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Phytoremediation of Heavy Metal-Contaminated Soils: An Overview of Principles and Expectations for Fundamental Techniques

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Abstract: The earth is currently dealing with a variety of issues and is losing its potential as a result of climate change brought on by increasing industrialization and urbanization. Harmful metals wastes generated by anthropogenic processes such as household, municipal, agricultural, industrial, and military operations penetrate the soil, decreasing its quality and usefulness. Because soil is the foundation of life, it necessitates excellent remediation activity. The problem of soil pollution is no longer being ignored because it is limited or no new land to replace. Therefore, the objective of this review paper is to explore the concepts and promises of basic phytoremediation approaches for heavy metal-contaminated soils. The use of living organisms, particularly plants (phytoremediation), is one of the remediation approaches that is now being used. In comparison to other soil remediation approaches, phytoremediation is an effective and affordable technology that can work with few maintenance costs once established, is suited for vast regions with low to moderate amounts of contaminants, and is ecologically benign. Phytoremediation, on the other hand, is a long-term remediation option, and not all of its remediation procedures are optimal. For example, in the case of phytovolatilization, air pollution may occur, while in the case of phytoextraction, pollutants collected in leaves may be released back into the environment during litterfall. Therefore, future concerns should be directed toward the modification and improvement of phytoremediation technologies that are likely to improve metal-binding abilities in plant tissues and phyto-transform toxic metals. Finally, it is critical to minimize or avoid the release of harmful compounds into the environment, in addition to enhancing and adapting various techniques.

Keywords: Heavy Metal, Pollutant, Phytoremediation, Toxicity

1. Introduction

Heavy metals are conventionally known as natural elements with metallic properties (ductility, conductivity, stability as cations, ligand specificity, etc), higher atomic weights, and a density five times greater than that of water [60, 115]. The most common and important heavy metals are As, Sr, Cs, U, Cd, Cr, Cu, Hg, Pb, and Zn [63, 96]. Some of these metals such as Zn, Cu, Mn, Ni, and Co are micronutrients necessary for plant growth and development while others (Cd, Pb, and Hg) have unknown biological functions [42]. As stated by Jayanthi *et al*. [56]; Shazia *et al*. [106], heavy metals are not only cytotoxic but also carcinogenic and mutagenic in nature even when present at trace amount [56, 106]. For instance, the U.S Environmental Protection Agency and International Agency for Research on Cancer declared certain heavy metals like Pb, Cd, Hg, As and Cr as the most toxic of all pollutants and termed them carcinogens due to their potential problems to human health [115].

Electronics, automotive, ceramics, glass, paints, pigments, fertilizers, reagents, alloys for diverse uses, and so on are examples of heavy metal resources attributed to the fundamental acquired usefulness that are produced directly or indirectly from heavy metals. As a result, human socioeconomic progression is becoming increasingly reliant on the use of various heavy metals, necessitating the extraction of enormous quantities of these resources as industrialization and urbanization progress [73]. However, most human activities emit non-recovered heavy metal-containing pollutants into the soil on a daily basis [78]. As a result, their negative consequences on human health and the environment are rapidly expanding [31] athering of minerals, erosions, and volcanic activity are the most significant natural sources, while mining, smelting, electroplating, excessive use of pesticides, fertilizer discharge, biosolids (livestock manures, composts, and municipal sewage sludge), atmospheric deposition, and other anthropogenic sources are also significant [38, 99]. To be sure, heavy metal pollution and its effects on environmental quality and human health are well-known global issues [20, 105].

Table 1. *Potential sources of heavy metals.*

Heavy Metal	Sources	References
Arsenic*	Mining, smelting, pesticides, bio-solids, wood preservatives, petroleum refining, food additives, coal-based power plants, volcanic eruptions.	[31, 37]
Mercury*	Volcanic activities, waste from caustic soda industry, Gold-Silver mining, medical waste, peat, burning of wood and coal.	[31, 36]
Lead*	Petroleum derivatives, mining, paints, smelting, industrial and municipal sewage, pesticides, wastes from batteries,	[31, 73]
Cadmium*	Smelting, sludge, combustion of fossil fuels, phosphate fertilizers, paint, pigments, plastic stabilizers, electroplating.	[31, 36]
Chromium*	Electroplating, sludge, solid wastes, fly ash, tanning, textile, steel and pulp processing industries.	[31, 73]
Copper**	Copper polishing, mining, paint, plating, printing operations	[31, 36]
Nickel**	Electroplating, non-ferrous metal, paints, porcelain enameling	[36, 23]
Selenium**	Coal combustion, mining	[31]
Silver**	Battery manufacture, mining, photographic processing, smelting	[85, 84]

Source: Ayansina and Olubukola, [10] **; Mukhtar *et al*. [79] *

Several strategies for cleaning up the environment from these types of toxins are already in use, but the majority of them are expensive and fall short of their potential. Chemical procedures produce significant volumes of sludge, which raises expenses [87]; chemical and thermal processes are technically challenging and costly, and they can destroy soils' valuable components [50]. Traditionally, heavy metal contaminated soils have been remedied by either onsite management or excavation and subsequent disposal to a landfill. This type of disposal only relocates the contamination problem, as well as the risks associated with transporting polluted soil and contaminant migration from the landfill into the surrounding ecosystem. Soil washing is an alternative to excavation and landfill disposal for clearing polluted soil. However, this process is expensive and produces a heavy metal-rich residue that will require further treatment. Furthermore, because these physio-chemical procedures for soil remediation remove all biological activity, they render land unusable as a substrate for plant growth [42].

Concerns about environmental pollution have prompted the development of devices to determine the presence and mobility of metals in soil [108]. Phytoremediation is now an effective and cost-effective technological technique for removing metal contaminants from polluted soil. Because the expenses of cultivating a crop are low compared to the costs of soil removal and replacement, plant-based remediation solutions can operate with little upkeep once established. Phytoremediation is ten times cheaper than engineering-based remediation technologies such soil excavation, soil washing or burning, or pump-and-treat systems because biological processes are ultimately solar-driven [41].

The fact that phytoremediation is done in situ adds to the cost-effectiveness of the process and may limit the amount of polluted substrate that is exposed to humans, wildlife, and the environment [82]. It is not, however, always the greatest answer to a contamination issue. The application of phytoremediation is limited by the meteorological and geological characteristics of the cleaning site, such as temperature, altitude, soil type, and agricultural equipment accessibility [100]. Furthermore, soil factors such as pH, organic matter, and clay concentration influence heavy metal bioavailability [8]. The use of a phytoremediation strategy may cause some issues. Woods that accumulate contaminants, for example, might be utilized as fuel, while pollutants gathered in leaves can be released back into the ecosystem during litterfall [100]. Many of the limits of phytoremediation can be summarized as follows: pollutants must be accessible to a plant and its root systems [82].

The problem of soil pollution is no longer being ignored because it is limited or no new land to replace. Furthermore, it is self-evident that the "used up" soil resource must be refined in an environmentally responsible and cost-effective manner in order to sustain life on Earth. Therefore, the major objective of this review paper is to explore the concepts and promises of basic phytoremediation approaches for heavy metal-contaminated soils.

2. Phytoremediation of Soils Polluted with Heavy Metals

2.1. An Overview of Phytoremediation Technology

Phytoremediation is a newly evolving field of science and technology that uses plants and their associated rhizospheric microorganisms to extract, sequester, and/or detoxify a wide variety of environmental contaminants [72]. A set of ecological techniques that employ plants in situ to promote pollutant breakdown, immobilization, and removal from the environment. It is a green technology that is frequently the most cost-effective treatment for metal-polluted soils, especially in cases of widespread pollution [27]. Because many cropping cycles may take several years to decrease metals to acceptable regulatory levels, phytoremediation should be seen as a long-term remediation strategy.

Plants have a unique ability to concentrate elements and compounds from the soil and metabolize the molecules in their tissues, which is used in phytoremediation [45]. Plant roots can play a key role in metal removal via filtration, adsorption, and cation exchange, as well as plant-induced chemical changes in the rhizosphere, because the majority of plant roots are located in the soil [32, 129]. Physiological adaptations also regulate hazardous metal accumulations in the roots by sequestering metals [43]. Variations in plant species, plant growth stage, and element characteristics may all influence metallic pollutant absorption, accumulation, and translocation.

The greatest progress in phytoremediation has been made with heavy metals [17, 128]. Soil-focused phytoremediation technologies are suitable for large areas which have been contaminated with low to moderate levels of contaminants. Phytoremediation will not be able to remediate extremely contaminated sites since the harsh conditions will prevent plant development and survival. The amount of soil that can be cleansed or stabilized is limited to the root zone of the plants. This depth might range from a few inches to many meters, depending on the plant [102].

Table 2. *List of plant species utilized for phytoremediation of heavy metals.*

Heavy Metal	Plant Species	References
Fe, Al, Cu, Mn, Cr, As, Zn, Hg	Jatropha (*Jatropha curcas* L.) **	[55, 131]
Cu, Fe, Mn, Zn, Ni, Cd, Pb, Co, As	Lettuce (*Lactuca sativa* L.) **	[3, 86, 88]
Pb, Cu, Zn, Fe, Cd, Ni, As, Cr	Pea (*Pisum sativum* L.) **	[39, 49, 66, 103, 127]
Cd, Cu, Fe, Ni, Pb, Zn, Cr	Spinach (*Spinacia oleracea* L.) **	[1, 54, 80, 81, 95]
As, Cd, Fe, Pb, Hg	Cress (*Lepidium sativum* L.) **	[44, 111]
As, Cd, Fe, Pb, Cu	Radish (*Rapanus sativus* L.) **	[44, 47]
Cd, Cu, Pb, Zn	*Salix* spp. (*S. viminalis, S. fragilis*) *	[94, 123]
	Populus spp. (*P. deltoides, P. nigra, P. trichocarpa*)*	[94]
	Brassica juncea L.**	[11, 103, 109, 118]
	Canola (*Brassica napus*) **	[29, 107, 118]
	Zea mays L.**	[1, 117]
Cd, Cu, Ni, Pb	Jatropha (*Jatropha curcas* L.)*	[2, 55]
Cd, Pb, Cr, Cu	Chickpea (*Cicer aeritinum* L.)**	[28, 57, 126]
Cd, Pb, Zn	*Zea mays**	[74]
As, Cd	pigeon pea (*Cajanus Cajan*)**	[39]
Cu, Cd	Rice (*Oryza sativa* L.)**	[65]
Pb	Lantana (*Lantana camara* L.)**	[6]
	Lentil (*Lens culinaris* Medic.)**	[125]
Cd	Castor (*Ricinus communis*)*	[52]
	Alfalfa (*Medicago sativa* L.)**	[40]
Hg	*Populus deltoides**	[22]
Se	*Brassica juncea, Astragalus bisulcatus**	[15]
Zn	*Populus canescens**	[16]

Source: Dixit *et al.* [31] *; Sumiahadi and Acar, [112] **

Plants have a range of potential mechanisms at cellular level that might be involved in the detoxification and tolerance to heavy metal stress. These are all involved in preventing toxic amounts from accumulating at sensitive sites in the cell, thereby preventing harmful effects [46]. When metals build up in tissues, they induce toxicity both directly and indirectly by destroying cell structure and replacing critical nutrients [113].

Heavy metal build-up can be avoided in a variety of ways [46, 75]. Metal accumulation can be avoided by restricting metal movement to roots with the help of mycorrhizal fungi. Huang et al. [52], for example, described a Zn exclusion strategy in arbuscular mycorrhizal fungi associated with Zea mays. According to Marques et al. [67], reducing the influx through the plasma membrane as well as binding to cell wall and root exudates could be viable avoidance methods for Zn retention in Solanum nigrum cell walls. Plants may also use other strategies to avoid metal build-up, such as stimulating metal efflux into the apoplast. Benaroya et al. [12] demonstrated that this stimulation happened and that the apoplastic accumulation of Pb in Azolla filiculoides was significant, as well as the chelation of different ligands in the cytosol. Metal detoxification abilities in plants are aided by ligands such as phytochelatins and metalotheins, as demonstrated by the engineered Nicotiana tabacum [75]. The transport and buildup of metals in the vacuole is one proposed avoidance tactic. Thlaspi goesingense, for example, improves Ni tolerance by transferring and compartmentalizing most of the internal leaf Ni into the vacuole [59].

2.2. Principles and Promises of Fundamental Phytoremediation Processes

Generally, a number of phytoremediation strategies are possible with distinct mechanism of action for the remediation of metal-polluted soils [69, 122]. Phyto-stabilization, in which plants are utilized to stabilize rather than clean contaminated soil, is one of them. Phyto-volatilization, in which plants extract certain metals from soil and then release them into the atmosphere [124]; phyto-extraction, in which plants absorb metals from soil and translocate them to harvestable shoots, where they accumulate [61]; phyto-filtration, which includes rhizo-filtration (use of plant roots), blasto-filtration (use of seedlings), and caulo-filtration (use of excised plant shoots) [76]. and phyto-degradation, which involves the breakdown or modification of metals within tissues by enzymes [7].

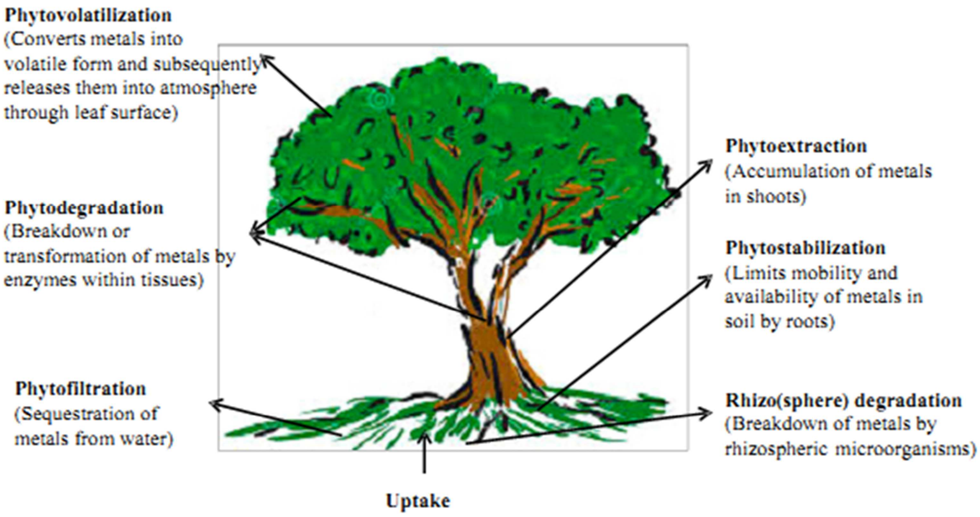


Figure 1. *Various processes of heavy metals' phytoremediation [31].*

2.2.1. Phyto-stabilization of Heavy Metals

Phyto-stabilization refers to grow plants on soils polluted by heavy metals [64] with principal purpose to stabilize the contaminants by limiting their mobility [5] and bioavailability [64] via the plant roots [4]. For effective stabilization, plants should be resistant to heavy metals [64]. It is predominantly applicable for remediation of heavy metals including Ar, Cr, Cd, Zn and Cu [62]. The research of Smith and Bradshaw [110], led to the development of two cultivars of *Agrostis tenuis* Sibth. and one *Festuca rubra* L. which are used for phyto-stabilization of Pb, Zn, and Cu.

Phyto-stabilization can help in a variety of circumstances involving large areas of surface contamination [26]. Phyto-stabilization is not a possibility in some highly contaminated locations since plant growth and survival are impossible [14]. Phyto-stabilization has several advantages over other soil-remediation techniques, including cost, environmental impact, ease of implementation, and aesthetic appeal [14, 101]. It also minimizes soil erosion and heavy metal migration to far-flung locations [90].

2.2.2. Phyto-extraction of Heavy Metals

Phyto-extraction, the most commonly recognized of all phytoremediation technologies, is predominantly applicable for the clean-up of polluted soils [4]. It concerned with to the use of hyper-accumulator plants [70] that are adapted to uptake large quantities of heavy metals from soil through their roots [19] and subsequently, translocate them to the above ground portions [5] where they can be stored [31] in large concentrations. As a result, the plant biomass is increased [19] and then the above-ground portions are harvested and removed so as to assure permanent deletion of metals from the site [73]. However, in some cases, the disposal of contaminated material may become an issue. As a result, some studies propose burning of harvested plant tissue, which drastically minimizes the volume of waste that must be disposed of [61]. If important, valuable metals can be recovered from the metal-rich ash and serve as a source of revenue, thereby compensating the expense of cleanup [24, 25].

Phyto-extraction should be seen as a long-term remediation activity that will take many cropping cycles to achieve acceptable metal concentrations [61]. The amount of time required for remediation varies depending on the kind and extent of metal contamination, the length of the growing season, and the efficiency with which plants remove metal; however, it typically takes 1 to 20 years [17, 61]. Because plant growth is not sustained in extremely polluted soils, this approach is suited for the restoration of broad areas of land that are damaged at shallow depths with low to moderate amounts of metal pollutants [17, 61]. Metals in the soil should also be bioavailable, or able to be absorbed by plant roots.

Pollutants that dissolve in water are easily extracted by plants [5]. In the usual range of soil pH, for example, Pb is very insoluble and unavailable for plant uptake. As a result, plants growing in extremely contaminated locations frequently has shoots with less than 50 mg Pb g-1 [26]. When grown in Pb-contaminated soil, even plants with the genetic capacity to accumulate Pb, such as B. juncea, will not have much Pb in their roots or shoots. The finding that certain soil-applied chelating chemicals dramatically accelerate the translocation of heavy metals, particularly Pb, from soil into shoots, provided the answer to the metal availability problem [18].

For the process to be efficient, plant should be able to tolerate high metal concentrations [70] and be efficient at translocating them from roots to the harvestable above-ground portions of the plant [17]. Furthermore, the plants are desirable to cope with difficult soil conditions (soil pH, salinity, soil structure, water content, etc) plus disease and insect problems. In fact, the success of phyto-extraction is inextricably linked to two key plant features. These abilities include the ability to rapidly create enormous amounts of biomass and the ability to accumulate high amounts of heavy metals in shoot tissues [18, 71]. Brassica juncea, while having one-third the Zn concentration in its tissue, is more successful in removing Zn from soil than Thlaspi caerulescens, a recognized hyper-accumulator of Zn, according to Ebbs et al. [34]. The fact that B. juncea produces ten times more biomass than T. caerulescens contributed to this advantage.

Adsorption: Root surfaces with enormous surface areas and high-affinity chemical sensors evolved specifically to absorb elemental contaminants from soils [30] and many elemental contaminants attach to root surfaces during the adsorption process [48, 97]. For example, Indian mustard (Brassica juncia) can rapidly concentrate Cd^{2+}, Ni^{2+}, Pb^{2+}, and Sr^{2+} into root tissues at 500 times the amounts seen in the liquid media in which it grows [97]. Sunflower roots concentrate uranium from water contaminated with low but highly dangerous levels of this oxyanion by a factor of 30,000 [33]. Similarly, tobacco roots treated to low concentrations (1–5ppm) of ionic mercury (Hg[II]) in liquid medium reduced the medium's Hg[II] content roughly 100-fold in just a few hours [48]. Because root surfaces compete for nutrients with a variety of particulate soil components, these adsorption mechanisms in soils are orders of magnitude less efficient than in liquid medium [89].

Uptake and Translocation: The plant cell plasma membrane contains a variety of specialized proteins involved in ion uptake and transport. These include proton pumps (ATPases that use energy and generate electrochemical gradients), co- and anti-transporters (proteins that employ the electrochemical gradients formed by ATPases to induce active ion uptake), and channels are all examples of these (proteins that facilitate the transport of ions into the cell). The interplay of ionic species during the ingestion of various heavy metal pollutants is a fundamental issue. Because root biomass cannot be harvested, translocation into shoots is desirable after uptake by roots. Metal ions are transferred from roots to shoots in a variety of ways, but little is known about them [119].

Most organic chelators, in contrast to citrate, promote metal ion absorption and translocation in plants. Plants release phytosiderophores like mugenic and avenic acids in response to metal ion shortages [35, 58]. Metal chelators boost the bioavailability of metal nutrients that are otherwise strongly bound to the soil and aid in their transport into plant tissues. Synthetic chelators can also be utilized to facilitate metal uptake and translocation. When ethylene diamine tetra-acetic acid (EDTA) is applied to lead-contaminated soils, for example, the absorption and transport of lead + EDTA-chelate into stems and leaves increases 100-fold [51, 121]. In addition to citric acid's involvement in lowering aluminum uptake, plants whose secretion of specific organic acids is raised would likely show higher uptake and translocation of metal contaminants.

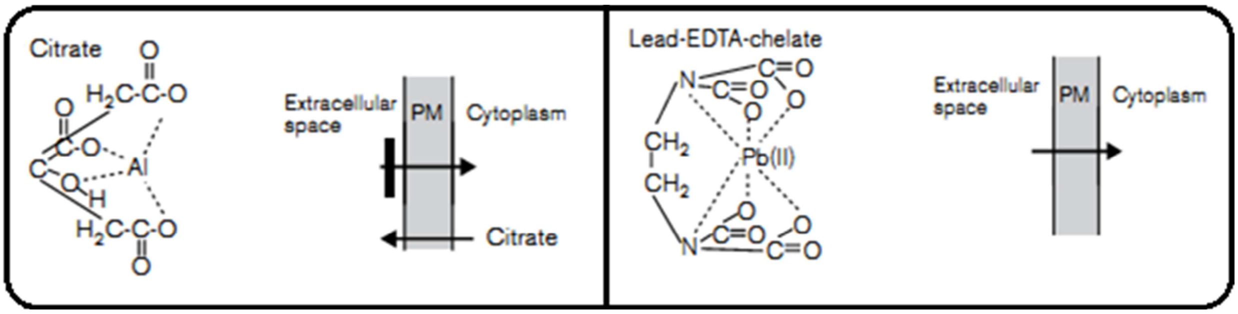


Figure 2. *Metal ion uptake and translocation in plants (Richard, 2000).*

2.2.3. Phyto-volatilization of Heavy Metals

Phyto-volatilization involves the uptake of pollutants from soil into plant body [4], then transform them into low boiling [31], less harmful compounds [48], and consequently discharge them into air [31, 48] through leaves or/ and shoots [5] with the help of transpiration. Phyto-volatilization is the most contentious of all phytoremediation processes, as there is concern about the safety of releasing gaseous contaminants (As, Hg, and Se) into the atmosphere [128]. For instance, Hg is present in soil in combination with methyl group which makes it extremely toxic, but modified tobacco plants are capable to uptake and transform methyl mercury into less toxic molecular form and ultimately release it into the atmosphere [5].

Members of the Brassicaceae are capable of emitting up to 40 g Se ha^{-1} day^{-1} as different gaseous chemicals, according to Terry et al. [116]. Cattail (Typha latifolia L.) is a nice example of an aquatic plant that can help in Se phytoremediation [83]. Unlike plants used for Se volatilization, those utilized for Hg volatilization are genetically engineered organisms. The bacterial organomecuriallyase (MerB) and mercuric reductase (MerA) genes have been inserted into Arabidopsis thaliana L. and tobacco (Nicotiana tabacum L.) [48, 93]. These plants take elemental mercury (II) and methyl mercury (MeHg) from the soil and release volatile mercury (Hg(0)) into the atmosphere through their leaves [48].

Hg^{2+}. R-CH_2-Hg^{+} ----merB---->R-CH_3 + Hg(II)

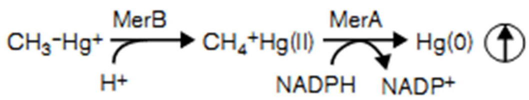
Hg(II) + NADPH ----merA---->Hg(0) + $NADP^{+}$ + H^{+}

Hg (0) (elemental mercury) can be volatilized by the cell

Because the inorganic forms of these elements are eliminated and the gaseous species are unlikely to be re-deposited at or near the site, the volatilization of Se and Hg is a permanent site solution [9, 48]. Furthermore, after the first planting, places that use this technology may not require much upkeep. This type of treatment has the added advantages of causing minimal site disturbance, reducing erosion, and eliminating the need to dispose of contaminated plant debris [48, 92]. According to Heaton et al. [48], adding Hg(0) to the atmosphere would have no substantial impact on the atmospheric pool. Those who favor this strategy, however, believe that it is not appropriate to use phyto-volatilization in population centers or in areas with peculiar meteorological circumstances that encourage the rapid deposition of volatile chemicals [48, 92].

2.2.4. Phyto-degradation of Heavy Metals

In this technique, heavy metals are either broken down enzymatically or converted to less toxic forms with the aid of enzymes present in plant tissues [31]. The effectiveness of the process relies exclusively on the nature of soil, plant type and the quantity and type of pollutant to be treated [5]. After the uptake, heavy metals are subjected to various catalytical reactions within the plant living tissues. MerA and merB, two laboratory-made genes from the well-characterized bacterial mer operon, are employed in plants for mercury transformation and remediation [72]. As illustrated below, the bacterial merA gene produces a NADPH-dependent mercuric ion reductase that transforms ionic mercury (Hg[II]) to elemental mercury (Hg[0]):



Methyl mercury ($CH3^{-}Hg^{+}$) is not only the most toxic natural form of mercury, but is biomagnified efficiently in the food chain.

2.2.5. Rhizo-filtration of Heavy Metals

Plant roots are utilized to either adsorb heavy metals on roots [64], accumulate them in the root zone [5], or convert them by bacteria in the root zone [5]. Surface water, extracted ground water, and less contaminated waste water are the most common applications [4]. Land plants with deep, hairy roots are ideal for this use [21]. This approach can be used to treat large amounts of Pb and Cr [5]. Although various plants such as sunflower, Indian mustard, tobacco, rye, spinach, and corn are capable of removing lead from soil and water but sunflower has been found to remove large amount of lead after one hour of exposure [21].

3. Conclusion

Climate change, exacerbated by increased industrialization and urbanization, is causing the world to face plenty of problems and robbing it of its potential. Furthermore, toxic metal wastes produced by anthropogenic processes such as residential, municipal, agricultural, industrial, and military operations enter the soil, reducing its quality and utility. Because soil is the foundation of life, competent remediation is required. One of the current remediation options is the utilization of living organisms, notably plants (phyto-remediation). Because, in compared to other soil remediation techniques, phyto-remediation is a cost-effective and low-maintenance method that is suitable for large areas with low to moderate levels of contaminants and is environmentally friendly. Phytoremediation, on the other hand, is a long-term cleanup alternative with a variety of remediation processes. For example, air pollution may result from phyto-volatilization, whereas pollutants gathered in leaves may be released back into the ecosystem after litter fall in the case of phyto-extraction.

Furthermore, contaminants must be accessible to the plant and its root systems, despite the fact that plant life and function are influenced by a variety of edaphic and plant circumstances. As a result, future concerns should focus on modifying and improving phyto-remediation technologies that are likely to improve metal binding abilities in plant tissues and phyto-transform hazardous metals. Finally, in addition to improving and adapting diverse approaches, it is vital to prevent or avoid the discharge of dangerous substances into the environment.

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