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Review

Phytoremediation: Curing soil problems with crops

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Among the different contaminants in the environment, heavy metals (HMs) are unique due to the fact that they cannot be broken down to non-toxic forms. According to the reports published worldwide, these metals are released into the environment by both natural and anthropogenic sources, especially, mining and industrial activities, and automobile exhausts (for lead). They leach into underground waters, moving along water pathways and eventually depositing in the aquifer, or are washed away by run-off into surface waters thereby, resulting in water and subsequently soil pollution. The HM contamination is increasing day by day because of increase in population, industrialization and urbanization. Therefore, posing a serious threat to health and environment. Researchers worldwide have used different methods for removing these hazardous elements. Although, these methods for cleaning up of contaminated environment including soil and water are usually expensive and do not give optimum results. Currently, phytoremediation is an effective and affordable technology used to remove inactive metals and metal pollutants from contaminated soil and water. It includes phytoextraction, rhizofiltration, phytostabilization, phytovolatization, and phytodegradation/ phytotransformation. This technology is ecofriendly and exploits the ability of plants to remediate pollutants from contaminated sites. More than 400 plant species have been identified to have potential for soil and water remediation. Among them, *Thlaspi*, *Brassica*, *Sedum alfredii* H., and *Arabidopsis* species have been mostly studied. Our paper aims to cover the causes of HM pollution and phytoremediation technology, including HM uptake mechanism and several reports describing its application at field level.

Key words: Phytoremediation, heavy metals, phytostabilisation, rhizofiltration, phytoextraction.

INTRODUCTION

Heavy metals (HM) are a unique class of toxicants since they cannot be broken down to non-toxic forms (Jabeen et al., 2009). Concentration of these toxic metals has accelerated dramatically since the beginning of the industrial revolution (Ana et al., 2009) thus, posing problems to health and environment (Nriagu, 1979). Once the heavy metals contaminate the ecosystem, they remain a potential threat for many years. HM contaminants causing ecological problems are of global concern. HM refers to metals and metalloids having densities greater than 5 g cm^{-3} and is usually associated with pollution and toxicity although, some of these elements (essential metals) are required by organisms at low concentrations (Adriano, 2001). The most common HM contaminants are: cadmium (Cd), chromium (Cr), copper (Cu), mercury (Hg), lead (Pb), nickel (Ni) and zinc (Zn) (USEPA, 1997; Lasat, 2002). Due to the awareness of the negative effects of environmental pollution, everyone is becoming aware about finding innovative methods for preventing pollution of the environment including soil (Gruca-Królikowska and Wacławek, 2006).

There are various factors leading towards environmental degradation and soil pollution in particular. The main factors contributing to soil pollution are the

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increased growth of industry; nearly 1000 new chemicals are being synthesized every year (Shukla et al., 2010). Almost 60,000 to 95,000 chemicals are in commercial use. According to Third World Network reports, more than one billion pounds (450 million kilograms) of toxins are released globally in air and water. Similarly, the excessive uses of pesticides in agriculture, wastes from de-acidifying soils are other factors leading to soil pollution (Szczygłowska et al., 2011). Among environmental pollutants, HMs play a major role in causing hazard to human and animal health due to their prolong existence in the soil (Gisbert et al., 2003; Halim et al., 2003). For instance, a very typical example of lead (Pb) pollution has been reported by plentiful researchers (Nandkumar et al., 1995; Yang et al., 2005). Due to the long term persistence nature of lead, it can persist up to 150 to 5000 years and was reported to a high concentration for as long as 150 years after application of sludge to the soil. Similarly, the biological half life of cadmium (Cd) has been reported to be about eighteen years in human body (Fostner, 1995; Yang et al., 2005).

Remediation of polluted soils has been a matter of concern and for its remediation, many technologies like pneumatic fracturing, soil flushing, solidification, vitrification, electrophoresis, chemical reduction, soil washing and excavation have been tried. But these traditionally used methods are limited in their application to selected areas because of some limitations. Currently, conventional remediation methods of HM contaminated soils are expensive and environmentally destructive (Bio-Wise, 2003; Aboulroos et al., 2006). Since then, scientists all over have been in search of some innovative, eco-friendly and low cost alternative technologies. One of them is the phytoremediation, which includes the use of plants to clean and cure the environment; and plants have been known for their property to absorb, accumulate and detoxify the impurities present in the soil, water and air through various physical, chemical and biological processes (Hooda, 2007). Phytoremediation, a fast-emerging new technology for removal of toxic HMs, is cost-effective, non-intrusive and aesthetically pleasing. It exploits the ability of selected plants to remediate pollutants from contaminated sites. Plants have inter-linked physiological and molecular mechanisms of tolerance to HMs. High tolerance to HM toxicity is based on a reduced metal uptake or increased internal sequestration, which is manifested by interaction between a genotype and its environment. The growing interest in molecular genetics has increased our understanding of mechanisms of HM tolerance in plants and many transgenic plants have displayed increased HM tolerance. Improvement of plants by genetic engineering, that is, by modifying characteristics like metal uptake, transport and accumulation and plant's tolerance to metals, opens up new possibilities of phytoremediation. Either naturally occurring or genetically engineered plants are used for cleaning contaminated environments. Phytoremediation can be used to remove not only metals (for example, Ag, Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni, Pb, Zn) but also radionuclides (for example, ^{90}Sr, ^{137}Cs, ^{239}Pu, ^{234}U, ^{238}U) and certain organic compounds (Andrade and Mahler, 2002). The phytoremediation efficiency of plants depends upon various physical and chemical properties of soil, plant, bioavailability of metals and capacity of plants to uptake, accumulate and detoxify metals. For selections of plants which are suitable for phytoremediation of polluted soils, one has to understand the mechanism underlying plant tolerance towards a particular metal. The HM pollution is a very vast subject, but in this review, we will try to focus on the sources of soil pollution, mechanism of metal uptake by the plants and the different types of phytoremediation and their practical application in soil remediation.

Where does the soil metal pollution come from?

HM contamination is a result of various geological and anthropogenic activities (Dembitsky, 2003). Some natural processes like volcanic eruptions and weathering of rocks may be the cause of metal contamination in the environment; but, human intervention is also a reason (Marchiol et al., 2004). Contaminants can spread in the environment through air, as dust and gases, and can also spread into the soil and water from the air through surface run-off. Anthropogenic metal contamination is broadly due to fuel production, industrial wastes, defense activities, coal mining, smelting, brick kilns, coal combustion, melting of metallic ferrous ores, municipal wastes, fertilizers, pesticides, sewage sludge and many small scale industries which release enormous effluents, causing HM contamination in the environment (Zhen-Guo et al., 2002; Peng et al., 2006). The main threats to human health from heavy metals are associated with exposure to lead, cadmium, mercury and arsenic (Jarup, 2003). Cigarette smoking is a major source of Cd exposure. Biological monitoring of Cd in the general population has shown that cigarette smoking may cause significant increases in blood Cd (B to Cd) levels, the concentrations in smokers being on average 4 to 5 times higher than those in non-smokers (Jarup et al., 1998). Food is the most important source of cadmium exposure in the general non-smoking population in most countries (WHO, 1992). Cadmium is present in most foodstuffs, but concentrations vary greatly, and individual intake also varies considerably due to differences in dietary habits (Jarup et al., 1998). Cd is released as a by-product of Zn (and occasionally Pb) refining; Pb is emitted during its mining and smelting activities from automobile exhausts (by combustion of petroleum fuels treated with tetraethyl Pb anti-knock) and from old lead paints; Hg is emitted by the degassing of the earth's crust. Generally, metals are emitted during their mining and processing activities (Lenntech, 2004). People are basically exposed to mercury through food; fish, being a major source of methyl mercury exposure (Sallsten et al., 1996) and dental amalgam. Many reports have revealed that mercury vapour is released from amalgam fillings, and that the release rate may increase by chewing (WHO, 1990). Energy production from fossil fuel and smelting of non-ferrous metals are the two major industrial processes that leads to arsenic contamination of air, water and soil; smelting activities being the largest single anthropogenic source of atmospheric pollution (Chilvers et al., 1987). The amount of arsenic contamination in air in rural areas ranges from <1 to 4 ng/m^3, whereas concentrations in cities may be as high as 200 ng/m^3. Much higher concentrations (>1000 ng/m^3) have been measured near industrial sources. Water concentrations are usually <10 µg/l, although, higher concentrations may occur near anthropogenic sources. Levels in soils usually range from 1 to 40 mg/kg, but pesticide application and waste disposal can result in much higher concentrations (WHO, 2001). One of the vital factors leading to soil pollution is the disposal of municipal wastage. Usually the municipal wastages are used for land filling or they are often dumped on road sides. The sewage coming out of municipal wastes is also used for irrigation. Harmful and toxic metals are a result of these wastes, hence, contaminating the soil. In addition, use of non-recommended pesticides, herbicides, fungicides and fertilizers are a major cause of soil contamination.

How do plants uptake metals?

Bioavailability of metals is the primary factor responsible for the uptake of metals. In soils, metals exist as a variety of chemical forms in a dynamic equilibrium governed by the physical, chemical and biological processes of the soil. Bioavailability of soil pollutants, a primary basis of remediation efficacy, refers to a fraction of the total pollutant mass in the soil and sediment available to plants. Uptake of metals by plants involves root interception of metal ions, entry of metal ions into roots and their translocation to the shoot through mass flow and diffusion.

Plants have evolved highly specific mechanisms to take up, translocate, and store these nutrients. For example, metal movement across biological membranes is mediated by proteins with transport functions. In addition, sensitive mechanisms maintain intracellular concentration of metal ions within the physiological range. In general, the uptake mechanism is selective and plants preferentially acquired some ions over others. Ion uptake selectivity depends upon the structure and properties of membrane transporters. These characteristics allow transporters to recognize, bind and mediate the trans-membrane transport of specific ions. For example, some transporters mediate the transport of divalent cations, but do not recognize mono- or trivalent ions. Hyperaccumulator plants do not only accumulate high levels of essential micronutrients, but can also absorb significant amounts of non-essential metals such as Cd. The mechanism of Cd accumulation has not been elucidated. It is possible that the uptake of this metal in roots is through a system involved in the transport of another essential divalent micronutrient, possibly Zn^{2+}. Cd is a chemical analogue of the latter, and plants may not be able to differentiate between the two ions (Chaney et al., 1994).

Plants possess several classes of metal transporters such as HM (or CPX-type) ATPases that are involved in the overall metal-ion homeostasis and tolerance in plants, natural resistance-associated macrophage-protein (Nramp) family, cation-diffusion facilitator (CDF) proteins family and the Zn-Fe permease (ZIP) family (Guerinot, 2000). Yang et al. (2005) found a correlation between uptake capacity and hyper-accumulation of ZIP family members in the plant, for example, *Thlaspi caerulescens*. Under Zn-replete conditions, two ZIP cDNA (ZNT1 and ZNT2) are expressed at significantly higher levels in the roots of different *T. caerulescens* accessions than those of the non-hyper-accumulating, *T. arvense*. Thus, over-expression of the uptake systems may result in enhanced accumulation of the metals. In *Escherichia coli*, the uptake of Zn is mediated by two major types of transporters; *ZnuACB*, which belongs to the cluster C9 family of (TroA-like) ATP-binding cassette (ABC) transporters, 107 and ZupT, which is a member of the ZRT/IRT-related proteins (*ZIP*) family of transporters. *ZIPs* are expressed amongst different organisms in order to maintain their metal homeostasis and thus, contribute greatly to their growth and development. *ZIPs* have also been found to play key roles in bacterial infections, as well as, the onset and progression of chronic diseases in humans (Iryna, 2011). Once the metal is bioavailable to the plant, the entry of metal ions inside the plant, either through symplast (intercellular) or apoplast (extracellular), depends on the type of metal and the plant species. The apoplast continuum of root epidermis and cortex is readily permeable for solutes. Apoplastic pathway is relatively unregulated, because water and dissolved substance can flow and diffuse without crossing the membrane. The cell walls of the endodermal layer act as a barrier for apoplastic diffusion into the vascular system. Apoplastic transport is limited by high cation exchange capacity (CEC) of the cell wall. In the symplastic transport, metal ions move across the plasma membrane, which usually has a large negative resting potential of approximately 170 mV (negative inside the membrane). This membrane potential provides a strong electrochemical gradient for the inward movement of the metal ions. Most metal ions enter plant cells by an energy-dependent process through specific or generic metal-ion carriers or channels. On entry into the roots, metal ions can either be stored in the root or forwarded to the shoot, primarily, through the xylem. The rate of metal translocation to the shoot may depend on metal concentration in the root. A phytochelatin (PC)-mediated metal binding in the xylem sap as a possible mechanism for metal translocation has been proposed. Nutrients destined for the developing cereal grain encounter several restricting barriers on their path towards their final storage sites in the grain. In order to identify transporters and chelating agents that may be involved in transport and deposition of Zn in the barley grain, expression profiles have been generated of four different tissue types; the transfer cells, the aleurone layer, the endosperm, and the embryo (Tauris et al ., 2009). Low molecular weight chelators such as citrate and free histidine as in *Alyssum lesbiacum* were associated with this process. Other chelating compounds like malate, citrate, and histidine may also have a role in the metal-ion-mobility in plants. Membrane transport systems are likely to play a central role in the translocation process. For cleaning and curing of the polluted sites, plants utilize several methods.

Phytoremediation technology can be subdivided, on the basis of the underlying process and applicability, (Figure 1):

1. Phytoextraction
2. Rhizofiltration
3. Phytostabilization
4. Phytovolatization
5. Phytodegradation/phytotransformation

Phytoextraction

Phytoextraction, or phytomining, is the process of planting a crop of a species that is known to accumulate contaminants in the shoots and leaves of the plants, and then harvesting the crop and removing the contaminant from the site. Unlike the destructive degradation mechanisms, this technique yields a mass of plant and contaminant (typically metals) that must be transported for disposal or recycling. This is a concentration technology that leaves a much smaller mass to be disposed of when compared to excavation and landfilling. This technology is being evaluated in a Superfund Innovative Technology Evaluation (SITE) demonstration, and may also be a technology amenable to contaminant recovery and recycling. Phytoextraction is the name given to the process where plant roots absorb metal contaminants from the soil and translocate them to their above soil tissues. Phytoextraction, also called phytoaccumulation, refers to the uptake of metals from soil by plant roots into above-ground portions of plants (Figure 2).

The concept of using plants to clean up contaminated environments is very old and cannot be traced to any particular source (Blaylock and Huang, 2000). Chaney (1983) was the first to reintroduce it as a remediation technique on metal-contaminated soils. Initially, the concept was based on metal hyper-accumulating plants, which are able to uptake and tolerate extremely high levels of metals. In the past, extensive research has been conducted in the field of phytoextraction: searching for new phytoextractors (Baker and Brooks, 1989); providing more fundamental knowledge about metal uptake, translocation, and tolerance by plants (Rauser, 1995; Kramer et al., 1996; Lasat et al., 1998; Salt et al., 1999) as well as, improving plant metal accumulation and tolerance by genetic transformations (Karenlampi et al., 2000; Clemens et al., 2002; Kramer, 2005). Another approach in the concept's development was based on high biomass-producing plants used together with chemical agents to enhance metal solubility and uptake by plants (Blaylock et al., 1997; Huang et al., 1997).

Certain plants, called hyper-accumulators, absorb unusually large amounts of metals in comparison to other plants. More than 400 plant species have been identified to have potential for soil and water remediation (Lone et al., 2008). As different plants have different abilities to uptake and withstand high levels of pollutants, many different plants may be used for phytoremediation. The strategies used in developing a phytoremediation plant are (a) screening of hyperaccumulator candidate plants, (b) plant breeding, and (c) development of improved hyperaccumulators using genetic tools. The hyperaccumulators that have been most extensively studied by scientific community include *Thlaspi* sp., *Arabidopsis* sp., *Sedum alfredii* sp. (both genera belong to the family of Brassicaceae and Alyssum). *Thlaspi* sp. are known to hyperaccumulate more than one metal, that is, *T*. *caerulescens* for Cd, Ni, Pb and Zn, *T*. *goesingense* for Ni and Zn, *T*. *ochroleucum* for Ni and Zn, and *T*. *rotundifolium* for Ni, Pb and Zn (Prasad and Freitas, 2003).

Metal phytoextraction involves: 1) cultivation of the appropriate plant/crop species on the contaminated site; 2) removal of harvestable metal-enriched biomass from the site; and 3) post-harvest treatments (that is, composting, compacting, thermal treatments) to reduce the volume and/or weight of biomass for disposal as a hazardous waste or for its recycling to reclaim valuable metals. Two basic strategies of metal phytoextraction have been suggested, continuous or natural phytoextraction and induced, enhanced, or chemically assisted phytoextraction (Salt et al., 1998). After the plants have been allowed to grow for some time, they were harvested and either incinerated or composted to recycle the metals. This procedure may be repeated as necessary to bring soil contaminant levels down to allowable limits. If plants are incinerated, the ash must be disposed of in a hazardous waste landfill, but the volume of ash will be less than 10% of the volume that would be created if the contaminated soil itself were dug up for treatment. In some cases, it is possible to recycle the metals through a process known as phytomining, though;

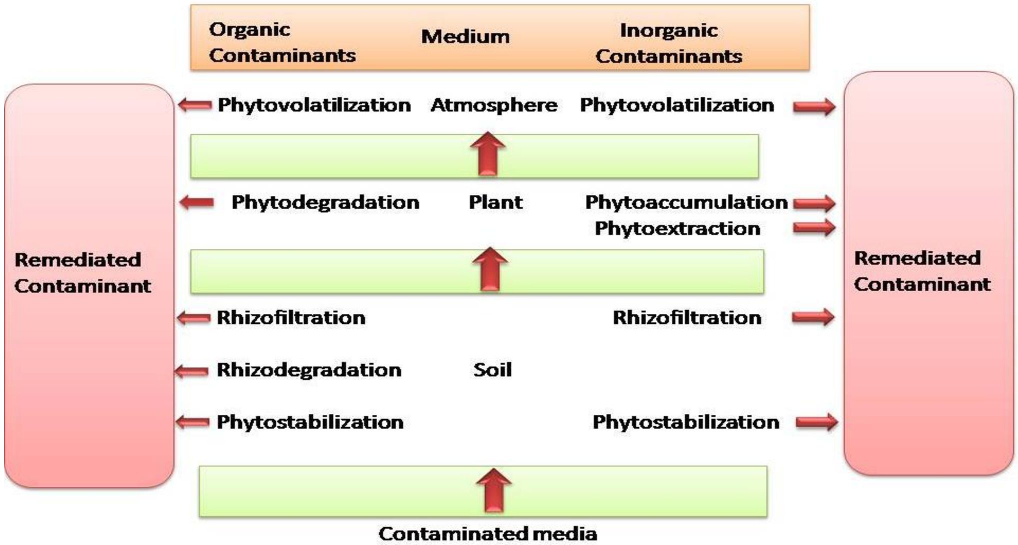

Figure 1. Phytoremediation Technology (ITRC, 2009).

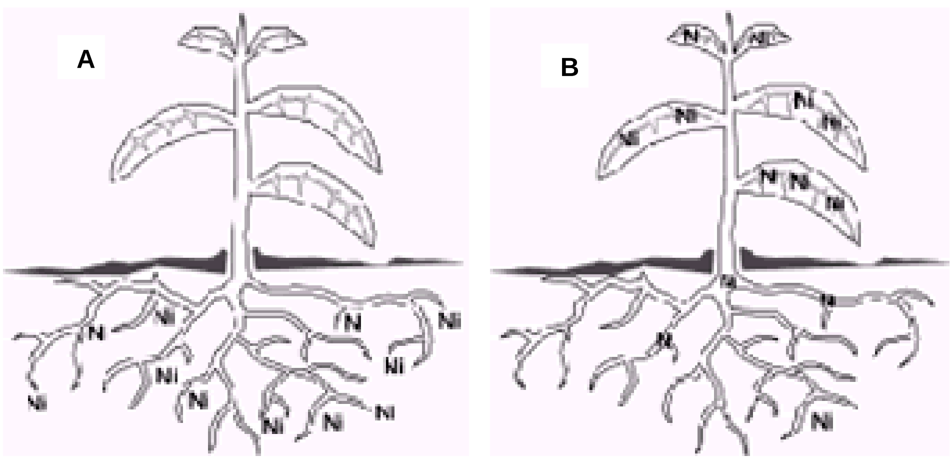

Figure 2. Uptake of metals Ni by phytoextraction. Nickel is removed from soil by moving up into plant roots, stems, and leaves. The plant is then harvested and disposed of and the site replanted until the Ni in the soil is lowered to acceptable levels.

this is usually reserved for use with precious metals.

Metals such as Ni, Zn, and Cu are the best candidates for removal by phytoextraction because the majority of the approximately 400 known plants that absorb unusually large amounts of metals have a high affinity for accumulating these metals. Plants that absorb Pb and Cr are currently being studied and tested. According to report, in the presence of vegetation, the exchangeable form of Cd was partly removed by plant uptake that accompanied with the intake of nutrition (Zhang et al., 2009). Cd-hyperaccumulating plant species are almost the only ones that can grow in soil solutions containing Cd concentrations as high as 35 µmol/L (3.9 mg/L) (Brown et al., 1994; Xiao et al., 2008). Zhang et al. (2009) expressed that as Cd phytoextraction is observed by maize, the percentage of exchangeable form of Cd decreased in the planted soil. Besides, plant root exudates and rhizosphere micro-organisms accelerated the stability process of added Cd in soils, which might make the exchangeable form transform to other relatively stable forms such as organic form and residual form and might help reduce the harm of Cd to soil and water environment. Similar finding of decrease in Cd level in soil planted with maize have also been reported by Mojiri (2011). Water soluble and exchangeable Pb are the only fractions readily available for uptake by plants. Oxyhydroxides, organic, carbonate, and precipitated forms of Pb are the most strongly bound to the soil. The capacity of the soil to adsorb Pb increases with increasing pH, CEC, organic carbon content, soil/water

Eh (redox potential) and phosphate levels. In the natural setting, Pb hyper-accumulation has not been documented. However, certain plants have been identified which have the potential for Pb uptake (Henry, 2000). From the results of experiment conducted by Mojiri (2011), it was observed that the concentration of extractable Pb significantly decreased in the planted soil after 60 days of culture. It was clear that the concentration of extractable Pb in soil under all treatments decreased between 39.2 to 40.9%. Accumulation of Pb in root is higher than that in shoot; this showed that the root of corn is more active than shoot to phytoremediation of Pb. Therefore, crop plants like maize play a vital role as accumulator plants for metal polluted soils.

The main bottlenecks limiting phytoextraction efficiency are 1) metal phytoavailability in the soil and 2) translocation of metals to the aboveground plant parts. To increase the "phytoavailability" and/or translocation of HMs, the use of soil amendments has been suggested and tested by several authors (Huang et al., 1997; Cooper et al., 1999; Kulli et al., 1999; Blaylock and Huang, 2000). Ethylenediaminetetraacetic acid (EDTA), in particular, has received much attention. It is a complexing agent that has been used in agriculture since the 1950s as an additive in micronutrient fertilizers (Wallace et al*.,* 1992; Bucheli-Witschel and Egli, 2001). Recently, an experiment was conducted on the effect of EDTA on the phytoextraction ability of *Eleusine indica* (grass). Results revealed that the grass showed relatively good response to EDTA application and the higher levels of Cu and Cr concentration in the root suggested that the grass may be a good metal excluder with the possibility of extracting Pb from contaminated soils (Garba et al., 2012). Other substances that have been reported in literature include different synthetic aminopolycarboxylic acids diethylene triamine pentaacetic acid, nitriloacetate, organic acids, chlorides, ammonium isothiocyanate, sodium cyanide, elemental sulfur, fluoride solutions, hydrogen peroxide, ammonium fertilizers, and many others. Some of these compounds show great potential to substitute or complement mobilization by EDTA.

Rhizofiltration

Rhizofiltration ('rhizo' means 'root') is the adsorption or precipitation onto plant roots (or absorption into the roots) of contaminants that are in solution surrounding the root zone. It is defined as the use of plants, both terrestrial and aquatic, to absorb, concentrate, and precipitate contaminants from polluted aqueous sources with low contaminant concentration in their roots. Rhizofiltration is similar 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. The plants to be used for clean-up are raised in greenhouses with their roots in water. Contaminated water is both collected from a waste site and brought to the plants, or the plants are planted in the contaminated area, where the roots then take up the water and the contaminants dissolved in it. As the roots become saturated with contaminants, they are harvested and disposed of safely. Rhizofiltration remediates metals like As, Pb, Cd, Ni, Cu, Cr, V and radionucliides (U, Cs and St). The ideal plants should produce significant amounts of root biomass or root surface area, be able to accumulate and tolerate significant amounts of target metals, involve easy handling and a low maintenance cost, and has a minimum of secondary waste that requires disposal. Terrestrial plants are more suitable for rhizofiltration because they produce longer, more substantial and often fibrous root systems with large surface areas or metal adsorption. *Pteris vittata*, commonly known as Chinese brake fern, is the first known As-hyper accumulator (Ma et al., 2001). Several aquatic species have the ability to remove HMs from water, including Water Pennywort (*Hydrocotyle umbellate* L.) (Dierberg et al., 1987), Duckweed (*Lemna minor* L.) (Mo et al., 1989) and Water Hyacinth (*Eichhornia crassipes* (Mart.) Solms) (Zhu et al., 1999). Indian mustard (*Brassica juncea*) and sunflower (*Helianthus annuus*) are most promising for metal removal from water. Indian mustard effectively removes Cd, Cr, Cu, Ni, Pb, and Zn (Dushenkov et al., 1995) whereas sunflower absorbs Pb (Dushenkov et al., 1995) and U (Dushenkov et al., 1997) from hydroponic solutions. Indian mustard could effectively remove a wide range (4 to 500 mg/L) of Pb concentration (Raskin and Ensley, 2000). Karkhanis et al. (2005) reported the result of their experiment conducted on rhizofiltration under greenhouse condition using pistia, duckweed and water hyacinth (*E. crassipes*) to remediate aquatic environment contaminated by coal ash containing HMs. The results showed that pistia has high potential capacity of uptake of the HMs (Zn, Cr, and Cu) and duckweed also showed good potential for uptake of these metals next to pistia. Rhizofiltration of Zn and Cu in case of water hyacinth was lower as compared to pistia and duckweed. In a recent study, the potential of water hyacinth (*E. crassipes*) weeds for phytoremediation of metal polluted soils by rhizofiltration method was reported by Mohanty and Patra (2011). The mine waste water at South Kaliapani chromite mining area of Orissa (India) showed high levels of toxic hexavalent (Cr^{+6}). Cr^{+6} contaminated mine waste water poses potential threats for biotic community in the vicinity. The weeds significantly reduced (up to 54%) toxic concentrations of Cr^{+6} from contaminated mine waste water when passed through succeeding water hyacinth ponds. The reduction of toxic Cr level varied with the plant age and passage distance of waste water. Cr phytoaccumulation and Bio-Concentration Factor (BCF) was maximum at growing stage of plant that is, 75 days old plant. High BCF

(10,924) and Transportation Index (32.09) for water hyacinth indicated that the weeds can be used as a tool of phytoremediation to combat the problem of *in situ* Cr contamination in mining areas (Mohanty and Patra, 2011). Therefore, plants like pistia/duckweed/water hyacinth can be effectively used for phytoremediation of HM polluted problem soils.

Phytostabilization

Phytostabilization, also referred to as in-place inactivation, is primarily used for the remediation of soil, sediment, and sludges (United States Protection Agency, 2000). It is the use of plant roots to limit contaminant mobility and bioavailability in the soil and water. Contaminants 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. The plants primary purposes are to (1) decrease the amount of water percolating through the soil matrix, which may result in the formation of a hazardous leachate, (2) act as a barrier to prevent direct contact with the contaminated soil and (3) prevent soil erosion and the distribution of the toxic metal to other areas (Raskin and Ensley, 2000). Phytostabilization can occur through the sorption, precipitation, complexation, or metal valence reduction. It is useful for the treatment of Pb as well as As, Cd, Cr, Cu and Zn. Some of the advantages associated with this technology are that the disposal of hazardous material/ biomass is not required (United States Protection Agency, 2000) and it is very effective when rapid immobilization is needed to preserve ground and surface waters. The presence of plants also reduces soil erosion and decreases the amount of water available in the system (United States Protection Agency, 2000). Phytostabilization has been used to treat contaminated land areas affected by mining activities and Superfund sites.

Smith and Bradshaw (1992) developed two cultivars of *Agrostis tenius* and one of *Festuca rubra,* which are used for phytoremediation of the Pb, Zn and Cu contaminated soils. Phytostabilization, though most effective at sites having fine-textured soils with high organic matter content, can treat a wide range of surface contamination (Cunningham et al., 1995; Berti and Cunningham, 2000).

Deep rooting plants could reduce the highly toxic Cr VI to Cr III, which is much less soluble and therefore, less bioavailable (James, 2001). Phytostabilization does not require soil removal and/or disposal of the hazardous material or the biomass. An experiment was conducted under green house condition using sorghum (fibrous root grass) to remediate soil contaminated by HMs and the developed vermicompost was amended in contaminated soil as a natural fertilizer (Jadia and Fulekar, 2008). It was reported that growth was adversely affected by HMs at the higher concentration of 40 and 50 ppm, while lower concentrations (5 to 20 ppm) stimulated shoot growth and increased plant biomass. Moreover, HMs were efficiently taken up mainly by roots of sorghum plant at all the evaluated concentrations of 5, 10, 20, 40 and 50 ppm. The order of uptake of HMs was: Zn>Cu>Cd>Ni>Pb. The large surface area of fibrous roots of sorghum and intensive penetration of roots into the soil reduces leaching via stabilization of soil and capable of immobilizing and concentrating HMs in the roots. Recently, a study was conducted by Cheraghi et al. (2011) on phytostabilization using different plant species. Their results indicated that *C. bijarensis, C. juncea, V. speciosum, S. orientalis, C. botrys, and S. barbata*, had a high bioconcentration factor and low translocation factor for Mn, therefore having potential for the phyto-stabilization of Mn.

Phytovolatilization

Phytovolatilization refers to the uptake and transpiration of contaminants, primary organic compounds by plants. The contaminant, present in the water taken up by the plant, passes through the plant or is modified by the plant, and is released to the atmosphere (evaporates or vaporizes). The contaminant may become modified along the way, as the water travels along the plant's vascular system from the roots to the leaves, whereby the contaminants evaporate or volatilize into the air surrounding the plant. The use of phytoextraction and phytovolatilization of metals by plants offers a viable remediation on commercial projects (Sakakibara et al., 2007). Phytovolatilization has been primarily used for the removal of murcury, the mercuric ion is transformed into less toxic elemental Hg (Ghosh and Singh, 2005). Phytovolatilization has been successful in tritium (3H), a radioactive isotope of hydrogen; it is decayed to stable helium with a half-life of about 12 years. Phytovolatilization is the most controversial of all phytoremediation technologies. Some metals, like As, Hg and Se, may exist as gaseous state in the environment. Some naturally occurring or genetically modified plants, like *Chara canescens* (muskgrass), *B. juncea* (Indian mustard) and *Arabidopsis thaliana*, are reported to possess capability to absorb HMs and convert them to gaseous state within the plant and subsequently release them into the atmosphere (Ghose and Singh, 2005).

Some plants growing in high Se media, for example, *A. thaliana* and *B. juncea*, produce volatile Se in the form of dimethylselenide and dimethyldiselenide. Similarly results from a study conducted on volatilization of heavy metals suggest that P. *vittata* is a plant species that is effective at volatilizing Arsenic (As); it removed about 90% of the total uptake of As from As-contaminated soils in the greenhouse, where the environment was similar to the subtropics (Sakakibara et al., 2007). However, if a large amount of arsenic had been released from the contaminated site into the atmosphere by the fern, the process may have caused a secondary As-contamination to the surrounding environments. Unlike other remediation techniques, once the contaminants have been removed via volatilization, one has no control over their migration to other areas. Similar cases of volatilization based soil remediation has also been reported in many recently published reports (Tangahu et al., 2011; Conesa et al., 2012)

Phytodegradation /phytotransformation

Phytodegradation is the breakdown of organic contaminants within plant tissue. Plants produce enzymes, such as dehalogenase and oxygenase that help catalyze degradation. It appears that both the plants and the associated microbial communities play a significant role in attenuating contaminants.It is referred to the degradation or breakdown of organic contaminants by internal and external metabolic processes driven by the plant (Prasad and Freitas, 2003). *Ex planta* metabolic processes hydrolyse organic compounds into smaller units that can be absorbed by the plant. Some contaminants can be absorbed by the plant and are then broken down by plant enzymes. These smaller pollutant molecules may then be used as metabolites by the plant as it grows, thus becoming incorporated into the plant tissues. Plant enzymes have been identified that breakdown ammunition wastes, chlorinated solvents such as TCE (Trichloroethylene), and others which degrade organic herbicideds. Plant enzymes that metabolise contaminants may be released into the rhizosphere, where they may play active role in transformation of contaminants. Enzymes, like dehalogenase, nitro-reductase, peroxidase, laccase and nitrilase, have been discovered in plant sediments and soils. Organic compounds such as munitions, chlorinated solvents, herbicides and insecticides and the inorganic nutrients can be degraded by this technology (Schnoor et al., 1995). The dissolved TNT (trinitrotoluene) concentrations in flooded soil decreased from 128 ppm within one week in the presence of the aquatic plant, *Myriophyllum aquaticum*, which produces nitroreductase enzyme that can partially degrade TNT (Schnoor et al., 1995). To engineer plant tolerance to TNT, two bacterial enzymes (PETN reductase and nitroreductase), able to reduce TNT into less harmful compounds, were over-expressed in tobacco plants. The two genes *onr* and *nfs* , under the control of a constitutive promoter, provided the transgenic plants with increased tolerance to TNT at a concentration that severely affected the development of wild type plants (Hannink et al., 2001).

The term “Green Liver Model” is used to describe phytotransformation, as plants behave analogously to the human liver when dealing with these xenobiotic compounds (foreign compound/ pollutant). After uptake of the xenobiotics, plant enzymes increase the polarity of the xenobiotics by adding functional groups such as hydroxyl groups (OH^-). This is known as Phase I metabolism, similar to the way that the human liver increases the polarity of drugs and foreign compounds. Whilst in the human liver, enzymes such as Cytochrome P450s are responsible for the initial reactions (Yoon et al., 2008). In plants, enzymes such as nitroreductases carry out the same role. Similar results showing the role of phytotransformation in soil remediation have also been reported recently (Shukla et al., 2010).

Phytoremediation is a potential remediation strategy that can be used to decontaminate soils contaminated with inorganic pollutants. Research related to this relatively new technology needs to be promoted and emphasized and expanded in developing countries since it is low cost. *In situ*, solar driven technology makes use of vascular plants to accumulate and translocate metals from roots to shoots. Harvesting the plant shoots can permanently remove these contaminants from the soil. Phytoremediation does not have the destructive impact on soil fertility and structure that some more vigorous conventional technologies have such as acid extraction and soil washing. This technology can be applied “*in situ*” to remediate shallow soil, ground water and surface water bodies. Also, phytoremediation has been perceived to be a more environmentally-friendly “green” and lowtech alternative to more active and intrusive remedial methods. The broader importance of protecting soils and improved management for the services they provide are currently receiving considerable attention from policy-makers. Soils provide fundamental ecosystem services, with extensive economic, ecological, and sociological influences on the wellbeing of the human society. Metal-contaminated soils provide a significant but previously neglected component of the global soil resource. There is much scope to optimize the utilization of this resource for improved services. Phytoremediation does have real applications, but it is vital that it emerges as a realistic technology and in the right context. It has been tested successfully in many places around the world for many different contaminants (Table 1). Some of the recent applications of different plants for phytoremediation of metals and radionuclides are shown in Table 2. The unending use of various forms of HMs in industries and agriculture has been a serious concern of environmental pollution worldwide. HM uptake by plants due to

Table 1. Extent of testing of phytoremediation across some sites in USA.

Location	Application	Pollutant	Medium	Plants
Ogden, UT	Phytoextraction and rhizodegradation	Petroleum and hydrocarbons	Soil and groundwater	Alfalfa, poplar, juniper, fescue
Anderson, ST	Phytostabilisation	HMs	Soil	Hybrid poplar, grasses
Ashtabula, OH	Rhizofiltration	Radionuclides	Groundwater	Sunflowers
Upton, NY	Phytoextraction	Radionuclides	Soil	Indian mustard, cabbage
Milan, TN	Phytodegradation	Expolsives waste	Groundwater	Duckweed, parrot feather
Amana, IA	Riparian corridor, phytodegradation	Nitrates	Groundwater	Hybrid poplar
Pennsylvania	Phytoextraction mine wastes	Zinc and cadmium	Soil	*Thlaspi caerulescens*
San Francisco, CA	Phytovolatization	Se	Refinery wastes and agricultural soils	*Brassica* sp.

(http://arabidopsis.info/students/dom/mainpage.html).

Table 2. Details of application of Phytoremediation.

Mechanism	Contaminant	Media	Plant	Status	Reference
Phytoextraction	Zn, Cd, and As	Soil	*Datura stramonium* and *Chenopodium murale*	Applied	Varun et al. (2012)
Phytodegradation	Pb, Cd	Soil	*Jatropha curcas* L.	Applied	Mangkoedihardjo and Surahmaida (2008)
Phytostabilisation	Cd	Soil	Sunflower	Applied	Zadeh et al. (2008)
Extraction-concentration in shoot and root	Cd, Co, Cu, Ni, Pb and Zn	Wetlands	*Ipomoea aquatica* Forsk, *Eichhornia crassipes*, (Mart.) Solms, *Typha angustata* Bory and Chaub, *Echinochloa colonum* (L.) Link, *Hydrilla verticillata* (L.f.) Royle, *Nelumbo nucifera* Gaerth. and *Vallisneria spiralis* L.	Field Demo	Kumar et al. (2008)
Phytodegradation	Total petroleum hydrocarbons (TPH)	Soil	*Anogeissus latifolia*, *Terminalia arjuna*, *Tacomella undulata,*	Field Demo	Mathur et al. (2 010)
Phytodegradation	Zn and Cd	Soil	*Vetiveria*, *Sesbania*, *Viola*, *Sedum, Rumex*	Field Demo	Mukhopadhyay and Maiti, 2010)
Phytodegradation	As	Soil	*Cassia fistula*	Applied	Preeti et al. (2011)
Phytoextraction	Cr	Soil	*Anogeissus latifolia*	Applied	Mathur et al. (2010)
Phytoextraction	^{137}Cs	Soil	*Catharanthus roseus*	Applied	Fulekar et al. (2010)
Phytodegradation	U	Soil	*Brassica juncea*	Field Demo	Huhle et al. (2008)
Phytoextraction	Uranium and Thorium	Soil	*Nyssa sylvatica, Liquidambar styraciflua*	Field Demo	Saritz (2005)
Phytostabilisation	Mn	Soil	*Cousinia bijarensis, Chondrila juncea, Chenopodium botrys*	Soil	Cheraghi et al. (2011)

phytoremediation technology emerged to be a potential tool to remediate HMs from the contaminated soil and water.

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