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Heavy metal pollution, a global problem and its remediation by chemically enhanced phytoremediation: A Review

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Abstract

Heavy metal contaminated soils are very hard to restore. This type of soil pollution is primarily attributed to anthropogenic activities, including, smelting, mining and various industrial activities. The world's heavily effected areas from heavy metal pollution have been proving as health risks to more than 10 million people in various countries. Linfen in China people faced extreme loads of pollution, In Haina of Dominican Republic, people suffered from a huge amount of lead poisoning due to, in Ranipet a city of India about 3.5 million people are being affected by tannery waste. Bioaccumulation of metal toxins in the food chain poses disastrous effects on human health. Plants accumulate some non essential heavy metals having no contribution in biological functions these heavy metals cause serious risks to plants, animals and human health. In order to remediate this problem in situ and ex situ techniques are being used but in situ methods are more effective than ex situ. Phytoremediation is one of the most successful and environmental friendly in situ method of modern era, coupled with chemical chealtores such as EDTA and Citrci Acid this method is being proved to be more useful and soil friendly.

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Introduction

Soils contaminated with heavy metals are very difficult to restore. Heavy-metal pollution of soil is mainly accredited to human activities, including, smelting, mining and various industrial activities (Wang *et al.*, 2005). With the new era of urbanization and industrialization, soils have become more tainted progressively by heavy metals which cause threats to ecosystems, surface, and ground waters, food safety and human health (Kachenko *et al.*, 2006).

Two of the main sources of heavy metal pollution are geological and anthropogenic activities (Dembitsky, 2003). Anthropogenic sources of heavy metal contamination come from industrial effluents, mining, fuel production, military operations, smelting processes, utilization of agricultural chemicals, brick kilns, small-scale industries and coal combustion (Zhen-Guo *et al.*, 2002). One of the dominant sources taking part in increased budget of soil pollution include municipal waste disposal, this may be roadside dumping or end up in land fills, while sewage consumed for irrigation purposes. These contaminants are although a handy source of nutrients, but are proved to be carcinogens and sources of toxic metals. Other types of pollution come from unsafe or excess application of fungicides, fertilizers and pesticides (Zhen-Guo *et al.*, 2002). Water polluted with sewage and industrial emissions, resulting in contaminated vegetables and soils are some other sources of heavy metal pollution (Bridge, 2004).

An increased accumulation of heavy metals can have lethal effects on soil fertility, ecosystem functions and poses a health risk to human beings and animals (Turan *et al.*, 2007).

A number of biological procedures are being used to treat soil. Phytoremediation is one of the efficient and potential process, which recommends the use of plants to extract, seize and detoxify pollutants (Jing *et al.*, 2007). Phytoremediation encompasses phytoextraction, phytovolatilization, rhizofiltration and phytostabilization (Chaney *et al.*, 1997). Phytoremediation proves to be useful due to low cost, and reliance on solar power to speed up the remediation, preservation natural characteristics of soil (Zhuang *et al.*, 2007). The success of phytoremediation depends upon bioavailability and the capacity of the plant to sequester the metals. Plants with high metal extraction capability frequently are slow growing and grow up in small quantities of biomass on metals polluted soil (Denton, 2007).

The major dilemma hampering plant remediation effectiveness is that some of the metals are static in soils and their accessibility and phytoextraction rate are restricted by solubility and diffusion to the root surface, chemicals were used to overcome this setback (Turan *et al.*, 2007). Numerous studies recognized that chelating agents such as ethylenediamine- tetraacetic acid (EDTA), citric acid (CA) N-(2-hydroxyethyl)- ethylenediaminetriacetic acid (HEDTA) can effectively enhance metal mobility, thereby boosting phytoextraction (Chen *et al.*, 2003).

Ethylene diamine tetraacetic acid (EDTA) is even though a proficient synthetic chelator (Haung *et al.*, 2005) however, its persistence for long time in soil and its slow degradation rate amplify its leaching hazard. On the other hand, LMWOA e.g. citric acid is a better substitute to EDTA for the phytoextraction of heavy metals (Luo *et al.*, 2005) beacuase it is effortlessly biodegradable in the environment.

Heavy Metals Problem Around The Globe

Heavy metals are recognized as toxic pollutants all over the world. The world's most contaminated areas pose health risks to more than 10 million people in various countries, according to research of U.S. environmental action group (ENS, 2006). According to this research, Linfen is a city of China faced extreme loads of pollution; Haina in Dominican Republic, is a place of automobile battery recycling industries previously where people suffer from a huge amount of lead poisoning; in Ranipet a city of India about 3.5 million people are being effected by tannery waste, Mailuu-Suu, Kyrgyzstan, is severely polluted by radioactive uranium wastes form mines; the Russian people of Rudnaya, Dalnegorsk and Pristan, suffer lead contamination from local lead mining, unsafe transportation of lead and from an old lead smelter; and in Zambia, lead and cadmium mining causes a widespread contamination (ENS, 2006). Mining activities threaten health through water by the techniques of extraction; pollution of local water bodies and having detrimental effects on our environment e.g. erosion of beach from sand mining or by biodiversity loss or reduction in population of fishes which are long-term effects of mining (WHO, 2008). Mining activities in coastal areas release toxic substances into our environment and lead to a number of harmful effects on living organisms via food chain (Dembitsky, 2003).Cadmium, lead, copper, nickel, zinc and chromium are regarded as vital environmental pollutants, specifically in areas of extreme anthropogenic activities (United States Environmental Protection Agency, 1997). Bioaccumulation of heavy metals in the food chain can have catastrophic effects on human health. Ingestion of food and water are general route of exposure to heavy metals in human (Pickering and Owen, 1997)

Toxic Effects of Heavy Metals

Plants are capable of accumulating "essential" metals (Ca, Co, K, Mo, Na, Mg, Mn, Ni, Se, Cu, Fe, V and Zn) form soil. Plants require different amounts of these for their growth and development. This capability of plants also permits accumulation of other "non-essential" metals (Al, Cd, Cr, As, Hg, Pt, Sb, Te, Pb, Pd, Tl, Au and U) which do not have any contribution in biological function (Djingova and Kuleff, 2000). Moreover, break down of metals is impossible and when levels inside cells of plant rise above threshold levels, the consequence may be direct toxicity to plant by destroying cell structure and hindering the function of many cytoplasmic enzymes (Assche and Clijsters, 1990). Moreover, indirect toxic effects may be evident by substitution of nutrients at cation exchange spots in plants (Taiz and Zeiger, 2002). It was suggested by Baker (1981), that some plants were able to tolerate presence of high levels of metals in their surrounding by three ways:

1. Exclusion, in which there is a restriction of metal transport and metal concentrations are constant and maintained in shoot area over various soil levels

2. Inclusion, whereby concentrations of metal in shoots reveal those in the soil solution and having a linear relationship.

3. Bioaccumulation, accumulation of metals in the roots and upperparts of plants at both low and high soil levels (Figure 1).

Increased heavy metal levels in the soil can cause elevated crop uptake and it can pose stress on plant growth (Schmidt 2003). At higher quantities, they inhibit growth, obstruct metabolic processes and sometimes plant death may occur (Schaller and Diez, 1991). High levels of metals in human nutrition can prove to be toxic and result in acute and chronic disorders (Schmidt, 2003). Zn is one of the essential trace elements for both higher plants and animals. A huge number of enzymes require zinc (Mengel and Kirkby, 1982) and take a vital part DNA transcription. Leaf chlorosis is caused by Zn toxicity (Cobbett and Goldsbrough, 2002).

Cu is an essential trace metal for plants, but can cause toxicity at higher levels. Copper (Cu) plays important role in a number of physiological functions in plants including, respiration, photosynthesis, nitrogen, carbohydrate distribution, seed production, cell wall metabolism, and also in disease resistance (Kabata-Pendias and Pendias, 2001). Cadmium is not a micronutrient for metabolic processes of plant and can cause toxicity in plants and rapid death (Kuzovkina *et al.*, 2004). It can interfere enzyme activities, reduce microorganism's DNA-mediated transformation, inhibit symbiosis between plants, and microorganisms, enhance plant predisposition to fungal attack (Kabata-Pendias and Pendias, 2001). Pb is one of the toxic heavy metals even in trace levels for microorganisms and nonessential element for metabolic processes. Pb proved to be toxic for plants causing necrosis, chlorosis, inhibited growth of root/shoot, and reduced biomass production on *Helianthus annuus*, and *Vetiveria zizanioides* (Boonyapookana *et al.*, 2005).

Treatment methods

Ex-situ method

It requires removal of contaminated soil for treatment on or of site, and returning the treated soil to the resorted site. For the remediation of polluted soils, conventional methods of ex-situ are applied that depend on excavation, detoxification and devastation of pollutant chemically or physically, which will lead contaminant to become stable, solid, immobile and demolish (Gosh and Singh, 2005).

Table 1. Types of Phytoremediation.

No.	Process	Mechanism	Contaminant
1.	Rhizofiltration	Rhizosphere accumulation	Organics/Inorganics
2.	Phytostabilisation	Complexation	Inorganics
3.	Phytoextraction	Hyper-accumulation	Inorganics
4.	Phytovolatilization	Volatilisation by leaves	Organics/Inorganics
5.	Phytotransformation	Degradation in plant	Organics

In-situ method

Remediation of contaminated site without excavation is in situ. It has been defined as devastation or alteration of the pollutant, immobilization to decrease availability to living organisms and partition of the toxin from the huge mass of soil (Reed *et al.*, 1992). In-situ processes have edge on ex-situ processes because they have low cost and have less effect on our ecosystem. On the other hand, the ex-situ process which involves excavation of soil effected with heavy metal pollutants and burial of contaminants in landfill, but the landfil is not an ideal option because it only transfers the pollutants problem to some other areas. It also poses risk to other areas by the transport of polluted soil (Williams, 1988). Reducing the concentration of heavy metal contaminants to safe level by bringing in the healthy soil and blending with the polluted soil can be a substitute to on-site method (Musgrove, 1991). On-site technique of remediation provide a substitute, it includes the cover of inert material on soil (Body *et al.*, 1988). Heavy metal polluted soils can be remediated by making inorganic contaminant immobile.This can be done by making complexes of the contaminants, or by liming for enhancing the pH of soil (Alloway, 1991). Higher pH of soil reduces the solubility of metal elements like Ni, Cu, Cd, and Zn. Many of conventional methods of remediation are costly to execute and form the basis for further interference to previously effected environment (Mench, 1994; Alloway, 1991). Bioremediation technologies based on plants have been jointly called as phytoremediation, this involves the utilization of green plants and micro biota associated with them for the in-situ remediation of polluted soil and water (Sadowsky, 1999). The concept of using hyper accumulator plants to get rid of heavy metals contaminants and other toxins was first initiated in 1983, but in fact the idea has been applied for past three centuries (Henry, 2003). The common phrase 'Phytoremediation' comprises of the prefix phyto (plant) of Greek origin, adjacent to the Latin basis remedium (to remove or correct an evil) (Cunningham *et al.*, 1996). This method can be implemented to both inorganic and organic contaminants in soil, water and air (Salt, 1998). The physico-chemical processes for soil treatment make the land worthless for growth of plant as they inhibit all biological functions, including activities of functional microorganisms such as mycorrhiza, fungi, nitrogen fixing bacteria and soil fauna in the course of remediation (Burns, 1996). Phytoremediation consists of five main processes (Figure 2) (Gosh and Singh, 2005).

Types of Phytoremediation

Phytoremediation comprises of variouse types (Trapp and Karlson, 2001) that are given below

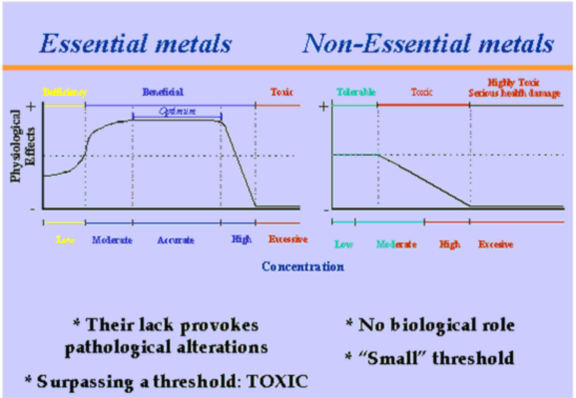

Fig. 1. Conceptual response strategies of metal concentrations in plant tops in relation to increasing total metal concentrations in the soil.

Phytoextraction

Phytoextraction is a process of uptake, translocation, and concentration of organic and inorganic pollutants in plants. It builds up products, which accumulates the pollutants, may be consumed or treated further. The method is commonly applied for metals contaminants.

Rhizofiltration

It is the sorption of toxins to the roots or some other parts of plants, or the precipitation of contaminants in root zone. E.g. This process is handy in the extraction of heavy metals or lipophilic complexes from water.

Phytostabilization

Phytostabilization is firstly immobilization and then stabilizing the compounds in soil itself in order to put off erosion. First case is done by transfer of compounds into non-soluble fractions through the process of redox milieu in rhizosphere.

Rhizo and phytodegradation

Phytodegradation is the breakdown of toxic compounds by plants. The degradation of pollutants in the rhyzosphere or root zoon is called rhyzodegradation, this may be done either by activities of microbes or by roots, or by both. In rhyzosphere, various processes speed up breakdown of some contaminants. These both methods are often implemented for breakdown of organic pollutants e.g. BTEX, PAH, chlorinated solvents, TNT and pesticides (EPA, 2000).

Phytoremediation enhanced by chemical chelaters

In consideration of improving the accessibility of contaminants in soil and increasing transportation from rhyzosphere to shoots, the use of chemical chelators have been suggested, these include ethylenediaminetetraacetic acid (EDTA), nitrilotriacetic acid (NTA), diethylenetrinitrilopentaacetic acid (DTPA), pyridine-2,6-dicarboxylic acid, ethylenediamine disuccinate (EDDS) (Kayser *et al.*, 2000; Puschenreiter *et al.*, 2001; Grcˇman *et al.*, 2003; Meers *et al.*, 2005; Saifullah *et al.*, 2009). Allocation of metals is influenced by these agents in soils because they make them soluble from insoluble form (Liu *et al.*, 2006). EDTA is capable of releasing metals from insoluble solid fractions by making dissolved compounds when it is applied in greater concentrations; this is due to its high binding affinity with heavy metals (Nowack, 2002). In the same way insoluble metals can become soluble by treating with elemental sulfur, thus enhancing the soil solution levels, by reducing pH of soil followed by formation of sulfate through microbial oxidation of sulfur into sulfate (Kayser *et al.*, 2000). As a result, toxic metals could be up taken by roots of plants in the soil solution subsequently transported to the shoots.

Studies conducted by Satroutdinov *et al.*, (2000) not only proved the presence of EDTA towards degradation by living organisms but also elaborated that stable compounds of EDTA and metals must detach before consumed by bacteria. Consequently, metal-EDTA compounds that may be located in pores of soils leached out even after five months of EDTA application (Lombi *et al.*, 2001). This reduced decomposition rate and increased persistence enhances the risk of leaching that is linked with application of EDTA soil conditions. However Synthetic chemical chelators like methylglycinediacetate (MGDA), and ethylenediaminedissuccinate (EDDS) are considered as substitute for EDTA (Groman *et al.*, 2003; Tamura *et al.*, 2005). Even though to the best knowledge, these chelating agents have not been evaluated comprehensively, they demonstrate promise to phytoextraction that is environmental friendly, specifically for lead (Pb) polluted soils.

Conclusion

The pleasures of industrialization and urbanization have also brought new types of problems for our environment. These demerits include deterioration of our soil, water and air quality as a result plants, animals and even human are bearing the impacts of these advancements. Heavy metal pollution is one of the problems that are rendering our environment enormously. There is a need for new methods for the remediation of polluted sites and phytoremediation enhanced by organic and inorganic chemicals is proved to be a better option for this purpose. This technique should be implemented all over the world in order to restore the quality of soil, water and air.

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