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Phytoremediation Mechanisms of Heavy Metal Contaminated Soils: A Review

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Abstract

Phytoremediation is a green emerging technology used to remove pollutants from environment components. Mechanisms used to remediate soils contaminated by heavy metal are: phytoextraction, phytostabilisation, phytovolatilization and rhizofiltration. The two first mechanisms are the most reliable. Many factors influence the choice of the suitable phytoremediation strategy for soil decontamination. It depends on soil properties, heavy metal levels and characteristics, plant species and climatic conditions. The present review discusses factors affecting heavy metals uptake by plant species, the different phytoremediation strategies of heavy metal contaminated soils and the advantages and disadvantages of phytoremediation and each of its mechanisms.

Keywords

Heavy Metal, Soils, Contamination, Phytoremediation

1. Introduction

Heavy metals are the major environmental contaminants and pose a severe threat to human and animal health by their long-term persistence in the environment [1]. The remediation of soils contaminated by heavy metals is a cost-intensive and technically complex procedure [2]-[5]. Conventional remediation technologies are based on biological, physical, and chemical methods, which may be used in conjunction with one another to reduce the contamination to a safe and acceptable level [6]. In spite of being efficient, these methods are expensive, time consuming and environmentally destructive [7] [8]. At the same time they are usually harmful to the natural soil

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environment, and generate large amounts of waste [9]. Recently, phytoremediation, which is an emerging technology, should be considered for remediation of contaminated sites because of its cost effectiveness, aesthetic advantages and long term applicability [10]-[13].

The aim of this paper is to provide a brief view about factors affecting heavy metals uptake by plant species, to discuss the different phytoremediation strategies of heavy metal contaminated soils and the advantages and disadvantages of phytoremediation and each of its mechanisms.

2. Heavy Metals: Definition and Origins

Heavy metals are natural constituents of the earth's crust [14] [15]. Their principal characteristics are an atomic density greater than 5 $g \cdot cm^{-3}$ [16] [17] and an atomic number >20 [14]. The most common heavy metal contaminants are Cd, Cr, Cu, Hg, Pb, and Zn. From the geochemical point of view, trace elements are metals whose percentage in rock composition does do not exceed 0.1% [18]. The occurrence of heavy metals in soils can result of two main sources:

Natural source: Heavy metals occur naturally in the soil environment from the pedogenetic processes of weathering of parent materials at levels that are regarded as trace (<1000 $mg \cdot kg^{-1}$) and rarely toxic [19] [20].

Anthropogenic sources: Human activities, such as mining, smelting, electroplating, energy and fuel production, power transmission, intensive agriculture, sludge dumping, and melting operations, are the main contributor to heavy metal contamination [15] [21]-[23]. Heavy metals in the soil from anthropogenic sources tend to be more mobile, hence bioavailable than pedogenic, or lithogenic ones [19] [24] [25]. The industry of mining and processing metals is a major source of farmland heavy metal contamination [26].

3. Heavy Metal Phytotoxicity

Metals are natural components in soil. Based on their role on physiological activities, they can be divided in two groups: 1) Essential heavy metals (Fe, Mn, Cu, Zn, and Ni) which are micronutrients necessary for vital physiological and biochemical functions of plant growth [1] [27] [28]. They are constituents of many enzymes and other proteins [29] and all plants have the ability to accumulate them from soil solution [30]; 2) Non-essential metals (Cd, Pb, As, Hg, and Cr) have unknown biological or physiological function [1] [31] and consequently are non-essential for plant growth.

Both groups are toxic to plants, animals and humans above certain concentrations specific to each element [17] [25] [32]. High contents of both essential and non-essential heavy metals in the soil may inhibit plant growth and can lead to toxicity symptoms in most plants [15] [29] [33] [34]. The general effects of various metals in plant are given in **Table 1**. However, some plant species have the ability to grow and develop in metalliferous soils such as near to mining sites [35]. Such plants can be used to clean up heavy metal contaminated sites. Willow (*Salix viminalis* L.), maize (*Zea mays* L.), Indian mustard (*Brassica juncea* L.), and sunflower (*Helianthus annuus* L.) has been found to be highly tolerant to heavy metals [36]. Vetiver grass (*Vetiveria zizanioides*) showed tolerance to Pb and Zn and it can be used for revegetating Pb/Zn mine tailings [37]. Populus species are examples of plants widely used to remediate heavy metal contaminated soils [38].

4. Factors Affecting Heavy Metal Phytoavailability

Bioavailability and phytoavailability are terms used to describe the degree to which contaminants are available for absorption or uptake by living organisms that are exposed to them [46]-[48]. Plants respond only to the fraction that is "phytoavailable" to them [48] [49]. For heavy metal phytoremediation (and phytoextraction in particular), bioavailability of metals in contaminated soils, is a crucial factor regulating heavy metal uptake by plant roots [50]-[52]. However, metal phytoavailability is a complex phenomenon that is dependent on a cascade of related factors [53].

4.1. Soil Properties

4.1.1. Soil pH

Soil pH directly influences the phytoavailability of metals as soil acidity determines the metal solubility and its ability to move in the soil solution [54]. Metal cations are the most mobile under acidic conditions while anions

Table 1. Functions and effects of heavy metals on plant growth [14] [35] [39]-[45].

Heavy metals		Functions in plant	Effects on plant
Essential metals	Copper (Cu)	- Constituent of enzymes; - Role in photosynthesis and several physiological processes; - Involved in reproductive and in determining yield and quality in crops (disease resistance)	- Disruption of photosynthesis, plant growth and reproductive processes; - Decreases thylakoid surface area
	Nickel (Ni)	- Constituent of enzymes - Activation of urease	- Reduction of: - seed germination; - protein production; - chlorophyll and enzyme production; - accumulation of dry mass
	Zinc (Zn)	- Constituent of cell membranes; - Component of a variety of enzymes; - DNA transcription; - Involved in reproductive phase and in determining yield and quality of crops; - Resistance against biotic and abiotic stress; - Legume nodulation and nitrogen fixation	- Reduces nickel toxicity and seed germination
Non-essential metals	Cadmium (Cd)	-	- Decreases seed germination, lipid content and plant growth - Disturb enzyme activities, - Inhibit the DNA-mediated transformation in microorganisms, - Interfere in the symbiosis between microbes and plants, - Increase plant predisposition to fungal invasion
	Chromium (Cr)	-	- Causes decrease in enzyme activity and plant growth; - Produces membrane damage, chlorosis and root damage.
	Lead (Pb)	-	- Reduces chlorophyll, chlorosis, necrosis; - Inhibit root and shoot growth - Less biomass production - affecting seed germination

tend to sorb to oxide minerals in this pH range [55]. Thus at low pH, metal bioavailability increases as more metals are released into the soil solution due to competition with H+ ions [56] [57]. At high pH, cations precipitate or adsorb to mineral surfaces and metal anions are mobilized [58]-[60]. At neutral or alkaline pH, most of the metals in soil are not available to plants, especially Pb and Cr are inherently immobile [61].

4.1.2. Soil Texture

Texture reflects the particle size distribution of the soil and thus the content of fine particles like oxides and clay [62]. Particle size distribution can influence the level of metal contamination in a soil. Fine particles (<100 µm) are more reactive and have a higher surface area than coarser material. As a result, the fine fraction of a soil often contains the majority of contamination [58] [62] reported that the fine textured soils contain higher amounts of Pb (3889 $mg \cdot kg^{-1}$) and coarse textured soil contains (530 $mg \cdot kg^{-1}$) lower amount of Pb.

4.1.3. Soil Organic Matter

Soil organic matter is frequently reported to have a dominant role in controlling the behavior of trace metals in the soil [62] [63]. The organic matter is one of the factors that may reduce the ability of metals to be phytotoxic in the soil due to metal-organic complexation [64]. The presence of organic carbon increases the cation exchange capacity of the soil which retains nutrients assimilated by plants [65]. Increasing the amount of organic matter in the soil helps to minimize the absorption of heavy metals by plants. Land rich in organic matter actively retains metallic elements [66]. Soils with relatively low organic matter concentration are more susceptible to contamination by trace elements [67]. Compost amendments to contaminated soils containing labile elements reduce the overall bioavailabilities of metals due to sorption processes [68].

4.1.4. Redox Potential

The redox potential is one of the most soil properties that affect changes metal speciation [69]. Redox potential in soil is established by oxidation-reduction reactions resulting from microbial activity [25] [66]. These redox reactions convert contaminants into non-hazardous or less toxic compounds that are more stable, less mobile and/or inert [70]. However, in soil environments, these reactions tend to be relatively slow [67]. Lack of oxygen in the soil causes start-up and increase the mobility of the large part of heavy metals [66].

4.1.5. Root Zone

Plant root can influence heavy metal phytoavailability [54] by modifying the soil properties in the rhizosphere [68]. The plant enzymes exuded from the roots should play a key role in the transformation and chemical speciation of heavy metals in soils, which facilitate their uptake by plant [71]-[73]. Plant root activities that potentially increase metal solubility and may change heavy metal speciation include acidification/alkalinisation, modification of the redox potential, exudation of metal chelants and organic ligands [74]-[76]. However, the process of root exudation and composition of exudates remains poorly understood for most of the environmentally relevant heavy metals [61] [73] showed that the increased mobility of heavy metals was not necessarily associated with their increased uptake in plants.

4.2. Heavy Metal Properties

The mobility of trace metals, their bioavailability and related eco-toxicity to plants depend strongly on their specific chemical forms [77]. Forms of occurrence of heavy metals in soil significantly influence their mobility. The most mobile elements include the Cd, Zn and Mo, while the least mobile are Cr, Ni and Pb [66]. Soil pH influences heavy metal mobility. In soils with low pH, metal mobilty decreases in the order: Cd > Ni > Zn > Mn > Cu > Pb. According to their phyto-availability, [78] have defined four groups of heavy metal (cited by [47]):

- weakly soluble in soil, absorbed by plants in trace amounts (Cr, Ag);
- elements relatively easily absorbed by roots but weakly transported to shoots (Hg, Pb);
- elements easily absorbed and transported to shoots (Zn, Cu, Ni);
- elements posing a risk to the food chain (Co, Cd).

However, the effect of pH on the mobility of metallic elements in the soil is highly variable, depending on the content and type of organic matter [66]. Heavy metals in the solid phase of organic-amended soils occur in various chemical forms, including exchange sites, specific adsorption sites, occluded or adsorbed on to soil oxides, biological residues and substituted into primary and secondary minerals [79]. The chemical speciation of heavy metals determines their bioavailability. It is related to the different natures of the metals, their bonding strength, and either in free ionic form or complexed by organic matter, or incorporated in the mineral fraction of the sample [63].

4.3. Plants Species

Plant species differ widely in their ability to accumulate heavy metals [80]. Many authors concluded that concentrations of metals in plants growing in the same soil vary between species and even between genotypes of a species [42] [81]. Some of the mechanisms, which may be responsible for plant species differences in metal concentrations, have been identified. These mechanisms include differences in: 1) root architecture; 2) water use efficiency; 3) rhizosphere chemistry; 4) expression and affinity of root surface transporter proteins for metals; 5) xylem loading of metals and translocation within the plant [82]. Also, the age and the growth stage of the plant can affect concentration of metals in plants [54] [80].

5. Phytoremediation

5.1. Definition and Concept

Phytoremediation can be defined as the process, which uses green plants for the relief, transfer, stabilization or degradation of pollutants from soil, sediments, surface waters, and groundwater [54] [83] [84]. Some plant roots can absorb and immobilize metal pollutants, while other plant species have the ability of metabolizing or accumulating organic and nutrient contaminants. Multifarious relationships and interactions between plants, microbes, soils and contaminants make these numerous phytoremediation processes possible.

The term phytoremediation, from the Greek phyto, means "plant", and the Latin suffix remedium, "able to cure" or "restore" [44]. This concept was first proposed by Chaney (1983) and then developed through the study of plant species ability to remove pollutants from environment components. It can be used for a wide range of organic [10] and inorganic contaminants [44]. Phytoremediation processes are most effective where contaminants are present at low to medium levels, as high contaminant levels can inhibit plant and microbial growth and activity [85]. Mechanisms involved in the uptake, translocation, and storage of micronutrients are the same involved to translocate and storage heavy metals [1].

5.2. Mechanisms of Phytoremediation

Phytoremediation is a general term including several processes, in function of the plant-soil-atmosphere interactions. For heavy metal contaminated soil, four processes of phytoremediation are recognized. Phytoextraction, phytostabilisation, phytovolatilization and rhizofiltration. The two first mechanisms are the most reliable. The different forms of phytoremediation require different general plant characteristics for optimum effectiveness [86]. **Table 2** summarizes definition and principle characteristics of each process.

5.3. Advantages and Limitations of Phytoremediation Mechanisms

Phytoremediation, like other remediation technologies, has a range of both advantages and disadvantages. The most positive aspect of using phytoremediation is as follow: 1) more cost-effective; 2) more environmentally friendly; 3) applicable to a wide range of toxic metals and 4) more aesthetically pleasing method. On the other hand, phytoremediation presents some limitations. It is a lengthy process, thus it may take several years or longer to clean up a site and it is only applicable to surface soils. Advantages and disadvantages of using phytoremediation for remediation a heavy metals contaminated area and each mechanism are shown in **Table 3** and **Table 4**.

6. Plant Selection Considerations

Plant species for phytoremediation are selected based on their root depth, the nature of the contaminants and the soil, and regional climate. The root depth directly impacts the depth of soil that can be remediated [83]. It varies greatly among different types of plants, and can also vary significantly for one species depending on local conditions such soil structure, depth of a hard pan, soil fertility, cropping pressure, contaminant concentration, or other conditions [86]. The cleaning depths are approximately <3 feet for grasses, <10 feet for shrubs and <20 feet for deep rooting trees. The nature of on-site contaminants is a principal factor in the selection of a plant for phytoremediation [103].

It has been reported that for phytoremediation, grasses are the most commonly evaluated plants [104]. They have been more preferable in use for phytoremediation because compared to trees and shrubs, herbaceous plants, especially grasses, have characteristics of rapid growth, large amount of biomass, strong resistance, effective stabilization to soils and ability to remediate different types of soils [54]. They are pioneers and usually are adapted to adverse conditions such as low soil nutrient content, stress environment and shallow soils [105]-[109]. The large surface area of their fibrous roots and their intensive penetration of soil reduces leaching, runoff, and erosion via stabilization of soil and offers advantages for phytoremediation [110]. Wild plants such as grasses can produce closures above ground quickly and reduce dispersion the dust of tailings [111].

Shrubs and trees produce extensive canopy cover and produce deep roots to prevent erosion in the long term. In addition, shrubs or trees provide high nutrient to the grass while lowering water stress and improve soil physical properties [111] [112]. Many trees can grow on land of marginal quality, have massive root systems, and their above-ground biomass can be harvested with subsequent resprouting without disturbance of the site [113]. However, the cost for planting trees is high and the growth rate is low.

To achieve a stable persistent cover it is important to use a mixed culture, and combine grasses, shrubs and trees in revegetation programs of mining soils because they represent two functional types of plants with different roles in the improvement of mine soils. For a longer duration, as considered for most phytoremediation

Table 2. Definition and main characteristics of phytoremediation processes [1] [23] [44] [54] [70] [83] [85] [87]-[96].

Process	Definition	Process goal	Contaminants	Media	Selection criteria of plant species
Phytoextraction	Uptake of a contaminant by plant roots from the environment and its translocation into harvestable plant biomass	Contaminant extraction and capture	Organic and inorganic pollutants	- Soils; - Sediments; - Water; - Sludges.	- Tolerance to high concentrations metals; - High metal-accumulation capability; - Rapid growth rate; - Accumulation of trace elements in the above ground parts; - Easy to harvest; - Extended root system for exploring large soil volumes; - High translocation factor; - Easy agricultural management; - Good adaptation to prevailing environmental and climatic conditions; - Resistance to pathogens and pests; - Rrepulse herbivores to avoid food chain contamination.
Phytostabilization	Reduction of mobility and bioavailabilit y of pollutants in environment either by physical or chemical effects	Contaminant containment	Heavy metals; Chlorinated solvents	- Soil; - Sediments; - Sludges.	- The ability to develop extended and abundant root systems; - The ability to keep the translocation of metals from roots to shoots as low as possible; - The capacity to retain the contaminants in the roots or rhizosphere (excluder mechanism) to limit the spreading through the food chain.
Phytovolatilization	The process of absorption of pollutants by plants and volatilization into the atmosphere by the foliar system	Contaminant extraction from media and release to air	Chlorinated solvents; Inorganic compounds	- Grouwndwat er - Soil - Sediments - Sludges	
Rhizofiltration	The use of plant roots to absorb or adsorb contaminants that are in solution surrounding the root zone	Contaminant extraction and capture	Heavy metals; Ogranic compounds	- Surface Waters; - Wastewaters.	- Metal-resistant plants; - High adsorption surface; - Tolerance of Hypoxia; - Terrestrial plants are preferred because they have a fibrous and much longer root system, increasing the amount of root area.

processes, it cannot be expected to clean up the soil only by one plant species used exclusively in monoculture [114]. Grasses, with their highly developed root system, can stabilize the soils and reduce erosion, while legumes can add nitrogen to the soil, preparing the establishment of other plant species typical of later stages of succession [115]-[117].

Perennial grasses develop a large plant biomass in a relatively short time and are recognized as heavy metal tolerant biosystems, accumulating high levels of these elements [54]. However, the shorter growing period of the seasonal flowering plants is a better option in phytoremediation over perennial plants, as it can be harvested yearly or seasonally, and the area can be replanted with subsequent seasonal flowering plants [109].

For phytoremediation, it is better to use plant species adapted to the climatic and soil conditions of the

Table 3. Advantages and limitations of phytoremediation [11] [12] [23] [54] [56] [84] [97] [98].

Advantages	Limitations
Cost	Time
- Low capital and operating cost; - Metal recycling provides further economic advantages.	- Slower compared to other techniques and seasonally dependent; - Most of the hyperaccumulators are slow growers.
- Low capital and operating cost; - Metal recycling provides further economic advantages.	- Slower compared to other techniques and seasonally dependent; - Most of the hyperaccumulators are slow growers.
Performance	
- Permanent treatment solution; - Capable of remediating bioavailable fraction of contaminants; - Capable of mineralizing organics; - The potential to treat sites polluted with more than one type of pollutant; - It is restricted to the rooting depth of remediative plants; - Highly-specialized personnel not required; - Can be used for site investigation or after closure.	- Not capable of 100% reduction; - High contaminant concentration may be toxic to plants; - Soil phytoremediation is applicable only to surface soils; - Restricted to sites with low contaminant concentrations; - Requires technical strategy, expert project designers with field experience that choose the proper species and cultivars for particular metals and regions.
Application	
- In situ application avoids excavation and transport of polluted media; - Relatively easy to implement. -	- The presence of multiple types of heavy metals and organic contaminants may pose a challenge; - Climatic conditions are a limiting factor.
Impact in the environment and population	
- Reduce the risk of spreading the contamination; - Eliminate secondary air or water borne Wastes; - Public acceptance due to aesthetic reasons.	- Metals can be washed by rain and transported back into the soil du the decomposition of plant biomass; - The use of invasive, non-native species can affect biodiversity; - Risk of food chain contamination in case of mismanagement and lack of proper care.

area to be de-polluted [54] [86] [118]. Use of indigenous plant species is generally favoured because they show tolerance to imposed stress conditions, require less maintenance and present fewer environmental and human risks than non-native or genetically altered species [119]. However, particular non- native plant may work best remediation of specific contaminant and can be safely used under circumstances where the possibility of invasive behaviour has been eliminated [120].

7. Conclusion

Phytoremediation is a promising green technology that can be used to remediate heavy metal contaminated soils. In developing countries like Morocco, this technology can provide low-cost solution to remediate contaminated area, especially abandoned industrial sites (mines and landfills). The complexity of factors that control the efficiency of this technique, such as soils properties, plant species and climatic conditions, fact that more researches need to be conducted. More species that have remediative abilities need to be identified, especially the plants that can contribute to social and economic development of local population, such as industrial species. Also, in the future, research should focus on developing agricultural techniques to enhance phytoremediation efficiency and reduce time and cost of heavy metal removal from soils. The valorization of some industrial residue in order to increase the heavy metal phytoavailability can be investigated.

Table 4. The advantages and limitations of various mechanisms of phytoremediation [54] [85] [89] [99]-[102].

Mechanisms	Advantages	Limitation
Phytoextraction	- The cost of phytoextraction is fairly Inexpensive; - The contaminant is permanently removed from the soil ; - The amount of waste material that must be disposed of is substantially decreased (up to 95%); - The contaminant can be recycled from the contaminated plant biomass.	- Metal hyperaccumulators are generally slow-growing with a small biomass and shallow root systems; - Plant biomass must be harvested and removed, followed by metal reclamation or proper disposal of the biomass; - Metals may have a phytotoxic effect.
Phytostabilization	- The disposal of hazardous material or biomass is not required ; - 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; - Soil removal is unnecessary; - It has a lower cost and is less disruptive than other more-vigorous soil remedial technologies; - Revegetation enhances ecosystem restoration; - Method with good results in prevention of acid mine discharges and metal stabilization.	- The contaminants remain in place; - The vegetation and soil may require long-term maintenance to prevent rerelease of the contaminants and future leaching; - Vegetation may require extensive fertilization or soil modification using amendments; - Plant uptake of metals and translocation to the aboveground portion must be avoided; - The root zone, root exudates, contaminants, and soil amendments must be monitored to prevent an increase in metal solubility and leaching; - Phytostabilization might be considered to only be an interim measure; - Contaminant stabilization might be due primarily to the effects of soil amendments, with plants only contributing to stabilization by decreasing the amount of water moving through the soil and by physically stabilizing the soil against erosion.
Phytovolatilization	- The contaminant, mercuric ion, may be transformed into a less toxic substance; - Contaminants could be transformed to less-toxic substances; - Contaminants or metabolites released to the atmosphere might be subject to more effective or rapid natural degradation processes such as photodegradation.	- The contaminant or a hazardous metabolite might be released into the atmosphere; - The contaminant or a hazardous metabolite might accumulate in vegetation and be passed on in later products such as fruit or lumber; - Low levels of metabolites have been found in plant tissue.
Rhizofiltration	- The ability to use both terrestrial and aquatic plants for either in situ or ex situ applications; - Species other than hyperaccumulators may be used; - An ex situ system can be placed anywhere because the treatment does not have to be at the original location of contamination.	- The constant need to adjust pH to obtain optimum metals uptake; - Plants may first need to be grown in a greenhouse or nursery; - Periodic harvesting and plant disposal are required; - Tank design must be well engineered; - A good understanding of the chemical speciation/interactions is needed; - The chemical speciation and interaction of all species in the influent have to be understood and accounted for; - Metal immobilization and uptake results from laboratory and greenhouse studies might not be achievable in the field.

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