

Remediation of heavy metal contaminated ecosystem: an overview on technology advancement

A. Singh · S. M. Prasad

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Abstract The issue of heavy metal pollution is very much concerned because of their toxicity for plant, animal and human beings and their lack of biodegradability. Excess concentrations of heavy metals have adverse effects on plant metabolic activities hence affect the food production, quantitatively and qualitatively. Heavy metal when reaches human tissues through various absorption pathways such as direct ingestion, dermal contact, diet through the soil–food chain, inhalation and oral intake may seriously affect their health. Therefore, several management practices are being applied to minimize metal toxicity by attenuating the availability of metal to the plants. Some of the traditional methods are either extremely costly or they are simply applied to isolate contaminated site. The biology-based technology like use of hypermetal accumulator plants occurring naturally or created by transgenic technology, in recent years draws great attention to remediate heavy metal contamination. Recently, applications of nanoparticle for metal remediation are also attracting great research interest due to their exceptional adsorption and mechanical properties and unique electrical property, highly chemical stability, and large specific surface area. Thus, the present review deals with different management approaches to reduce level of metal contamination in soil and finally to the food chain.

Keywords Heavy metal · Toxicity · Remediation · Nanotechnology

Introduction

Environmental pollution occurs due to industrialization and extraction of natural resources in large scale, and it is responsible for degradation of environmental health. Among all kinds of pollution, heavy metals make a significant contribution to the environmental pollution (Nedel-Koska and Doran 2000). The metal present in soil–plant system can easily enter into food chain and also cause risk for humans, animals, plants and whole environment of our modern society (Farouk et al. 2011).

Heavy metals are listed as priority pollutants by the United States Environmental Protection Agency (UEPA). There are more than 70,000 chemicals in use in the world (Cairns et al. 1988). For the level of toxicity, lead, mercury, arsenic and cadmium are ranked first, second, third, and sixth, respectively, in the list of US Agency for Toxic Substances and Disease Registry (ATSDR), which generally lists all hazards present in toxic waste sites on the basis of their prevalence and severity of toxicity. The problem of heavy metal pollution is emerging as a matter of concern at local, regional and global scales. In aquatic and terrestrial ecosystems, high levels of heavy metals can act as ecological toxins (Nazemi 2012; Veschasit et al. 2012). In the present scenario, anthropogenic inputs of metals exceed natural inputs.

Data of central pollution control board (CPCB 2011) show that Gujarat, Maharashtra and Andhra Pradesh contribute 80 % of hazardous waste (including heavy metals) in India. Apart from industries, roadways and automobiles contribute substantially to environmental burden of heavy metals since particulate matters in traffic emissions include heavy metals like lead, cadmium and arsenic (Onat et al. 2013). Application of sewage sludge in agricultural fields resulted in the accumulation of heavy metals in the soil and

A. Singh · S. M. Prasad (✉)
Ranjan Plant Physiology and Biochemistry Laboratory,
Department of Botany, University of Allahabad,
Allahabad 211002, India
e-mail: sheomohanp@yahoo.co.in



consequently to plants (Arvas et al. 2013; Nogueira et al. 2013). The concentrations of trace metals in sewage water and sludge samples from River Kubanni drainage basin in Zaria City, Nigeria were studied by Adamu et al. (2013). Groundwater can be contaminated with metals directly by infiltration of leachate from land disposal of solid wastes, liquid sewage or sewage sludge, leachate from mine tailings and other mining wastes, deep-well disposal of liquid wastes, seepage from industrial waste lagoons or from other spills and leaks from industrial metal processing facilities (e.g., steel plants, plating shops, etc.).

Total extractable trace metals (mg kg^{-1}) in sewage sludge were 403.3, 184.2, 303.4, 129.0 and 19.7 for Zn, Ni, Cu, Pb and Cd, respectively (Adamu et al. 2013). In recent years, use of energy-saving compressed fluorescent lamp (CFL) bulbs has gone up enormously. Hence, the production of CFL bulbs has increased from 19 million in 2002 to 500 million in 2010. Each bulb contains 3–12 mg of mercury. With no system to recover these bulbs and safe disposal, it may prove to be a major health hazard.

The problem of heavy metal pollution is continuously worsening due to a series of human activities, leading to an intensification of research dealing with the phytotoxicity of these contaminants and with mechanisms used by plants to counter their detrimental effects (Rascio and Navari-Izzo 2011). Transfer of toxic elements to human food chain is a concrete danger that has to be faced in the near future. Living organisms require varying amounts of few heavy metals. Iron, cobalt, copper, manganese, molybdenum and zinc are required by humans in trace amounts. All metals are toxic at higher concentrations (Singh et al. 2011). Other heavy metals such as mercury, plutonium, arsenic, cadmium and lead are toxic metals that have no known vital or beneficial effect on organisms, and their accumulation over time in the bodies of animals can cause serious illness. Heavy metals disrupt metabolic functions in human beings. Excess accumulation disrupts the function of vital organs and glands such as heart, brain, kidneys, bone, liver, etc. These metals displace the vital nutritional minerals from their original place, and hinder their biological function. These metals can enter into our body through consumption of foods, beverages, skin exposure and inhaled air. Among different heavy metals, chronic exposure to low doses of cancer-causing heavy metals may induce many types of cancer. Park et al. (2004) found an increased lifetime risk of lung cancer death resulted from occupational exposure to dusts and mists containing hexavalent chromium. The risk of postmenopausal breast cancer may increase due to consumption of cadmium-contaminated rice and other foods (Hiroaki et al. 2014). Acute and chronic exposure of arsenic could also cause numerous human health problems. These included dermal, respiratory, cardiovascular, gastrointestinal, hematological, hepatic, renal, neurological,

developmental, reproductive, immunological, genotoxic, mutagenic and carcinogenic effects (such as liver cancer) (Lin et al. 2013).

So, there is a need of technology to clean environment up to safer limit with suitable techniques, which must be easy to handle, cost-effective and feasible. A range of technologies is available for remediation of metals-contaminated soil. The comparison of different kind of technologies is given in Table 1. General approaches to remediation of metal contamination include isolation, immobilization, toxicity reduction, physical separation and extraction. These general approaches can be used for many types of contaminants but the specific technology selected for treatment of a metals-contaminated site will depend on form of the contamination and other site-specific characteristics.

The present review covers the whole scenario of metal contamination and its effects on plant responses. It also includes remediation technologies which can be easily applied in the metal-contaminated areas.

Metal toxicity through food chain contamination (soil → plant → consumer)

Due to continuous industrialization and urbanization activities, heavy metal pollution becomes a major cause of environmental degradation. Different countries showed different level of metal contamination. The South and Southeast Asian countries, like Peninsular Malaysia, Vietnam, India, Thailand, Philippines, Indonesia, Bangladesh and Pakistan have taken much care regarding monitoring of the contamination of agricultural soils and crops by heavy metals.

Kapungwe (2013) has studied metal (Co, Cr, Cu, Pb and Ni) contamination of water, soils and crops at two wastewater-irrigated study sites (New Farm Extension in Mufulira and Chilumba Gardens in Kafue) in Zambia. The results indicated that heavy metals were present in the water, soil and crops at the two study sites and exceeded acceptable limits. Zeid et al. (2013) reported that in agricultural research center of Giza, Egypt, wastewater usage for irrigation has resulted metal accumulation in soils and plants beyond maximum permissible limits, for livestock consumption.

Among different metals, it was suggested that Cd would be the most mobile element in the soil and more available to crop. Industrial emissions of contaminant to the atmosphere which is finally deposited on soil or dumping of industrial wastes on disposal land may cause problem in the environment beyond limit. In India, many urban and dense cities with significant industrial waste generation have been found to have contaminated soil.



Table 1 Comparative analysis of different methods used for metal remediation

	Way of treatments	Detail and result of treatment	Advantage	Disadvantage	References
Physical	Mechanical separation	Reduction in metal contamination in soil	Significant volume reduction in contaminated soil	It could not applied in case of homogenous distribution of pollutants in soil	Ottosen and Jensen (2005)
	Electro kinetic remediation	Reduction in metal contamination in soil	This method is applicable to different metals	Any heterogeneity of the soil body decreases the effectiveness of the method and considerable acidification of the remediated soil is a side effect of this method	Tahmasbian and Nasrazadani (2012)
Chemical	Soil washing (ex situ technique)	For removing inorganic contamination, such as heavy metals, radio-nuclides, toxic anions and others	Highly effective method for cleaning up strongly contaminated soils	High costs of construction of the cleaning installation and utilization	Wuana and Okieimen (2011)
	Soil flushing (in situ technique)	For removing inorganic contamination, such as heavy metals, radio-nuclides, toxic anions and others	Relatively low invasive method	A large amount of liquid and semi-liquid wastes are generated	Wuana and Okieimen (2011)
Soil amendments	Addition of lime	Reduce the mobility of Cd, Cu, Ni, Pb, Zn		Changes the physico-chemical properties of soil	Guo et al. (2006)
	Addition of chelating agents (ethylene diamine tetra acetic acid; EDTA)	Reduce the mobility of Pb and Cu			Sukumara et al. (2012)
	Addition of biological products a. Bark saw dust b. Cattle manure c. Rice hulls	a. Reduce the mobility of Cd, Pb, Hg, Cu b. Reduce the mobility of Cd c. Reduce the mobility of Cd, Cr and Pb	Increases the binding property of soil with metals	Some physico-chemical properties of soil is changed	Nagh and Hanafiah (2008) Angelova et al. (2010)
Biological method	By using micro-organism	Removes the metal contaminants as a result of sorption and/or transformation	Removes the contaminants as a result of sorption and/or transformation. Soil retains its properties and could be replaced on the reclaimed site	Construction of a special installation is required. Large amounts of wastes (solid, liquid) are generated	
Phytoremediation	a. Phytostabilisation b. Phytoextraction c. Phytovolatilization	Contaminants are absorbed into roots and precipitated in the roots' area contaminants are picked up by the roots of plants and transported to their overground parts, and then removed together with the crops. Uptake and transpiration of such elements by plants. The element is taken up by plant roots, transported through the xylem and is finally released to the atmosphere from cellular tissues (evaporates or vaporizes)	Low-cost method. Practically no side effects Relatively low costs The method is environmentally friendly	Contaminants are not removed from the soil but only immobilized Plants and soil require long-term monitoring	Fasaei (2012) Jiang et al. (2010) Rahimi et al. (2013)



Table 1 continued

	Way of treatments	Detail and result of treatment	Advantage	Disadvantage	References
Biotechnological approach	By using genetic tools	Transgenic plants removed up to 6 % Zn and 25 % Cd of the soil metal; Tobacco callus showed more resistance to methyl mercury (CH_3Hg^+) and accumulated more mercury from CH_3Hg^+ -containing medium	Transgenic plants might be able to contribute to the wider and safer application of phytoremediation	Not studied	Kupper and Kochian (2010); Nagata et al. (2010)
Nanotechnology approach	Use of particles with at least one dimension in the range of 1–100 nm, to affect the mobility, toxicity and/or bioavailability of contaminants in their natural environment	Use of nano-ZVI, bimetallic nanoparticles, and emulsified zero-valent nanoparticle reduces the metal contamination from soil and groundwater	Very efficient for removing the metal	Not studied	Xiong et al. (2009); Agarwal and Joshi (2010)

The levels of Pb, As, Cr, Cd and Zn were determined in vegetables: leek (*Allium ampeloprasum*), coriander (*Coriandrum sativum*), parsley (*Petroselinum crispum*), cress (*Lepidium sativum*), basil (*Ocimum basilicum*), radish leaf (*Raphanus sativus*) and beet leaf (*Beta vulgaris*) collected from North East of Iran (Nazemi 2012). The heavy metal concentration in vegetable samples showed a range of Cr (2.4–5.88), Zn (54.27–170.23), As (1.92–5.49), Cd (1.94–2.43) and Pb (18.48–21.3) in mg kg^{-1} . The study showed that vegetables grown in this region are a health hazard for human consumption (Nazemi 2012). The accumulation of As, Cd, Cr, Pb and Zn in soils and vegetables in vicinity of Enyigba lead mine was observed by Wilberforce and Nwabue (2013), in the edible vegetables such as *Telfaria occidentalis* (fluted pumpkin); *Talinum triangulare* (water leaf); *Amaranthus hybridus* (Amaranth or pigweed); *Vernonia amygdalina* (bitter leaf) and *Solmun nigrum* (garden egg leaf). The results revealed that heavy metal values (mg kg^{-1}) in vegetable ranged from 0.035 to 0.400, 0.001 to 0.01, 0.023 to 0.273, 0.105 to 0.826 and 0.016 to 0.174 for As, Cd, Cr, Pb and Zn, respectively. The levels of arsenic and lead in bitter leaf and garden egg leaf exceeded WHO maximum limit. Karimi et al. (2013) have collected plant and soil samples from uncontaminated and contaminated sites of the Dashkasan mining area, western Iran. Total and water-soluble arsenic in the soil ranged from 7 to 795 and from 0.007 to 2.32 mg kg^{-1} , respectively. The highest arsenic concentration in soil was found at the ore dressing area (up to 1,180 mg kg^{-1}) and lowest at an uncontaminated area (up to 11 mg kg^{-1}). Among all collected plants, the highest arsenic concentrations were found in *Hyoscyamus kurdicus* Bornm (up to 205 mg kg^{-1}) and *Helichrysum oligocephalum* DC (up to 162 mg kg^{-1}). These two accumulator species could have potential for soil cleanup by phytoextraction.

A geochemical investigation has been carried out in and around the Patancheru industrial development area of Andhra Pradesh to find out the extent of chemical pollution in the soil by Govil et al. (2001). It was found that contaminated soil showed two to three times higher level of toxic elements than normal and some metals like Cr, V, Fe, As, Cd, Se, Ba, Zn, Sr, Mo and Cu were found to be present above normal distribution in the soil. Singh et al. (2002) reported that stream sediments from Lucknow, Kanpur, Delhi and Agra in India were classified as highly polluted to dangerous sediments. The soil samples were collected from Pali Industrial area, present in the western state of Rajasthan (Krishna and Govil 2004). The result showed that soil in the study area is significantly contaminated with high concentrations of heavy elements like Pb, Cr, Cu, Zn, Sr and V. Similar study was done by Lokeshwari and Chandrappa (2006) around the city of Bangalore to assess heavy metal contamination of vegetation and soil due to irrigation with sewage-fed lake water on agricultural land. The results showed significant amount of heavy metals, above the Indian Standard limits in both the soil as well as the vegetation samples. In 2007, soil samples were collected from the industrial area of Surat city, present in the western state of Gujarat by Krishna and Govil (2007). It was found that soil in the study area is significantly contaminated with high concentrations of heavy elements like Ba, Cu, Cr, Co, Ni, Sr, V and Zn. Metal contamination is also studied near wastewater-irrigated sites of Varanasi city (Sharma et al. 2009). In this study, soil samples of major irrigation sites in sub-urban areas of Varanasi were taken and analyzed for heavy metal contamination. Samples of irrigation water and portion of vegetables being grown were also collected. Apart from concentration of Cd, rest of the heavy metals was present within the Indian standards.



Singh et al. (2010) have also reported that concentration of Cd, Pb and Ni is above safe limit in the vegetables collected from wastewater-irrigated sites of Dinapur sites of Varanasi city.

Soil to plant transfer is the major component of animal and human exposure to heavy metals through the food. It was shown by Fig. 1. Chronic intakes of heavy metals have damaging effects on human beings and other animals (John and Andrew 2011; Liu et al. 2013). Jolly et al. (2013) have investigated the concentration of Si, Ba, K, Ca, Mg Fe, Sc, V, Cr, Cu, Zn, As, Mn, Co, Ni, Se, Sr, Mo and Cd metals in agricultural soil and vegetables collected from agricultural land at Ruppur area of Pabna District of Bangladesh and also evaluated the possible health risks to human body through food chain transfer. Among all metals, the daily intake of Cd was estimated 0.178 mg/g and HQ value for Cd calculated was 2.543, which is much higher than the safe value. Cd is a very toxic element, its long-term exposure to lower level leads to build up in kidneys and possible kidney disease, lung damage and fragile bones.

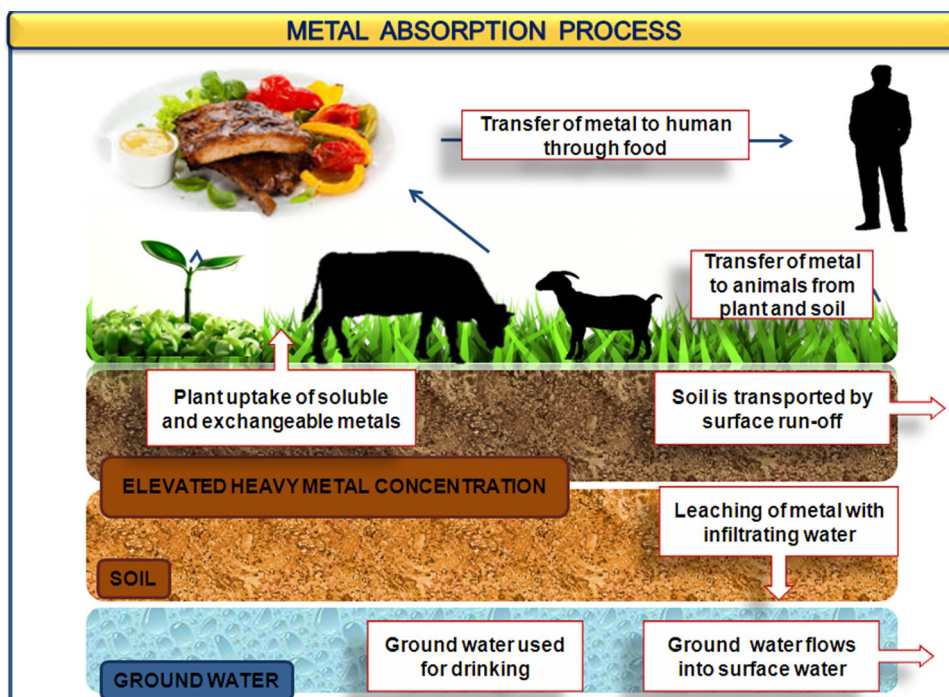
Harmanescu et al. (2011) have calculated daily metal intake for normal daily intake consumption of contaminated vegetable collected from copper and lead extraction and processing industry in Banat country, south West part of Romania. They have found that value of daily metal intake for Fe, Mn and Pb exceeded the upper tolerable daily intake.

Heavy metals were analyzed by Jan et al. (2011) in different food crops, milk and meat, and blood samples

collected from different age group subjects such as children (1–12 years), adolescent (12–18 years), adults (18–45 years) and old age (above 45 and 55 years for males and females, respectively) from polluted and relatively less polluted areas. The results revealed that consumption of contaminated food crops, meat and milk have significantly increased concentrations of selected metals in the human blood. Cu, Zn and Mn concentrations were significantly higher ($p < 0.05$) in the blood samples collected from the polluted area as compared to control area. Old people had accumulated high concentrations of metals as compared to the younger ones within the same area.

Javed and Usmani (2013) examined the contamination of rivulet situated at Kasimpur, Aligarh (27.218°N; 79.378°E). It receives the wastewater of Harduaganj Thermal Power Plant (HTPS) containing fly ash and heavy metals. Among the heavy metals estimated in the rivulet water, Fe (8.71 mgL^{-1}) was present in the highest concentration followed by Cu (0.86 mgL^{-1}), Zn (0.30 mgL^{-1}), Mn (0.21 mgL^{-1}), Ni (0.12 mgL^{-1}), Co (0.11 mgL^{-1}) and Cr (0.10 mgL^{-1}). Bioaccumulation of these heavy metals was detected in tissues such as gills, liver, kidney, muscle and integument of the fish *Mastacembelus armatus*. Accumulation of Fe ($213.29\text{--}2,601.49 \text{ mg kg}^{-1}$) was highest in all the organs. Liver was the most influenced organ and integument had the least metal load. The accumulation of Fe, Zn, Cu and Mn observed in the tissues was above the values recommended by FAO/WHO (Javed and Usmani 2013).

Fig. 1 Metal absorption process from water, soil and air to food chain and finally to humans



Entrapment strategy to reduce metal availability from soil

By using chelating materials

The chelating agents have a property to desorb toxic metals from soil solid phases by forming strong water-soluble complexes. After complex formation, it can be removed from the soil by plants through enhanced phytoextraction or by using soil washing techniques. In the process of phytoextraction with the help of chelant, it was applied to the soils. First, chelant can desorb metals from the soil matrix, and the mobilized metals move to rhizosphere for uptake by plant roots (Tahmasbian and Sinegani 2013). The amounts of bio-available metals in soil solution are mainly determined by the properties of the soil and applied chelant (Tandy et al. 2004; Luo et al. 2005). In order to reduce discharge of metal chelants into ground water and for reducing impact of chelant on soil micro-organisms, its selection, its amount and process of their application are important (Evangelou et al. 2007; Luo et al. 2007). Sukumara et al. (2012) have observed that Ethylene Diamine Tetra Acetic acid (EDTA) is one of the most powerful and commonly used chelating agents, which forms complexes with many of metal contaminants within the natural environment. It was found that application of EDTA as chelating agent increases the efficiency of an emergent wetland plant species such as *Typha* sp. and floating wetland macrophytes like *Pistia* sp., *Azolla* sp., *Lemna* sp., *Salvinia* sp. and *Eichhornia* sp. in phytoremediation of lead and copper (Sukumara et al. 2012).

The conventional complexing agents have some undesired features such as their persistence or slow transformation in the environment, remobilization of toxic metal ions mainly from sediments and soils as well as radionuclides from radioactive waste are of great concern, therefore, their replacement and the use of chelating agents with improved biodegradability is necessary (Reinecke et al. 2000). It should be stressed that most of the aminopolycarboxylic acids (such as EDTA—ethylene diamine tetra acetic acid, IDA—iminodiacetic acid, DTPA—diethylenetriaminepentaacetic acid) are resistant to conventional biological and physicochemical methods. Luo et al. (2005) found that EDTA is more efficient than [S, S]-EDDS (ethylenediamine disuccinic acid) in extraction of Pb and Cd, but [S, S]-EDDS is more effective in the extraction of Cu and Zn. It was found that combined application of EDTA and [S, S]-EDDS led to a higher level of efficiency (i.e., a synergy effect) in phytoextraction of Cu, Pb, Zn and Cd that could be obtained by the application of either chelant alone (Luo et al. 2005). Gupta and Sinha (2006) used five different metal extractants from different tannery sludge amendment. The result showed that metal

extraction efficiency of each extractants was highest in EDTA followed by DTPA > NH_4NO_3 > NaNO_3 > CaCl_2 . Dede et al. (2012) have done a pot experiment to investigate the influence of elemental sulfur, gypsum and chelating agent (ethylenediaminetetraacetic acid: EDTA) on copper, zinc, nickel, cadmium, chromium and lead uptake by *Brassica juncea* from sewage sludge. Sulfur addition acidified the sludge, which caused the pH decrease to 5.4 with an initial pH 6.7. Applications of EDTA and sulfur resulted in a considerable increase in copper and lead concentrations in the plant. The result showed that elemental sulfur will be more effective amendment for phytoextraction of heavy metals from sewage sludge.

By using natural products

To replace the conventional adsorbents now special attention has been focused on the use of natural sorbents as an alternative depending upon their availability in environment and economic cost (Babel and Kurniawan 2003; Singh and Prasad 2013a). Natural materials like farmyard manure (FYM) that are available in large quantities or certain waste products from industrial or agricultural operations such as saw dust and rice husk, etc. may have potential as inexpensive sorbents. Due to their low cost, these materials at end of their lifetime can be disposed of in agricultural fields for metal remediation purposes. The abundance and availability of agricultural by-products make it good sources of raw materials for natural sorbents. The organic substance present in the soil has a significant impact on absorption and translocation of heavy metal (Cu, Zn, Pb and Cd) in soil and it turns into more stable forms and leads to accumulation of metals in organic horizons of soil and peat (Kabata-Pendias 2001). Angelova et al. (2010) have found that concentration of Pb and Cu decreased in potato peel and tubers with 10 % compost or 10 % vermicompost amendment in soil (Angelova et al. 2010). The removal and stabilization of metals can be done by using compost, biosolids and recycled paper waste (Jones and Healey 2010). Mineral amendments have been used in agriculture for remediation of heavy metal (Paulose et al. 2007). The mineral amendments can reduce the risk of exposure to humans or biota by reducing availability of metals to the soil, water or air (O'Day and Vlasopoulos 2010).

Other natural products such as saw dust and rice husk act as binding agent to reduce uptake of heavy metal from contaminated site (Nagh and Hanafiah 2008). Bio-availability of metal ions in soils is largely governed by chemical equilibrium of metal ions in solid and solution phases, adsorption reactions are important to determine availability of metal to plants and their mobility throughout the soil. Shubhan and Pradeep (2011) have shown that SD and RH act as biosorbent in hydroponic system and



suggested that saw dust (SD) and rice husk (RH) could also be used to reduce metal availability. The appreciable reduction in availability of Cd in rice husk and saw dust amended soil is due to basic nature of complex compound: cellulose, hemicellulose, lignin, mineral ash containing large amount of SiO₂ and tannins (containing hydroxyl groups). The lignin is known to interact with cations by exchanging with protons and subsequently by chelating with the metallic ions (Rafatullah et al. 2009). These organic components are actively involved in ion exchange. Lignin is the third major component of the wood cell wall and it is built up from the phenylpropane nucleus; an aromatic ring with a three carbon side chain, which is promptly available to interact with cationic metal ions (Fateme et al. 2008). Sidiras et al. (2013) have used autohydrolyzing Scots Pine (*Pinus Sylvestris*) sawdust for removing hexavalent chromium from water and wastewater media. Singh and Prasad (2013b) have also reported that application of natural products such as FYM, SD and RH in Cd-contaminated soil reduced the level of Cd by 36 % under FYM, 23 % under RH and 14 % under SD amended soil.

To determine the chemical forms of Cu, Zn, Ni and Cd in fly ash stabilized sludge, sequential extraction method was used (Su and Wong 2003). The experiments have been performed in order to grow corn under greenhouse condition by amending the loamy acid soil with fly ash stabilized sludge. The result showed that sewage sludge amended with coal fly ash could reduce availability of Cu, Zn, Ni and Cd in sludge. With increasing rate of fly ash amendment, the DTPA extractable metals (Cu, Zn, Ni, and Cd) were reduced. The application of fly ash amended sludge also resulted into increase in dry mass of corn along with decrease in concentration of Zn and Cu in shoot tissues. Therefore, the amendment of fly ash in contaminated soil significantly reduced the availability of heavy metal by chemical modification of their chemical speciation into less available forms (Su and Wong 2003).

By using nanotechnology

The application of nanotechnology being mainly focused on animal science and medical research nanotechnology can also be applied to plant science research in order to analyze plant genomics and gene function as well as improvement of crop species (Monica and Cremonini 2009). The application of nanotechnology for remediation of contaminants may give promising results in the future. Nanotechnology can provide a way to purify the air and water resources by utilizing nanoparticles as a catalyst and/or sensing systems (Fulekar et al. 2014). The search for new and advanced materials is an important task of contemporary research in the environmental protection. Yang

et al. (2006) have found that application of nanostructured materials can be used as adsorbents or catalysts to remove toxic and harmful substances from wastewater and air and finally from soil. In order to understand possible benefits of applying nanotechnology to agriculture, the first step should be to analyze the level of penetration and transport of nanoparticles in plants. It is established that these particles tagged to agrochemicals or to other substances could reduce injury to plant tissues and amount of chemicals released into the environment. Some contact is, however, inescapable, due to the strong interaction of plants with soil growth substrates (Monica and Cremonini 2009). In the field of nanotechnology, production of nanomaterials and products containing them are rapidly developing fields, which provides many opportunities for new innovation. For the abatement of pollution, production in the field of nanotechnology is just a beginning. It can be explored to catalyze the important changes in the field of environment. The major factor which defines capability of nanoparticles as an extremely versatile remediation tool includes their very small particle sizes (1–100 nm) in comparison to a typical bacterial cell which has a diameter on the order of 1 µm (1,000 nm). Hence nanoparticles can be transported effectively by the groundwater flow. Despite their minuscule status, nanoscale particles may hold potential to cost-effectively address some of the challenges of site remediation (Tina and Zhang 2003). Applications of nanotechnology in water treatment and purification have witnessed significant developments in recent years (Theron et al. 2008; Mauter and Elimelech 2008). However, little progress has been made regarding application of nanoparticles to improve agricultural soil quality and to reclaim drastically disturbed lands.

Liu and Zhao (2007) prepared and tested a new class of iron phosphate (vivianite) nanoparticles for in situ immobilization of Pb⁺² in soils. Batch test results showed that the nanoparticles could effectively reduce the leachability and bioaccessibility of Pb⁺² from soils. Liu (2011) also reported an effective remediation of a lead-laden soil from a shoot range using synthesized apatite nanoparticles. Salam (2013) have used multi-walled carbon nanotubes (CNTs) that were used successfully for the removal of Copper(II), Lead(II), Cadmium(II), and Zinc(II) from aqueous solution. Yu et al. (2013) also used CNTs and their composites to remove metals from contaminated water. These nanotubes attracted great attention due to their excellent adsorption performance. The removal efficiency for metal ions by CNTs was observed around 10–80 %, which could be improved to approach 100 % by selectively functionalizing CNTs with organic ligands. Rathore et al. (2013) have found that the application of carbon nanoparticles resulted into 75–92 % reduction in Ni contamination from soil and about 99 % reduction from water



system. Carbon nanoparticle have exceptional adsorption and mechanical properties due to its unique electrical property, highly chemical stability and large specific surface area (Tofighy and Mohammad 2011; Salam 2013). The nanoparticles provided from *Euphorbia macroclada* plants were kept in experimental pots for 2 weeks and then the amount of their heavy metals were compared with that of the control pots. The data showed that concentrations of all the subjected metals decreased (Pb, 92 %; Zn, 76.05 %; Cu, 74.66 %; Cd, 69.08 %; Ni, 31.50 %) among which Pb showed the highest decrease. Nanoparticles of *E. macroclada* is suggested for removing and detoxification of heavy metals (especially Pb, Cd, Cu and Zn), from polluted environments (Mohsenzadeh and Rad 2011). Similarly, Singh et al. (2013) have also used zero-valent iron nanoparticles for removing Cr from contaminated soil. They have reported about 99 % removal of Cr.

Strategies to reduce metal contamination from aquatic system

When wastewater is released to land without treatment, it leads to the accumulation of metals in the soil for years. Untreated wastewater contaminated with heavy metals is released into aquatic system. The micro-organisms and plants present in the contaminated aquatic system have ability to accumulate and magnify the level of heavy metals in their habitats. It may not only affect productivity and reproductive capacities of these organisms, but may also ultimately affect health of man (Davies et al. 2006). Higher levels of essential and non-essential metals are toxic to aquatic organisms as well as humans and it may potentially damage human physiological and biological systems (Fatoki et al. 2002). The heavy metal from aqueous solution can be removed by passive binding with non-living biomass through biosorption process (Kumar and Oommen 2012). The technique of using micro-organism to reduce level of metal contamination is better than conventional separation techniques because of reusability of biomaterial, low operating cost and improved selectivity for specific metals of interest and short operation time (Srinath et al. 2002). The biosorption process is a new technology, which can easily use as a refining treatment in shallow bodies of water (Nirmal Kumar et al. 2006).

The dried, non-living, or pretreated microbial biomass frequently displays a higher affinity for metal ions compared with living one and seems to be a preferred alternative use of living cells in industrial applications for the removal of heavy metal ions from wastewaters. Living cells are likely to be more sensitive to metal ion concentration and adverse operating conditions of pH and temperature. The extent of metal binding is dependent on metal chemistry, nature of binding and metal affinity for binding sites on the cell

surface. Furthermore, a constant nutrient supply is required for using living cells. Recovery of metals and regeneration of biosorbent is complicated for living cells. Higher affinity of non-living cells for metal ions compared with living one probably due to the absence of competing protons produced during metabolism (Das et al. 2007).

Heavy metal removal from aquatic system by algae includes sedimentation, flocculation, absorption and cations and anion exchange, complexation, precipitation, oxidation/reduction, microbiological activity and uptake. Microalgae remove heavy metals directly from polluted water by two major mechanisms: the first is a metabolism-dependent uptake into their cells at low concentrations and the second is biosorption which is a non-active adsorption process (Mitra et al. 2012).

The algae have many features that make them ideal candidates for selective removal and concentration of heavy metals, which include high tolerance to heavy metals, ability to grow both autotrophically and heterotrophically, large surface area/volume ratios, phototaxy, phytochelatin expression and potential for genetic manipulation. The ability of macroalgae to accumulate metals within their tissues has led to their widespread use as biomonitors of metal availability in marine systems. Therefore, *Chlorophyta* and *Cyanophyta* are hyperabsorbents and hyperaccumulators for Arsenic and Boron, absorbing and accumulating these elements from their environment into their bodies. These algae can be hyperphytoremediators and their presence in water reduces water arsenic and boron pollutant (Chekroun and Baghour 2013). Some algal species may convert mercuric or phenylmercuric ions into metallic mercury which is then volatilized out of cell and from the solution. The blue green algae *Phormidium* successfully can hyperaccumulate heavy metals like Cd, Zn, Pb, Ni and Cu (Chekroun and Baghour 2013). *Caulerpa racemosa* var. *cylindracea* as a low-cost biomaterial could be used for the removal of boron species from aqueous solution (Bursali et al. 2009).

Strategies to reduce metal contamination from agricultural land system

By using naturally grown hyperaccumulator plants

Plants can be used to remove, transfer and stabilize heavy metals from contaminated soils (Jadia and Fulekar 2009; Garbisu et al. 2002). Phytoaccumulator plants have more tendencies to accumulate metals in their shoots and high tolerance to heavy metals (Baker et al. 2000). On the other hand, many hyperaccumulator plants tend to be slow growing and produce low biomass. Phytoremediation is the use of special type of plants to decontaminate soil or water by inactivating metals in the rhizosphere or translocating



them in their aerial parts. The families like Asteraceae, Brassicaceae, Caryophyllaceae, Cyperaceae, Cunouniaceae, Fabaceae, Flacourtiaceae, Lamiaceae, Poaceae, Violaceae and Euphorbiaceae showed remediation property (Sarma 2011). Phytoremediation is a promising technology using plants and microbes to clean up contaminated air, soil and water (Behera 2014). To reduce the level of metal from polluted soil by these techniques are cheaper, efficient and a more environment friendly (Lone et al. 2008; Jing et al. 2007). Through phytoremediation technique, the metals are extracted or inactivated from the soil (Lombi et al. 2001; Bennett et al. 2003). It was reported that high concentration of Cd and Ni is accumulated by *Sedum alfredii* and *Alyssum bertolonii*, respectively (Deng et al. 2007; Kramer 2010). The ratio of metals between soil and plants parts should be more than one for phytoremediating species (Barman et al. 2000). The roots of Indian mustard are effective in removal of Cd, Cr, Cu, Ni, Pb and Zn (Prasad and Freitas 2003). There are different categories of phytoremediation which includes: phytoextraction, phytoremediation, phytostabilisation and phytovolatilisation.

Phytoextraction involves the use of plants that has ability to extract the heavy metal from contaminated lands. As compared to the conventional techniques cost involved in phytoextraction would be more than ten times less per hectare (Salt et al. 1995). The level of metal contaminants can be reduced by the successive cropping and harvesting of phytoextracting plants (Vandenhove et al. 2001). *Brassica napus* is selected as major plant for accumulating high concentration of Cd, and Pb, Zn and Cd was accumulated more in *Andrographis Paniculata* (Selvam and Wong 2008; Tang et al. 2009). The plant *Amaranthus retroflexus*, *B. juncea* and *Phaseolus acutifolius* were found to most effective for extracting ^{137}Cs and ^{90}Sr (Fuhrmann et al. 2002). Lee et al. (2002) have reported that plutonium is accumulated ten times higher in Indian mustard (*B. juncea*) than sunflower (*Helianthus annuus*) grown in hydroponic media. Wuana and Okieimen (2010) have found that *Zea mays* (maize) is able to phytoextract the metals from contaminated soils. For recovery of metals from phytoremediating plants, the shoot biomasses are harvested for proper disposal in special site or are burnt (Islam et al. 2007).

For reducing the metal contamination from tannery waste contaminated site, the *Sesamum indicum* L. var. T55 (sesame) was used by Gupta and Sinha (2006). The trend of metal accumulation showed that it was highest for K followed by $\text{Na} > \text{Fe} > \text{Zn} > \text{Cr} > \text{Mn} > \text{Cu} > \text{Pb} > \text{Ni} > \text{Cd}$. The soil quality can be maintained by phytoextraction method. Jiang et al. (2010) have shown that quality of soil is maintained by using successive cropping of hyperaccumulator plant *Sedum plumbizincicola* for two-year period. The physico-chemical properties (microbial biomass, basal respiration and enzymatic activities) of soil

increased in the soil, where hyperaccumulator plant is grown (Jiang et al. 2010).

Jing et al. (2007) have shown that from aqueous solution, the metal can be removed by phytoremediation technique. It involves the use of plants to absorb, concentrate or precipitate metals. Both terrestrial as well as aquatic plants can be used for this technique (Jadia and Fulekar 2009). Ensley (2000) have found that only lower contamination from groundwater, surface water and wastewater can be removed by rhizofiltration. The plants that can be used for removing the metal through rhizofiltration are sunflower, Indian mustard, tobacco, rye, spinach, and corn, which are able to remove lead from water (Jadia and Fulekar 2009). The fibrous and much longer root present in the terrestrial plants are responsible for increasing remediation property of these kinds of plants (Raskin and Ensley 2000).

Phytostabilization technique is based on the use of plants to reduce mobility of heavy metal through absorption and precipitation by plants, thus reducing their bio-availability (Bennett et al. 2003; Jing et al. 2007). Whereas in case of volatilization, plants are used to absorb contaminants from the soil and transferred it into volatile forms and finally into the atmosphere through transpiration process (United States Environmental Protection Agency 2000).

The characteristics of plants involved in stabilization of heavy metals are that it should decrease the amount of water percolating through soil matrix. It acts as a barrier to prevent direct contact with contaminated soil and it should also prevent soil erosion and distribution of the toxic metal to other areas (Raskin and Ensley 2000). Jadia and Fulekar (2008) have observed that due to large surface area of fibrous roots of sorghum and intensive penetration of roots into the soil, it reduces leaching via stabilization of soil and capable of immobilizing and concentrating heavy metals in the roots. Heavy metals were efficiently absorbed by roots of sorghum plant at all concentration of 5, 10, 20, 40 and 50 mg kg^{-1} used and order of uptake of heavy metals was $\text{Zn} > \text{Cu} > \text{Cd} > \text{Ni} > \text{Pb}$ (Jadia and Fulekar 2008). For volatilization process, a laboratory experiment was performed with tobacco (*Nicotiana tabacum*) and a small model plant (*Arabidopsis thaliana*). In genetically modified plants, a gene for mercuric reductase converted ionic mercury (Hg(II)) to less toxic metallic mercury (Hg (0)) and volatilized it (Meagher et al. 2000).

There are various biotechnological approaches for remediation of metal that include biomineralization (mineral synthesis by living organisms or biomaterials), biosorption (dead microbial and renewable agricultural biomass), phytostabilization (immobilization in plant roots), hyperaccumulation (exceptional metal concentration in plant shoots), dendroremediation (growing trees in polluted soils), biostimulation (stimulating living microbial population), rhizoremediation (plant and microbe),



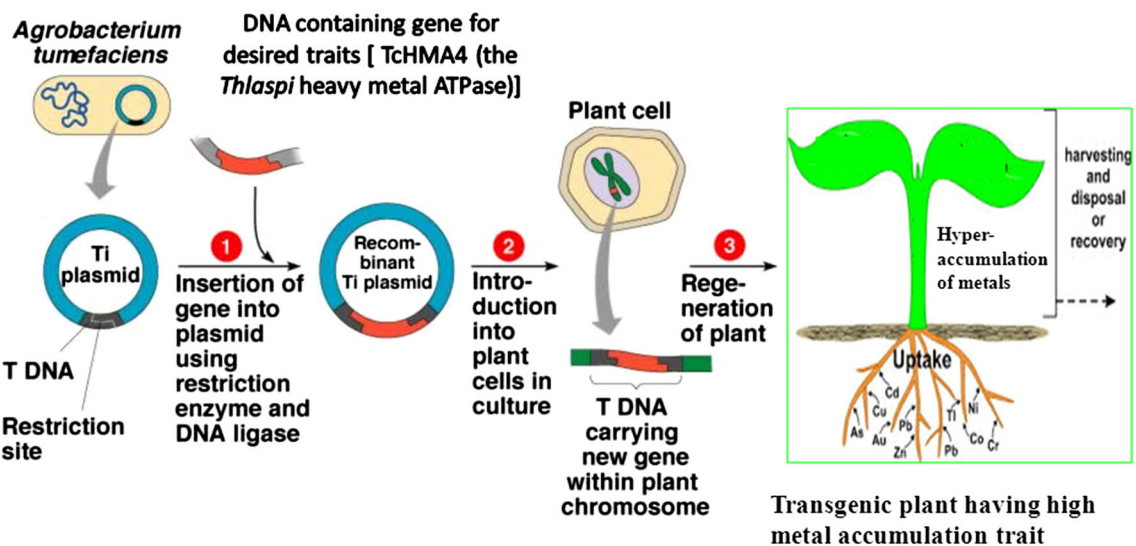


Fig. 2 A diagram to show application of genetically modified plants in heavy metal management

mycoremediation (stimulating living fungi/mycelial ultra-filtration), cyanoremediation (stimulating algal mass for remediation) and genoremediation (stimulating gene for remediation process). To clean the environment, cooperation, integration and assimilation of such biotechnological advances are required (Mani and Kumar 2013).

By using biotechnologically modified plants

Biotechnological tools include genetic engineering in order to improve the performance of plants in effective removal of metals from environment. With the help of this technique, overall functioning of plants can be altered. Addition of new genotype and phenotype by transferring the gene from metal-hyperaccumulating plants and microbes increases the remediation property of plants (James and Strand 2009). Aken (2008) has observed that transgenic plants can be safer for phytoremediation purpose. Isolation of quantitative trait loci (QTL) associated with tolerance of Zn metal in *Arabidopsis halleri* can be used for identifying the main genes responsible for adaptation against the metal stress (Nancy et al. 2007). When the bacterial merAB operon was transferred to the chloroplast genome of tobacco plant, then the plants showed more resistant toward highly toxic organic mercury (Heaton et al. 2005). To transfer the gene first DNA or gene of interest is spliced into a small, circular carrier DNA molecule which is known as a vector. After that the vector is introduced into plant cells either by physical means or biological means. When the foreign gene is entered into cell and integrated into the plant chromosome, the desired gene is “expressed” in a subset of the cells; these cells are selected in tissue culture and used to regenerate whole plants for subsequent breeding.

The extremely high level of Cd tolerance and hyperaccumulation in yeast is due to the presence of partial peptides from the C terminus of the TcHMA4 (the *Thlaspi* heavy metal ATPase) protein, which contains numerous possible His and Cys repeats residues for heavy metal binding. So this gene can be used for enhancing metal tolerance and phytoremediation potential of higher plants via expression of TcHMA4 (Fig. 2). It has great potential in metal remediation studies (Papoyan and Kochian 2004). Thomas et al. (2003) have shown that transgenic plants expressing metallothioneins exhibited enhanced tolerance to high metal concentrations. To increase metal uptake, the yeast metallothionein CUP1 was introduced into tobacco plants, and this gene is expressed in plants. Expression of these genes increases phytoextraction of Cu and Cd. By integrating dehaloperoxidase gene from salt marsh worm (*Amphitrite ornata*) into *Arabidopsis* and tobacco model systems, there was an enhancement in remediation property of experimental plants (Czako et al. 2006).

To remediate the methylmercury pollution, the tobacco plant was genetically modified by integrating a bacterial *merB* gene. The genetically modified tobacco callus showed more resistance to methylmercury (CH_3Hg^+). It accumulates more mercury from CH_3Hg^+ -containing medium than the wild-type. The *merB* gene encoded the MerB enzyme that degraded the CH_3Hg^+ to Hg^{2+} . After that it was accumulated in the form of less toxic Hg-polyP complex in the tobacco cells (Nagata et al. 2010).

By using micro-organisms

This remediation strategy includes application of micro-organisms. Bioremediation has been regarded as an environment-friendly, inexpensive and efficient means of



environmental restoration (Hryniewicz and Baum 2014). The role of micro-organisms is indirect as they support the growth of phytoaccumulator plants thus they help in the remediation of heavy metal (Yan-de et al. 2007; Zhuang et al. 2007). The micro-organisms, which are closely associated with roots, have been termed plant growth-promoting rhizobacteria (PGPR). Plant growth-promoting rhizobacteria include a diverse group of free-living soil bacteria that can improve host plant growth and development in heavy metal contaminated soils by mitigating toxic effects of heavy metals on plants. The association of plant growth-promoting bacteria with plant roots may exert beneficial effects on plant growth and nutrition by N_2 fixation, production of phytohormones and siderophores, and transformation of nutrient elements (Koo and Cho 2009). In mine tailings areas contaminated with heavy metal to increase growth of plant the PGPR are introduced to seeds of *Atriplex lentiformis* and *Buchloe dactyloides* at sowing stage (Grandlic et al. 2009). With improvement the growth and yield of the *Cicer arietinum*, *Vigna radiata* and *Pisum sativum*, metal toxicity is also decreased with the help of PGPR (Gupta et al. 2004; Wani et al. 2007, 2008). With the help of PGPR the increase in the growth and reduction in the metal toxicity is due to enhancement in soil nutrient so it is one of the most suitable choices for bioremediation (Zaidi et al. 2003; Khan et al. 2009). Heshmatpure and Rad (2012) have also observed that the *Pseudomonas fluorescence* plant growth-promoting rhizobacterium increases the resistance against high levels of Cd and reduces its adverse effect in canola (*B. napus* L.) plant. This rhizobacterium enhances the efficiency of phytoremediation in the presence of Cd. Kanmani et al. (2012) have also found that microbes, especially bacteria capable of Chromium (VI) reduction, belonging to a heterogeneous group. They exhibit plasmid-mediated chromate resistance and the reduction in Cr is enzymatically mediated.

Conclusion

Increasing public awareness of environmental pollution influences search and development of technologies that help in cleanup of contaminants such as heavy metals. Heavy metal contamination of ecosystem is a major environmental concern. In order to reduce the level of metal contamination, several remediation technologies have been implemented. These techniques include immobilization methods with the help of low-cost absorbent, application of some chelating agent and biology-based technique, i.e., phytoremediation. The techniques at the level of molecular and nanotechnology are also used to enhance remediation properties and open up new possibilities for metal remediation technique. The aim of all the remediation

technology should be linked with agricultural production, food security and scale down land tenure problems. Among all techniques, an alternative and eco-friendly remediation technology should be promoted in the developed and particularly developing countries, where heavy metal contamination is a serious problem with pace of population explosion and human developmental activities.

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