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RESEARCH ARTICLE

PHYTOREMEDIATION OF HEAVY METAL: PRINCIPLES AND PRESPECTIVES

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ABSTRACT

Acute and diffuse contamination of soil and water by heavy metals and metalloids cause wide, environmental and social concern. Among the techniques used to cleanup affected sites, phytoremediation has recently emerged as a new tool which is cost-effective as well as environment-friendly alternative. After a short introduction to the types of plant-based cleanup techniques, this review focuses on metal hyper accumulator plants and their potential use in phytoextraction technology. Phytoextraction using hyper accumulating plants is seen as a promising technique; a lack of understanding of the basic physiological, biochemical, and molecular mechanisms involved in the removal of heavy metal from environment. The discovery of hyper accumulator plants, which contain high levels of heavy metals that would be highly toxic to other plants, prompted the idea of using certain plant species to extract metals from the soil and, in the process, clean up soil for other less tolerant plants. The best-long term strategy for improving phytoextraction is therefore to understand and exploit the biological processes involved in metal acquisition, transport and shoot in plants.

INTRODUCTION

Land and water are precious natural resources on which rely the sustainability of agriculture and the civilization of mankind. Unfortunately, they have been subjected to maximum exploitation and severely degraded or polluted due to anthropogenic activities. The pollution includes point sources such as emission, effluents and solid discharge from industries, vehicle exhaustion and metals from smelting and mining, and nonpoint sources such as soluble salts (natural and artificial), use of insecticides/pesticides, disposal of industrial and municipal wastes in agriculture, and excessive use of fertilizers (McGrath *et al.,* 2001; Nriagu and Pacyna, 1988; Schalscha and Ahumada, 1998). Each source of contamination has its own damaging effects to plants, animals and ultimately to human health, but those that add heavy metals to soils and waters are of serious concern due to their persistence in the environment and carcinogenicity to human beings. They cannot be destroyed biologically but are only transformed from one oxidation state or organic complex to another (Garbisu and Alkorta, 2001; Gisbert *et al.,* 2003). Therefore, heavy metal pollution poses a great potential threat to the environment and human health (Lone Iqbal *et al*, 2008). "Phytoremediation", is an emerging technology in which the plants are employed to absorb and bio-magnify elements from a polluted environment and metabolize them into various biomolecules in their tissues (Pant Pandey *et al.,* 2011).

At many hazardous waste sites requiring cleanup, the contaminated soil, groundwater, and/or wastewater contain a mixture of contaminant types, often at widely varying concentrations. These may include salts, organics, heavy metals, trace elements, and radioactive compounds. The simultaneous cleanup of multiple, mixed contaminants using conventional chemical and thermal methods are both technically difficult and expensive; these methods also destroy the biotic component of soils. Phytoremediation, an emerging cleanup technology for contaminated soils, groundwater, and wastewater that is both low-tech and low-cost, is defined as the engineered use of green plants (including grasses, forbs, and woody species) to remove, contain, or render harmless such environmental contaminants as heavy metals, trace elements, organic compounds, and radioactive compounds in soil or water (Hinchman and Negri., 1997; Hussain *et al*., 2010).Several comprehensive studies have been done, summarizing many important aspects of this novel plant based technology (Meagher, 2000; Navari-Izzo and Quartacci, 2001; Lasat , 2002; McGrath *et al.,* 2002; McIntyre, 2003; Singh *et al*., 2003; Prasad and Freitas, 2003; Alkorta *et al*., 2004; Ghosh and Singh, 2005; Pilon smits, 2005; Rai and Pal, 2001; Padmavathiamma and Li, 2007). Present work shall give a general guidance, recommend for using phytoremediation technique highlighting the process associated with applicants and identifying biological mechanisms.

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SOURCES OF HEAVY METALS AND SOIL WATER POLLUTION

Land and water pollution by heavy metals is a worldwide issue. All countries have been affected, though the area and severity of pollution vary enormously. In Western Europe, 1, 400, 000 sites were affected by heavy metals (McGrath *et al.,* 2001), of which, over 3,00,000 were contaminated, and the estimated total number in Europe could be much larger, as pollution problems increasingly occurred in Central and Eastern European countries (Gade, 2000). In USA, there are 6, 00,000 brown fields which are contaminated with heavy metals and need reclamation (McKeehan, 2000). According to government statistics, coal mine has contaminated more than 19 000 km of US streams and rivers from heavy metals, acid mine drainage and polluted sediments. More than 1, 00, 000 ha of cropland, 55,000 ha of pasture and 50,000 ha of forest have been lost (Ragnarsdottir and Hawkins, 2005). The problem of land pollution is also a great challenge in China, where one-sixth of total arable land has been polluted by heavy metals, and more than 40% has been degraded to varying degree due to erosion and desertification (Liu, 2006). Soil and water pollution is also severe in India, Pakistan and Bangladesh, where small industrial units are pouring their untreated effluents in the surface drains, which spread over near agricultural fields. In these countries raw sewage is often used for producing vegetables near big cities.

Heavy metals that have been identified in the polluted environment include As, Cu, Cd, Pb, Cr, Ni, Hg and Zn. The presence of any metal may vary from site to site, depending upon the source of individual pollutant. Excessive uptake of metals by plants may produce toxicity in human nutrition, and cause acute and chronic diseases. For instance, Cd and Zn can lead to acute gastrointestinal and respiratory damages and acute heart, brain and kidney damages. High concentrations of heavy metals in soil can negatively affect crop growth, as these metals interfere with metabolic functions in plants, including physiological and biochemical processes, inhibition of photosynthesis, and respiration and degeneration of main cell organelles, even leading to death of plants (Garbisu and Alkorta, 2001; Schmidt, 2003; Schwartz *et al.,* 2003). Soil contamination with heavy metals may also cause changes in the composition of soil microbial community, adversely affecting soil characteristics (Giller *et al.,* 1998; Kozdrój and van Elsas, 2001; Kurek and Bollag, 2004).

PHYTOREMEDIATION TECHNIQUE

The word's Phytoremediation comes from the Greek word "phyto" = plant, and Latin "remedium" = restoring balance, or remediation. Phytoremediation consists in mitigating pollutant concentrations in contaminated soils, water or air with plants able to contain, degrade or eliminate metals, pesticides, solvents, explosives, crude oil and its derivatives, and various other contaminants, from the media that contain them. Phytoremediation works best at sites with low to medium amounts of pollution. Plants remove harmful chemicals from the ground when their roots take in water and nutrients from polluted soil, streams, and groundwater. Plants can clean up chemicals as deep as their roots can grow. Tree roots grow deeper than smaller plants, so they are used to reach pollution deeper in the ground (A Citizen's Guide to Phytoremediation [EPA 542-F-01-002]).Phytoremediation is a set of processes that uses plants to remove, transfer, stabilize and destroy organic/inorganic contamination in ground water, surface water, and soil (Vishnoi and Srivastava, 2008).

Once inside the plant, chemicals can be:

- stored in the roots, stems, or leaves
- changed into less harmful chemicals within the plant
- changed into gases that are released into the air as the plant transpires (breathes).

METHODS OF PHYTOREMEDIATION

The use of green plants to remove pollutants from the environment or render them harmless is defined as phytoremediation (Cunningham and Berti, 1993). Phytoextraction, phytostabilization and phytofiltration are three processes involved in phytoremediation (Salt *et al.,* 1998) processes which can help reduce metal content of respective environment. The general process of phytoremediation is depicted in Figure-1.

1. PHYTOEXTRACTION (PHYTOACCUMULATION):

Phytoextraction is the name given to the process where plant roots uptake metal contaminants from the soil and translocate them to their above soil tissues. As different plant have different abilities to uptake and withstand high levels of pollutants many different plants may be used. This is of particular importance on sites that have been polluted with more than one type of metal contaminant. Hyperaccumulator plant species (species which absorb higher amounts of pollutants than most other species) are used on may sites due to their tolerance of relatively extreme levels of pollution. Once the plants have grown and absorbed the metal pollutants they are harvested and disposed of safely. This process is repeated several times to reduce contamination to acceptable levels. In some cases it is possible to recycle the metals through a process known as phytomining, though this is usually reserved for use with precious metals. Metal compounds that have been successfully phytoextracted include zinc, copper, and nickel, but there is promising research being completed on lead and chromium absorbing plants (Meagher, 2000).

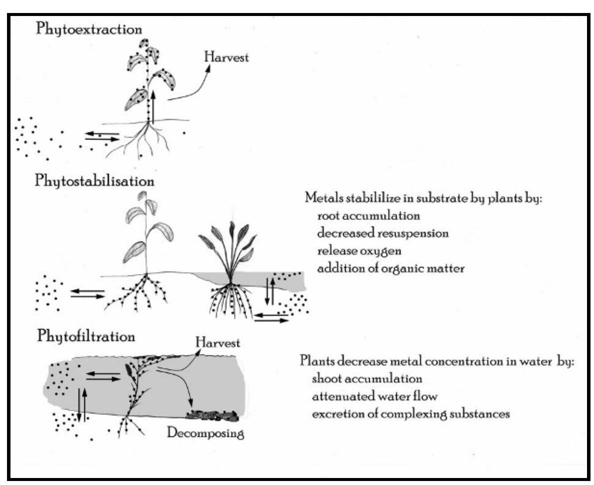


Fig.1. Principles of phytoextraction, phytostabilization, and phytofiltration

Table: 1 Advantage and Disadvantage/ Limitations of Phytoremediation

Sl. No.	Advantages	Disadvantage/Limitations
1	Amendable to a broad range of organic and inorganic contaminants including many metals with limited alternative options.	Restricted to sites with shallow contamination within rooting zone of remediative plants; ground surface at the site may have to be modified to prevent flooding or erosion.
2	In Situ / Ex Situ application possible with effluent/soil substrate respectively; soil can be left at site after contaminants are removed, rather than having to be disposed or isolated.	A long time is often required for remediation; may take up to several years to remediate a contaminated site.
3	In Situ applications decrease the amount of soil disturbance compared to conventional methods; it can be performed with minimal environmental disturbance; topsoil is left in a usable condition and may be reclaimed for agricultural use; organic pollutants may be degraded to CO_2 and H_2O, removing environmental toxicity.	Restricted to sites with low contaminant concentrations; the treatment is generally limited to soils at a meter from the surface and groundwater within a few meters of the surface; soil amendments may be required.
4	Reduces the amount of waste to be landfilled (up to 95%), can be further utilized as bio-ore of heavy metals.	Harvested plant biomass from phytoextraction may be classified as a hazardous waste hence disposal should be proper.
5	In Situ applications decrease spread of contaminant via air and water; possibly less secondary air and/or water wastes are generated than with traditional methods.	Climatic conditions are a limiting factor; climatic or hydrologic conditions may restrict the rate of growth of plants that can be utilized.
6	Does not require expensive equipment or highly specialized personnel; it is cost-effective for large volumes of water having low concentrations of contaminants; it is cost-effective for large areas having low to moderately contaminated surface soils.	Introduction of non-native species may affect biodiversity.
7	In large scale applications the potential energy stored can be utilized to generate thermal energy; plant uptake of contaminated groundwater can prevent off-site migration.	Consumption/utilization of contaminated plant biomass is a cause of concern; contaminants may still enter the food chain through animals/insects that eat plant material containing contaminants.

Source: Schwitzguébel (2000); Ghosh and Singh (2005).

2. PHYTOSTABILISATION

Phytostabilisation is the use of certain plants to immobilize soil and water contaminants. Contaminant are absorbed and accumulated by roots, adsorbed onto the roots, or precipitated in the rhizosphere. This reduces or even prevents the mobility of the contaminants preventing migration into the groundwater or air, and also reduces the bioavailability of the contaminant thus preventing spread through the food chain. This technique can also be used to re-establish a plant community on sites that have been denuded due to the high levels of metal contamination. Once a community of tolerant species has been established the potential for wind erosion (and thus spread of the pollutant) is reduced and leaching of the soil contaminants is also reduced (Mendez and Maier, 2008).

3. PHYTOFILTRATION (RHIZOFILTRATION):

Phytofiltration is similar in concept to Phytoextraction but is concerned with the remediation of contaminated groundwater rather than the remediation of polluted soils. The contaminants are either adsorbed onto the root surface or are absorbed by the plant roots. Plants used for phytofiltration are not planted directly in situ but are acclimated to the pollutant first. Plants are hydroponically grown in clean water rather than soil, until a large root system has developed. Once a large root system is in place the water supply is substituted for a polluted water supply to acclimatize the plant. After the plants become acclimatized they are planted in the polluted area where the roots uptake the polluted water and the contaminants along with it. As the roots become saturated they are harvested and disposed of safely. Repeated treatments of the site can reduce pollution to suitable levels as was exemplified in Chernobyl where sunflowers were grown in radioactively contaminated pools (Baker and Brooks, 1989).

PLANT SPECIES FOR PHYTOREMEDIATION

To identify plant populations with the ability to accumulate heavy metals, 300 accessions of 30 plant species were tested by Ebbs *et al*. (1997) in hydroponics for 4 weeks, having moderate levels of Cd, Cu and Zn. The results indicate that many *Brasssica spp.* such as *B. juncea* L., *B. juncea* L. *Czern, B. napus* L. and *B. rapa* L. exhibited moderately enhanced Zn and Cd accumulation. They were also found to be most effective in removing Zn from the contaminated soils. To date, more than 400 plant species have been identified as metal hyper accumulators, representing less than 0.2% of all angiosperms (Brooks, 1998; Baker *et al.*, 2000). The plant species that have been identified for remediation of soil include either high biomass plants such as willow (Landberg and Greger, 1996) or those that have low biomass but high hyper accumulating characteristics such as *Thlaspi* and *Arabidopsis* species.

PHYTOREMEDIATION OF POLLUTED WATER

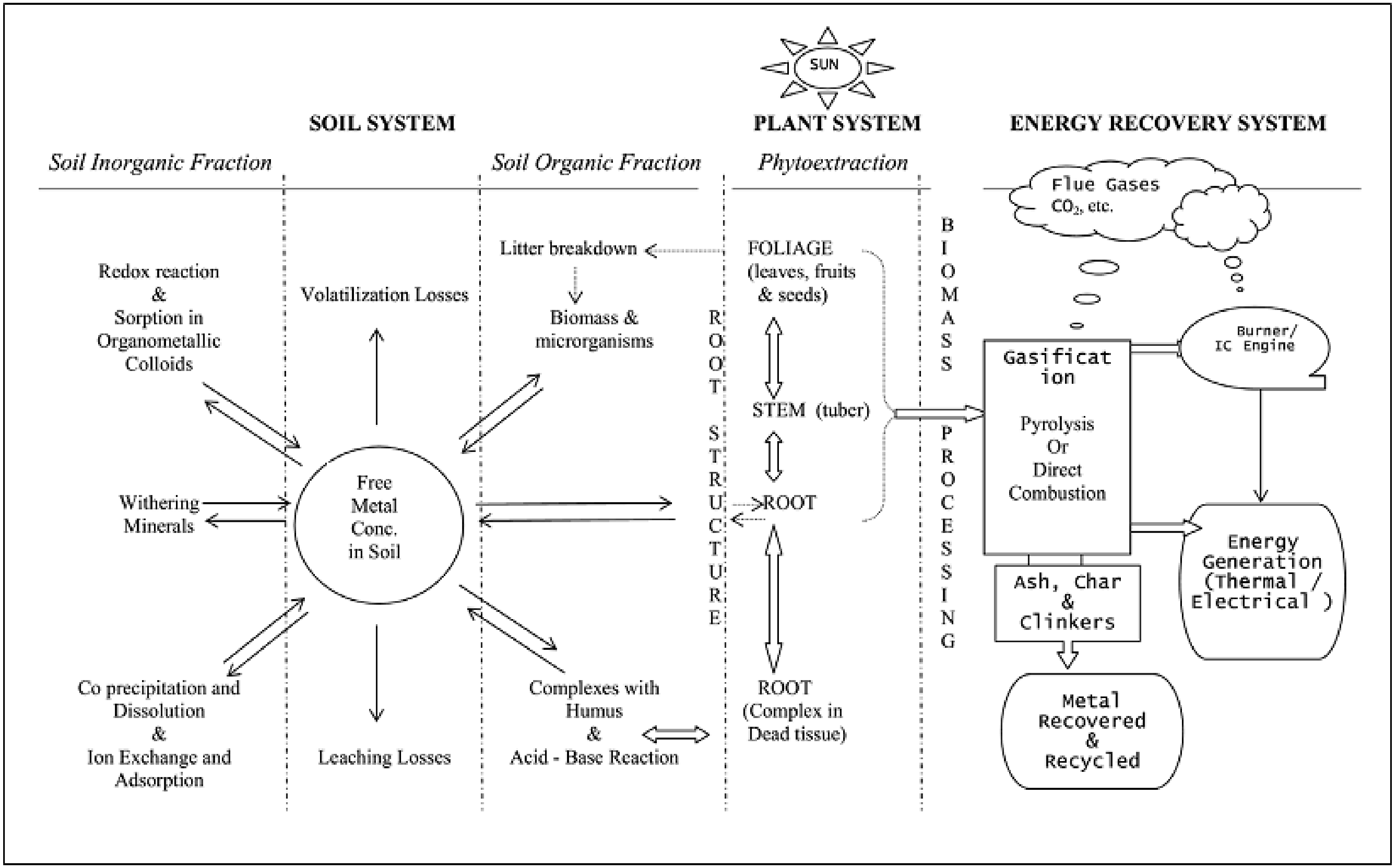
Rhizofiltration is the removal of pollutants from the contaminated waters by accumulation into plant biomass. Several aquatic species have been identified and tested for the phytoremediation of heavy metals from the polluted water. These include sharp dock (*Polygonum amphibium* L.), duck weed (*Lemna minor* L.), water hyacinth (*Eichhornia crassipes*), water lettuce (*P. stratiotes*), water dropwort [*Oenathe javanica* (BL) DC], calamus (*Lepironia articulate*), pennywort (*Hydrocotyle umbellate* L.) (Prasad and Freitas, 2003). The roots of Indian mustard are found to be effective in the removal of Cd, Cr, Cu, Ni, Pb and Zn, and sunflower can remove Pb, U, Cs-137 and Sr-90 from hydroponic solutions

Table 2. Overview of some phytoremediation process

Sl. No	Mechanism	Process Goal	Media	Contaminants	Plants	Status of Research
1.	Phytoextraction	Hyper-accumulation, Contaminant extraction and capture	Soil, sediment, sludges	**Inorganics:** Metals: Ag, Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni, Pb, Zn, **Radionuclides:** $^{\infty}$Sr, ^{137}Cs, ^{230}Pb, ^{238,234}U	Indian mustard, pennycress, alyssum, sunflower, hybrid poplars	**Laboratory, pilot and field applications**
2.	Rhizofiltration	Rhizosphere accumulation Contaminant extraction and capture	Groundwater, surface water	**Organics/Inorganics:** Metals, radionuclides	Sunflowers, Indian mustard, water hyacinth	**Laboratory, Pilot scale**
3.	Phytostabilization	Complexation, Contaminant destruction	Soil, sediment, sludges	**Inorganics:** As, Cd, Cr, Cu, Hs, Pb, Zn	Indian mustard, hybrid poplars, grasses	**Field application**
4.	Rhizodegradation	Contaminant destruction	Soil, sediment, sludges,groundwater	Organic compounds (TPH, PAHs, pesticides, chlorinated solvents, PCBs)	Red mulberry, grasses, hybrid poplars, cattail, rice	**Field application**
5.	Phytodegradation	Contaminant destruction	Soil, sediment, sludges,groundwater, surface water	Organic compounds, chlorinated solvents, phenols, herbicides, munitions	Algae, stonewort, hybrid poplar, black willow, bald cypress	**Field demonstration**
6.	Phytovolatilization	Volatilization by leaves, Contaminants extraction from media and release into air	Groundwater, soil, sediment, sludges	**Organics/Inorganics:** Chlorinated solvents, some inorganics (Se, Hg, As)	Poplars, alfalfa, black locust, Indian mustard	**Laboratory and field application**
7.	Hydraulic Control (plume control)	Contaminant degradation or containment	Groundwater, Surface water	Water-soluble organics and Inorganics	Hybrid poplar, cottonwood, willow	**Field demonstration**
8.	Vegetative cover (evapotranspiration cover)	Containment erosion control	Soil, sediment, sludges	Organic and inorganics compounds	Poplars, grasses	**Field application**
9.	Riparian corridors	Containment destruction	Surface water, groundwater	Water-soluble organics and inorganics	Poplars	**Field application**

Source: Kania *et al.* (2002); Ghosh and Singh (2005).

(Zaranyika and Ndapwadza, 1995; Wang *et al.,* 2002; Prasad and Freitas, 2003). The potential of duck weed was investigated by Zayed *et al.*(1998) for the removal of Cd, Cr, Cu, Ni, Pb and Se from nutrient-added solution and the results indicate that duck weed is a good accumulator for Cd, Se and Cu, a moderate accumulator for Cr, but a poor accumulator of Ni and Pb. Dos Santos and Lenzi (2000) tested aquatic macrophyte (*Eiochhornia crassipes*) in the elimination of Pb from industrial effluents in a green house study and found it useful for Pb removal. Water hyacinth possesses a well-developed fibrous root system and large biomass and has been successfully used in wastewater treatment systems to improve water quality by reducing the levels of organic and inorganic nutrients. This plant can also reduce the concentrations of heavy metals in acid mine water while exhibiting few signs of toxicity. Water hyacinth accumulates trace elements such as Ag, Pb, Cd, etc. and is efficient for phytoremediation of wastewater polluted with Cd, Cr, Cu and Se (Zhu *et al.,* 1999). Among the ferns, *Pteris vitta* commonly known as Brake fern has been identified as Arsenic (As) hyperacccumulator for As contaminated soils and waters. It can accumulate up to 7500 mg As/kg on a contaminated site (Ma *et al*., 2001) without showing toxicity symptoms. One fern



Source: Ghosh and Singh (2005)

Figure 2: The Soil, Plant and Energy Recovery System depicting the key components concerned with the mass transfer and dynamics of Phytoextraction

cultivar is available commercially for remediation of Arsenic (As) and has been successfully used in field trials (Salido *et al.,* 2003).

CONCLUSION AND PERSPECTIVE

The contamination of heavy metals to the environment, i.e., soil, water, plant and air is of great concern due to its potential impact on human and animal health. Cheaper and effective technologies are needed to protect the precious natural resources and biological lives. Acute and diffuse contamination of soil and water by heavy metals and metalloids cause wide, environmental and social concern. Among the techniques used to cleanup affected sites, phytoremediation has recently emerged as a new, cost-effective, environment-friendly alternative (Barceló and Poschenrieder, 2003). Substantial efforts have been made in identifying plant species and their mechanisms of uptake and hyper accumulation of heavy metals in the last decade. There are genetic variations among plant species and even among the cultivar of the same species. The mechanisms of metal uptake, accumulation, exclusion, translocation, osmoregulation and copartmentation vary with each plant species and determine its specific role in phytoremediation. In order to develop new crop species/plants having capabilities of metal extraction from the polluted environment, traditional breeding techniques, hybrid generation through protoplast fusions, and production of mutagens through radiation and chemicals are all in progress. With the development of biotechnology, the capabilities of hyper accumulators may be greatly enhanced through specific metal gene identification and its transfer in certain promising species. This can play a significant role in the extraction of heavy metals from the polluted soils. The use of cleaning technologies is site-specific due to spatial and climatic variations and is not economically feasible everywhere. Therefore, cheaper technologies are being sought for practical use. However, much research work is needed in this respect such as metal uptake studies at cellular level including efflux and influx of different metal ions by different cell organelles and membranes. Rhizosphere studies under the control and field conditions are also needed to examine the antagonistic and synergistic effects of different metal ions in soil solution and the polluted waters. In depth soil microbial studies are required to identify the micro-organisms highly associated with metal solubility or precipitations. To date the available methods for the recovery of heavy metals from plant biomass of hyper accumulators are still limited. Traditional disposal approaches such as burning and ashing are not applicable to volatile metals; therefore, investigations are needed to develop new methods for effective recovery of metals from the hyper accumulator plant biomass.

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