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Plant mediated detoxification of mercury and lead

Brajesh Kumar *, Kumari Smita, Luis Cumbal Flores *

Centro de Nanociencia y Nanotecnologia, Escuela Politécnica del Ejército (ESPE), Sangolqui, Ecuador

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KEYWORDS

Phytoremediation; Heavy metal; Phytoextraction; Toxicity; Biosorption **Abstract** In recent years, the development of efficient green chemistry methods for detoxification of metal poisoning has become a major focus of researchers. They have investigated in order to find an eco-friendly and recyclable technique for the removal of heavy metal (Pb^{2+} , Hg^{2+}) contamination from the natural resources. One of the most considered methods is the removal of Pb^{2+} , Hg^{2+} metal using green plants and their wastes. Among these plant wastes seem to be the best candidates and they are suitable for detoxification of heavy metals. Biosorption by plants involve complex mechanisms, mainly ion exchange, chelation, adsorption by physical forces and ion entrapment in inter and intra fibrillar capillaries and spaces of the structural polysaccharide cell wall network. The advantages of using green plants and their wastes for detoxification of heavy metal have interested researchers to investigate mechanisms of metal ion uptake, and to understand the possible utilization. In this review, we discuss the role of plants and their wastes for minimizing mercury and lead pollution with their toxic effect on both human beings and plants.

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1. Introduction

Environmental chemistry is an area of increasing interest both to chemists and to the general public. Nowadays, more and more people consider that the magnitude of pollution problem in our soils and water calls for immediate action. Among toxic substances reaching hazardous levels are heavy metals, including mercury, lead, chromium, arsenic, zinc, cadmium, uranium, selenium, silver, gold and nickel. The danger of heavy

E-mail addresses: krmbraj@gmail.com (B. Kumar), lhcumbal@espe.edu.ec (L. Cumbal Flores).

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metals is aggravated by their almost indefinite persistence in the environment due to their immutable nature. Unfortunately, the enormous cost associated with the removal of pollutants from soils and water by means of traditional physiochemical methods has been encouraging companies to ignore the problem. Conventional methods for heavy metal removal from aqueous solution and soil include chemical precipitation, electrolytic recovery, ion exchange/chelation, solvent extraction/liquid membrane separation and size exclusion processes (Esalah et al., 2000; Canet et al., 2002; Weirich et al., 2002; Shi et al., 2009; Li et al., 2009; Shao et al., 2010). But these methods are often cost prohibitive having inadequate efficiencies at low metal concentrations (Hammaini et al., 2003). Moreover, the resulting sludge has to be concentrated and its disposal or recovery of metals from the sludge represents an enormous problem (Cheng and Shang, 1994). The conventional technologies for effluent treatment are not economically feasible for small-scale industries that are prevalent

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^{*} Corresponding authors. Tel.: + 593 2 3989492, Mobile: + 593 095698124.

Table 1 Types	of heavy metals, permi.	Table 1 Types of heavy metals, permissible level, health hazards and sources.	
Metal contamina	Metal contaminant Permissible level (ppm) Health hazards) Health hazards	Major sources
Lead, Pb	0.1	Mental retardation in children, Liver, Kidney, gastrointestinal damage(GIT), causes sterility, anemia, muscle and joint pains, Hypertension	Paint, pesticides, smoking, batteries, water pipes, automobile emission, mining,
Mercury, Hg	0.01	Corrosive to skin, eyes and muscle membrane. Dermatitis, nervous and kidney damage, anorexia, protoplasm poisoning, severe muscle pain	outimus of coar, tamps Pesticides, batteries, paper and leather industry, thermometers, electronics, amalgam in denistry charmacenticals
Arsenic, As	0.02	Bronchitis, carcinogenic dermatitis, liver tumors, gastrointestinal damage (GIT)	Pesticides, fungicides, metal smelters, Coal fumes. Wood Preservatives
Zinc, Zn	5.0	Nervous membrane and skin damage, Causing short term illness called metal filme fever and restlessness	Refineries, brass manufacture, metal plating,
Cadmium, Cd	0.06	Kidney damage, bronchitis, carcinogenic, gastrointestinal disorder, bone marrow, cancer, weight loss	Welding, electroplating, pesticides, fertilizers, CdNi hatteries nuclear fission plant
Chromium, Cr	0.01	Allergic dermatitis, producing lung tumors, human carcinogens	Steel industry, mining, cement, paper, rubber, metal allov paints
Copper, Cu	3.0	Long term exposure causes irritation of nose, mouth, eyes, headache, stomachache, dizziness, diarrhea Brass manufacture, electronics, electrical pipes, additive for antifumoal	Brass manufacture, electronics, electrical pipes, additive for antifunoal
Nickel, Ni	3.0	Causes chronic bronchitis, reduced lung function, nasal sinus, cancer of lungs	Steel industry, mining, magnetic industry

Heavy metal ions are reported as priority pollutants, due to their mobility in natural water ecosystems and due to their toxicity. Heavy metals cannot be destroyed biologically, but only transformed from one oxidation state or organic complex to another. As a result of the alteration of its oxidation state. the metal may become either: (i) more water soluble and is removed by leaching, (ii) inherently less toxic, (iii) less water soluble so that it precipitates and then becomes less bioavailable or removed from the contaminated site, or (iv) volatilized and removed from the polluted area (Garbisu and Alkorta, 1997). Heavy metals are present in soil as natural components or as a result of human activity. Heavy metals even at low concentrations can cause toxicity to humans and other forms of life, their adverse effects on human health are quite evident from Table 1. The primary sources of metal pollution are the burning of fossil fuels, mining and smelting of metallic resources, downwash from power lines, municipal wastes, fertilizers, pesticides and sewage.

1.1. General aspects of phytoremediation

Phytoremediation is often also referred as botanical bioremediation or green remediation (Chaney et al., 1997) and defined as the use of green plants to remove pollutants from the environment or to render them harmless (Cunningham and Berti, 1993; Raskin et al., 1994), is being considered as a new highly promising technology for the remediation of polluted sites. This technology can be applied to both organic and inorganic pollutants present in soil (solid substrate), water (liquid substrate) or the air (Salt and Kramer, 1999). In this respect, plants can be compared to solar driven pumps which can extract and concentrate certain elements from their environment (Salt et al., 1995). However, the ability to accumulate heavy metals varies significantly between species and between cultivars within a species.

Phytoremediation is the use of plants to remove pollutants from the environment (Salt and Kramer, 1999) and is currently divided into the following areas (Table 2):

• *Phytoextraction:* the use of pollutant-accumulating plants to remove metals or organics from soil by concentrating them in the harvestable parts (Kumar et al., 1995). Pollutant-accumulating plants are utilized to transport and concentrate contaminants (metals or organics) from the soil into the above-ground shoots; the term is mostly used to refer to metal removal from soils. In some cases, roots can be harvested as well. Phytoextraction can be carried out either with or without added chelate complexant to assist in removing the metals. In certain cases the addition of chelating agents enhances the accumulation of metals by plants, especially if the chelate has a strong affinity for the targeted metal. Nevertheless, a consideration when

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Phytoremediation techniques	Action mechanism	Medium treated	Contaminant
Phytoextraction	Direct accumulation of contaminants into plant shoots with subsequent removal of the plant shoots	Soil	Inorganics
Rhizofiltration	Absorb and adsorb pollutants in plant roots	Surface water and water pumped through roots	Inorganics/ Organics
Phytostabilization	Root exudates cause metals to precipitate and biomass becomes less bioavailable	Groundwater, soil, mine tailings	Inorganics
Phytodegradation	Microbial degradation in the rhizosphere region	Groundwater within the rhizosphere and soil	Organics
Phytovolatilization	Plants evaporate certain metal ions and volatile organics	Soil, groundwater	Inorganics/ Organics
Phytotransformation	Plant uptake of organic contaminants and degradation	Surface- and groundwater	Organics
Removal of aerial contaminants	Uptake of various volatile organics by leaves	Air	_

using this method is the requirement that the chosen chelate must be biodegradable or readily removed from the contaminated site. Lead (Pb) is usually not available for plant uptake because it is extremely insoluble in the normal range of soil pH (Raskin et al., 1997). Thus, vegetation growing in heavily contaminated areas often has less than 50 mg/g Pb in shoots (Cunningham et al., 1995). Corn (Zea mays) and, to a lesser extent, ragweed (Ambrosia artemisiifilia) have been identified as good accumulators of Pb (Huang and Cunningham, 1996). But even plants, such as Brassica *juncea*, that have a genetic capacity to accumulate Pb, will not contain much Pb in roots or shoots if cultivated in Pb-contaminated soil (Raskin et al., 1997). A large proportion of many metals remains sorbed to solid soil constituents. The formation of metal-chelate complexes prevents precipitation and sorption of the metals thereby maintaining their availability for plant uptake (Salt et al., 1995).

- *Rhizofiltration:* the use of plant roots to absorb and adsorb pollutants, mainly metals (especially Pb), from water and aqueous waste streams (Dushenkov et al., 1995); which is the removal of pollutants from contaminated waters by precipitation, absorption and accumulation into plant biomass. Lead is accumulated in roots due to some physiological barriers against metal transport to aerial parts, while other metal such as Cd is easily transported in plants. Pelargonium (Arshad et al., 2008) and Brassica napus (Zaier et al., 2010) are characterized as Pb hyperaccumulators, and they can extract huge amounts of lead from contaminated soil without showing morphophytotoxicity symptoms. For most plant species, the majority of absorbed lead (approximately 95% or more) is accumulated in the roots, and only a small fraction is translocated to aerial plant parts, as has been reported in Viciafaba, Pisumsativum and Phaseolus vulgaris (Piechalaka et al., 2002; Maecka et al., 2008; Shahid et al., 2011), V. unguiculata (Kopittke et al., 2007), Nicotianatabacum, (Gichner et al., 2008), Lathyrussativus (Brunet et al., 2009), Z. mays (Gupta et al., 2009), Avicennia marina (Yan et al., 2010), non-accumulating Sedum alfredii (Gupta et al., 2010), and Allium sativum (Jiang and Liu, 2010).
- Phytostabilization: the use of plants to reduce the bioavailability of pollutants in the environment. Plants stabilize pollutants in soils, thus rendering them harmless and reducing

the risk of further environmental degradation by leaching of pollutants into the ground water or by airborne spread (Smith and Bradshaw, 1972). Lead may be immobilized by the formation of the lead phosphate mineral chloro pyromorphite in soils and within roots (Cotter-Howells et al., 1994), which has been shown to be formed in soils by *Agrostiscapillaris* growing on lead/zinc mining wastes (Cotter-Howells and Caporn, 1996).

- Phytodegradation: the use of plants and associated microorganisms (plant assisted bioremediation) to degrade organic pollutants. Plant roots in conjunction with their rhizospheric microorganisms are utilized to remediate soils contaminated with organics; the air purifying also uses some plants (Burken and Schnoor, 1997).
- *Phytovolatilization:* the use of plants to volatilize pollutants; and the use of plants to remove pollutants from air (Burken and Schnoor, 1999). It extracts volatile pollutants (e.g., selenium, mercury) from soil and volatilizes them from the foliage. By inserting an altered mercuric ion reductase gene (merA) into *Arabidopsis thaliana*, Rugh et al. (1996) reported the production of a mercury-resistant transgenic plant that volatilized mercury into the atmosphere.

Not only above groups are classified as phytoremediation but some authors also distinguish between indirect and direct phytoremediation (Stomp et al., 1994). In the case of indirect phytoremediation, plants participate in the detoxification of pollutants via their support of symbiotic, root-associated microorganisms that actually accomplish contaminant detoxification (plant-assisted bioremediation). On the other hand, plants could participate directly through contaminant uptake and subsequent contaminant immobilization or degradation within the plant. The development of phytoremediation is being driven primarily by the high cost of many other soil remediation methods, as well as a desire to use a 'green', sustainable process.

It is interesting to know that, phytotoxic element potential of hyperaccumulators is 100 times more than those found in nonaccumulators and metal concentration in the shoots of hyperaccumulator normally exceeds those in the roots. Also, it has been suggested that metal hyperaccumulation has the ecological role of providing protection against fungal and insect attack (Salt and Kramer, 1999; Chaney et al., 1997).

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Plant material	Metal ion	Result	Reference
Carica papaya wood	Hg (II)	96%	Basha et al. (2009)
Ricinus communis L. (Castor) leaves	Hg (II)	80%	Rmalli et al. (2008)
Sawdust (Acacia arabica)	Pb(II), Hg (II), Cr (VI), Cu(II)	Pb > Cr > Cu and Hg	Meena et al. (2008)
Oriza sativa husk	Pb(II)	98%	Zulkali et al.(2006)
Agricultural by product Humulus lupulus	s Pb(II)	75%	Gardea-Torresdey et al. (1998)
Agro waste of black gram husk	Pb(II)	Up to 93%	Saeed et al. (2005)
Febrifuga bark	Pb(II)	100%	Bankar and Dara (1985)
Waste tea leaves	Pb (II)	92%	Ahluwalia and Goyal (2005)
Rice bran	Pb (II), Cd (II), Cu (II), Zn (II)	>80.0%	Montanher et al. (2005)
Saw dust of Pinus sylvestris	Pb (II), Cd (II)	96%, 98%	Taty-Costodes et al. (2003)
Maple saw dust	Pb (II), Cu (II	80–90%	Yu et al. (2001)
Water hyacinth	Pb (II), Cu (II), Co (II), Zn (II)	70-80%	Kamble and Patil (2001)
Low cost sorbents (bark, dead biomass,	Pb (II), Hg (II), Cd (II), Cr (VI),	Good results	Bailey et al. (1999)
chitin, sea weed, algae, peat moss, leaf			
mold, moss			
Rice straw, soybean hulls, sugarcane bagasse, peanut and walnut shells	Pb (II), Cu (II), Cd (II), Zn (II), Ni (II) $Pb > Cu > Cd > Zn > 1$	Ni Johns et al. (1998)

Table 3 Some examples of selective detoxification of mercury and lead by biosorbents as plant material.

Hagemeyer and Hubner (1999) reported a conceivable redistribution of Pb in stems of spruce trees, possibly via the axial xylem sap stream or in rays. The metal transfer coefficients for Pb were considerably lesser than those for Cd and Zn (Labrecque et al., 1995). Huang et al. (1997) investigated the potential of adding chelates to Pb-contaminated soils to increase Pb accumulation in plants and showed that concentrations of lead in corn and pea shoots were greatly increased. Ethylenedia-mine tetra acetic acid (EDTA) was the most effective chelate in increasing Pb desorption from soil into the soil solution and also greatly increased the translocation of Pb from roots to shoots through prevention of cell wall retention.

1.2. General aspects of biosorption

Biosorption of heavy metals from aqueous solutions is a relatively new process that has proven to be very promising in the removal of contaminants from aqueous effluents. Adsorbent materials derived from low-cost agricultural wastes can be used for the effective removal and recovery of heavy metal ions from wastewater streams (Sud et al., 2008; Farooq et al., 2010).

Biosorption is not based on only one mechanism. It consists of several ones that differ quantitatively and qualitatively according to the type of biomass, its origin and its processing. Metal sequestration may involve complex mechanisms, mainly ion exchange, chelation, adsorption by physical forces and ion entrapment in inter and intra fibrilar capillaries and spaces of the structural polysaccharide cell wall network. Both living and dead biomasses (an inactive biomass) as well as cellular products such as polysaccharides can be used for metal removal. Various metal-binding mechanisms have been postulated to be active in biosorption (Gang and Weixing, 1998) by action of metallic ions toward the functional groups present in natural proteins, lipids and carbohydrates positioned on cell walls. Biomaterials previously investigated include use of fungal biomass (Guibal et al., 1992; Mathialagan and Viraraghavan, 2009), bacteria (Deleo and Ehrlich, 1994; Katircioglu et al., 2008; Rani et al., 2009), plants (Wankasi et al., 2006) and agricultural by-products (Horsfall and Abia, 2003; Pandey et al., 2007; Dang et al., 2009; Farooq et al., 2010).

Studies using biosorbents reveal that both living and dead microbial cells uptake metal ions, hence offering a potentially inexpensive alternative to conventional adsorbents. However, living cells often die due to the toxic effects of the heavy metals. In addition, living cells often require the addition of nutrients and hence increase the biochemical oxygen demand (BOD) and chemical oxygen demand (COD) in the effluent. Therefore the use of dead cells or non-living biomaterials as metal sequestering agents is fast gaining ground since toxic ions do not affect them (Folisio et al., 2008; Grimm et al., 2008). Most of these agricultural by-products are widely available and are of little or no economic value, and some of them in fact present a disposal problem (Table 3). Moreover, dead cells are cheaper, effective in reducing heavy metals to very low levels and require less care and maintenance. Furthermore, the dead biomass could be easily regenerated and reused (Wankasi et al., 2005; Horsfall et al., 2006).

1.2.1. General aspects of bioremediation

Bioremediation involves the use of biological remedies for pollution reduction (Shannon and Unterman, 1993). For metals this detoxification process must involve processes such as the oxidation or reduction of the metal center either to make it less water soluble, so that it precipitates and can be removed in solid form, or to convert it to a more volatile form that can be removed in the gas phase. In choosing a bioremediation strategy for metals, the biological system must be able to tolerate the concentration of metal that is present at the site.

2.1. Mechanism of biosorption binding

Metal biosorption is a complex process governed by several factors. Mechanisms involved in the biosorption process include chemisorption, complexation, adsorption–complexation on surface and pores, ion exchange, microprecipitation, heavy metal hydroxide condensation onto the biosurface, and surface adsorption (Gardea-Torresdey et al., 2004; Volseky, 2001). Plant cell walls are built by cellulose molecules, organized in microfibrils and surrounded by hemicellulosic materials (xylans, mannans, glucomannans, galactans, arabogalactans),

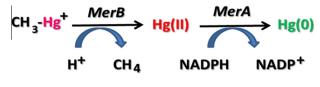


Figure 1 Phytoremediation of mercury.

lignin and pectin along with small amounts of protein (Noble, 1991). So, the functional groups (–OH or –COOH) present in the plant cell wall are responsible for metal binding via hydrogen bonding.

2.2. Mechanism for mercury phytoremediation

Elemental mercury is relatively inert, has very low solubility, and is gaseous at standard temperatures allowing its rapid evaporation from the bacterial habitat and dilution to normal, harmless atmospheric concentrations. The biochemical pathway for bacterial mercury resistance is conversion of methylmercury (MeHg) by MerB (organo mercurial lyase) to a still toxic product, ionic mercury [Hg(II)], then reduction by MerA (mercuric reductase) to the greatly detoxified volatile form, elemental mercury [Hg(0)] using NADPH as electron donor, as shown in Fig. 1. With respect to soil clean-up, the approach is still limited by a generally very low solubility of mercurial compounds in the soil solution. The reaction catalyzed by MerB limited the performance of the plants transformed with MerA and MerB. A specific enhancement in plant MerB activities was achieved by targeting the MerB protein to the cell wall or to the endoplasmatic reticulum, where the apolar organomercurials are believed to accumulate (Bizily et al., 2003).

2.3. Mechanism for lead phytoremediation

Lead forms various complexes with soil components, and only a small fraction of the lead is present as these complexes in the

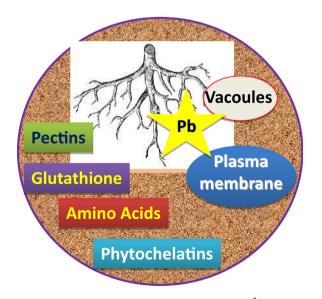


Figure 2 Schematic diagram of interaction of Pb^{2+} within the root of hyperaccumulators.

soil solution are phyto available. Despite its lack of essential function in plants, lead is absorbed by them mainly through the roots from soil solution and thereby may enter the food chain. So, there are several reasons why the transport of lead from roots to aerial plant parts is limited (Fig. 2). The absorption of lead by roots occurs via the apoplastic pathway or via Ca^{2+} -permeable channels. The behavior of lead in soil and uptake by plants are controlled by its speciation and by the soil pH, soil particle size, cation-exchange capacity, root surface area, root exudation, and degree of mycorrhizal transpiration. After uptake, lead primarily accumulates in root cells, because of the blockage by Casparian strips within the endodermis, sequestration in the vacuoles of rhizodermal and cortical cells by the formation of complexes (Seregin et al., 2004; Kopittke et al., 2007), immobilization by negatively charged pectins within the cell wall (Islam et al., 2007; Kopittke et al., 2007), accumulation in plasma membranes(Seregin et al., 2004; Islam et al., 2007; Jiang and Liu, 2010), binding by phytochelatins, glutathione, and amino acids (Clemens, 2006; Yadav, 2010), precipitation of insoluble lead salts in intercellular spaces (Kopittke et al., 2007; Islam et al., 2007; Mevers et al., 2008; Maecka et al., 2008) and synthesis of osmolytes.

3.1. Toxicity of Hg and Pb

The toxicological effects of mercury have resulted to cause various neurodegenerative diseases such as Amyotrophic lateral sclerosis, Alzheimer's diseases and Parkinson's disease (Mutter et al., 2004). Elemental mercury and inorganic mercury compounds have been reported to damage the immune system and kidneys (Holmes et al., 2009) while MeHg has been reported to pose a threat to the cardiovascular and nervous systems (Stem, 2005; Hogberg et al., 2010). Methylation results in the mercury being converted into a more lipophilic form that enters the food chain in products such as seafood. The greatest human health concerns are related to MeHg which has the ability to biomagnify in the food chain concerned with Minamata diseases in Japan. MeHg can be taken up by the aquatic organisms and further accumulate in fish. Therefore, populations living in areas of mercury contamination that consume a high amount of fish are at greatest risk of MeHg poisoning (Harada, 1995; Harada et al., 2001). Recent research has showed that rice will also accumulate MeHg from mercury contaminated soils in mercury mining areas (Zhang et al., 2010). Rice is now recognized as a major pathway for MeHg exposure in mercury mining areas of China (Zhang et al., 2010) where fish is not a major source of protein (Feng et al., 2008).

In nature, lead is predominantly found as a divalent cation with an affinity to bind to sulfhydryl groups on proteins, but without physiological function in the human body (Casas and Sordo, 2006). Lead is known to induce a broad range of toxic effects to living organism, including those that are morphological, physiological and biochemical in origin. Lead exposure decreases the concentration of divalent cations $(Zn^{2+}, Mg^{2+}, Ca^{2+}, and Fe^{2+})$ in human body. The biological half-life of Pb is about 35 days in blood, while in the brain it is about 2 years, and in bone lead lasts for decades (Rabinowitz et al., 1976).Use of lead paints in housing generates toxicity in young children's blood and children with high lead levels (six times) are more likely to have reading disabilities (Waldman, 1991). Indeed, the main target for lead toxicity

is the brain (Silbergeld, 1992), where it induces multiple effects. Pb causes oxidative stress (Ahamed and Siddiqui, 2007), affects calcium and zinc homeostasis (Godwin, 2001), neuro-transmission (Engle and Volpe, 1990), neurogenesis (Verina et al., 2007), damages mitochondria (Devi et al., 2005) and membrane integrity (Villeda-Hernández et al., 2001) and inhibits anti-oxidative enzymes (Godwin, 2001), finally leading to apoptosis, excitotoxicity, disruption of the blood brain barrier and neurodegeneration (Sanders et al., 2009).

3.2. Toxicity of Pb to plants

Lead is known to induce a broad range of toxic effects to living organism, including those that are morphological, physiological and biochemical in origin. This metal impairs plant growth, root elongation, seed germination, seedling development, transpiration, chlorophyll production, lamellar organization in the chloroplast and cell division (Sharma and Dubey, 2005; Krzesowska et al., 2009; Gupta et al., 2009, 2010; Maestri et al., 2010). It also causes phytotoxicity by changing the cell membrane permeability, by reacting with active groups of different enzymes involved in plant metabolism and by reacting with the phosphate groups of ADP or ATP, and by replacing essential ions. Lead toxicity causes inhibition of ATP production, lipid peroxidation and DNA damage by over production of reactive oxygen species (ROS). In addition, lead strongly inhibits seed germination, root elongation, seedling development, plant growth, transpiration, chlorophyll production and water and protein content.

3.3. Toxicity of Hg to plants

Although recognition of the toxicity of mercury to plants can be summarized as following: affect on the antioxidative system (Israr and Sahi, 2006); affect on the photosynthesis system (Patra et al., 2004); inhibition of plant growth and yield production and also an affect on nutrient uptake and homeostasis (Patra and Sharma, 2000); the inducement of genotoxicity (Sharma et al., 1990); some researchers also found that mercury in small quantity induces oxidative stress (Shiyab et al., 2009) and enhances lipid peroxidation (Cho and Park, 2000; Moreno-Jimenez et al., 2009) in plant cells, and subsequently increases the activity of antioxidant enzymes such as superoxide dismutase (SOD), ascorbate peroxidase (APX), glutathione reductase (GR), peroxidase (POD), as well as reduced glutathione (GSH). In terms of genotoxicity, a number of potentially reactive sites for mercury binding are present in DNA, depending on external conditions such as ionic strength, presence of different competing ions, and base composition (Sharma et al., 1990). Mercury, where present, could bind with DNA thus causing damage to chromosomes (Cenkci et al., 2009).

4. Conclusion

This review may generate useful information for the utilization of plant and its biomass wastes for the detoxification of heavy metals (lead and mercury). Phytoremediation and biosorption have many advantageous features that make it an appropriate and successful technology, giving practitioners a valuable option for remediation. These features make it to become the environmentally friendly method of choice because it is nonpolluting, low cost, does not require soil excavation, and is more acceptable to the public than chemical methods.

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