huang et al. (1998) that the addition of citric acid and its salts to the soil, increases uranium mobility and its uptake by the plant. They further suggested that the strong mobilization of uranium caused by citric acid is because of citrate-uranium complex formation rather than decreased pH. This indicates the affinity of the chelant for the target metal. Therefore, to increase efficiency of phytoextraction, synthetic chelants with high affinity for the metal of interest should be used. In the light of aforementioned information, a hypothetical protocol for the chelant assisted phytoextraction for a contaminated area is provided as (Salt et al., 1998) (Fig. III):

1. Evaluation of site and determination of suitable chelant / crop combination,
2. Preparation of site and cultivation of selected crop / plant,
3. When potential bio mass is produced suitable metal chelant is applied, and
4. Plant / crop is harvested after a short metal-accumulation phase (several days or weeks).

Moreover, phytoextraction could be continued by replanting on the site, depending on the crop and the season. Estimates suggest that remediation of sites contaminated with up to 2500 mg kg^{-1} Pb is possible in less than 10 years. The weight and volume of contaminated material can be further reduced by ashing or composting. Depending on economical feasibility plant residues, enriched with metals could be utilized for metal recovery. Along with the multifaceted benefits this strategy have potential risk of metal leaching to the ground water and there is still a lack of detailed studies regarding the persistence of metal chelating agent complexes in contaminated soil (Lombi et al., 2001). In addition to the risk of metal leaching, EDTA is an expensive chemical. Little discussion on the potential cost of EDTA induced phytoextraction occurred, but this issue seriously detracts from the feasibility of that technology (Chaney, 2007). Chaney et al. (2002) obtained the price of commercial quantities of EDTA and estimated the cost would be about $\$30000 \text{ ha}^{-1}$ for the amount of EDTA reportedly needed to attain over 10 kg Pb kg^{-1} dry shoots ($10 \text{ mmol EDTA kg}^{-1}$ soil for each cropping).

II. Using inorganic chelants

Enhancement of phytoextraction through inorganic amendments has a different solubilization mechanism. In this strategy, instead of complex formation, the solubilization of heavy metals relies on disruption through inorganic chelants like Sulphur, Ammonium sulphate and Chloride salts (Brummer et al., 1986; Hornburg Gray et al., 1999). Metals in solubilized form are potentially bioavailable and can either be absorbed by plants, leached into the ground water, or desorbed again by the exchange sites of the soil. In the light of literature the efficiency of

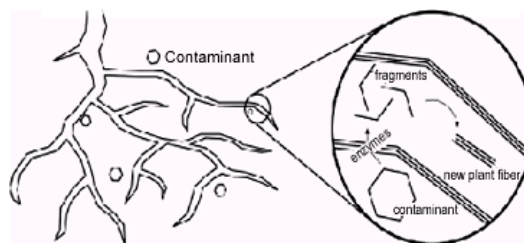


Fig. III. Destruction of organic contaminants by phytodegradation; Enzymes in plant roots break down (degrade) organic contaminants. The fragments are incorporated into new plant material (UNEP, 2002)

organic and inorganic heavy metals absorption is classified in Table 3, in which pollution caused by enhanced leaching is not assessed.

5. Conclusion

Heavy metals are persistent environmental pollutants which cannot be degraded and require complete removal for remedial purpose. Plants are exploited to rehabilitate the contaminated environment by the scientists of different inter-related fields. This resulted in a green technology called Phytoremediation. This fast emerging, innovative technology is a cost effective, eco-friendly and viable alternative to conventional remedial methods. At the same time, it is most suitable for a developing country like Pakistan. Enhanced phytoextraction is the important aspect for the modification and implementation of phytoremediation strategies because when accumulation rate of heavy metal in plants increases, the removal of pollutants also maximizes. It is also very crucial to minimize the ecological risk linked with enhanced phytoextraction. Further research is required to optimize the ecological and economical efficiencies of Phytoremediation.

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