



Phytoremediation of heavy metals polluted environments

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Abstract

The rapid industrial development and agricultural growth and the indiscriminate production of pollutants have faced problems for human societies and the environment. Accumulation and pollution of heavy metals in the environment are the main important problems that as a result of human activities through extraction from ore and processing for various applications has led to the release of these elements in the environment. Heavy metals are non-biodegradable, so they could accumulate in the environment and subsequently contaminate the food chain. Some heavy metals are known as carcinogens, endocrine disruptors and mutagens, and this is a serious threat for human health. Therefore, today, the removal of heavy metal pollutions from the environment has been received special attention by researchers. In the application of physicochemical methods for this purpose, there will be serious limitations such as the need for chemical substances, high cost, the need for specialized equipment and skills, changes in soil characteristics, and disruption of native soil microflora. In contrast, phytoremediation is a better solution to the problem. The use of plants and natural soil microbes to reduce the concentration or toxic effects of pollutants in the environment is called phytoremediation. It is considered as a cost-effective, efficient, new, environmentally friendly and highly adoptable technology. New efficient metal superaccumulator plants are being investigated for applications in phytoremediation and plant extraction. This review article comprehensively discusses the background, concepts, processes and mechanisms in plant remediation of heavy metals.

Keywords: Environmental pollution, Heavy metals, Phytoremediation, Environmentally friendly

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Introduction

The increase in world population has increased the need for food production and agricultural development. Humans to meet this need, need more water to irrigate agricultural land. Because water resources are scarce, it sometimes uses unconventional water and sewage (1). Heavy metals as the environmental pollutants found in

all parts of industrialized and developed societies (2). Weathering of rocks and minerals rich in heavy metals are other sources of heavy metals entering the biological cycle (3). In fact, heavy metal pollution is one of the most fundamental environmental problems that the modern world faces (4). The term of heavy metals refers to metals, quasi-metals and non-metals that generally

have a density of more than 5 grams per cubic centimeter (5). Some heavy metals are essential for the normal cells functioning in the body in low concentrations, however their excessive intake causes poisoning (Tables 1) (6, 7).

Some toxic and non-biodegradable heavy metals are known as a serious threat to the environment and public

health due to their accumulation in body tissues(8, 9). Heavy metals harms include neurological disorders, cell aging, carcinogenicity, respiratory damage, kidney and liver failure, depression and lethargy, disorders of the reproductive system and cardiovascular system, skin problems and even death (6, 10, 11).

Table 1. Classification of metals based on cell health impact index (12)

Metals without positive impact	Metals with possible positive effect	Necessary metals for the body
Al-Sb-As		Co-Cr-Cu-Fe
Ba-Be-Cd	B-Si-I	Mn-Mo-Se
Pb-Hg-Ag	V-Ni	Zn
Tl-Sr		

Since plants are considered to be the most important route for the transfer of heavy metals into the human life cycle and food chain, wastewater should not be used for irrigation of agricultural lands as much as possible (13). If we do not have access to safe water sources for

irrigation, sewage can be used to irrigate agricultural lands according to existing standards. However, it should be noted that long-term use of wastewater for irrigation, increases the concentration of heavy metals (14, 15).

Table 2. Permissible concentrations of heavy metals in wastewater used for irrigation of agricultural lands according to WHO and FAO standards (16)

Maximum allowable concentration (mg / l)	Metal	Maximum allowable concentration (mg / l)	Metal
2	Zn	5	Al
0.2	Mn	0.1	As
0.2	Cu	0.2	Ni
0.1	Cr	0.01	Cd

Access to safe drinking water and clean air is one of the most obvious rights of all human, and it is the duty of governments to produce and provide this needs for citizens (17). The simplest solution is to use plants called phytoremediation. Phytoremediation can be used to clean and remove a variety of contaminated environments such as groundwater, sewage sludge, soil, air and surface water (2). Phytoremediation refers to the use of plants and their associated microorganisms to reduce the concentration, removal, synthesis, deformation, metabolism, or elimination of toxicity of pollutants from contaminated media (18-20). Despite

the good mentality towards phytoremediation, unfortunately not many researches have been conducted in this field and there is not enough information to gain support for its commercialization, and this is one of the reasons for its slowly expansion (21).

History

Phytoremediation includes the Greek prefix Phyto meaning plant and the Latin suffix remedial or remedium meaning to cleanse, repair or remove an annoying and foreign agent. Although the phytoremediation term refers to a relatively new

technique, its application has a long history. The discovery of phytoremediation technique backs to 1948, when a number of Italian researchers first observed that the heavy metal nickel accumulated in the spiral plant *Alyssum bertolonii*. In 1962, research began using aquatic plants to purify radioactive contaminated waters in Russia's nuclear regions, they finding that some plants were able to accumulate large amounts of metals in their tissues without showing signs of toxicity. The Italians' findings were forgotten until 1977, until a researcher named Robert Brooks from Massey University in New Zealand obtained similar conclusions (22-24). Around 1980, the term called Phytoremediation was introduced for Hyperaccumulator plants (25).

Hyperaccumulator plants

Plants in phytoremediation technique not only could produce a large amount of biomass, but also they have ability to absorb high contaminants in their tissues

without the symptoms of toxicity. These plants can also transport large amounts of absorbed contaminants to the aerial organs and release them in the safe form. This type of plant is called hyperaccumulator and this process is called hyperaccumulation (26-28). Chaney was the first to introduce the Hyperaccumulator in 1983 to eliminate of pollutants from contaminated areas (22, 23). Hyperaccumulator plants could absorb hundreds of times more heavy metals than conventional plants (28).

In non-Hyperaccumulator and non-resistant plant species, heavy metals affect a wide range of plant cellular activities including photosynthesis, mineral nutrition, respiration, cell membrane attributes and structure, and gene expression (29). So far, more than 400 plant species belonging to 45 families such as Asteraceae, Brassicaceae, Caryophyllaceae, Fabaceae, Lamiaceae have been identified (30, 31). The name of some hyperaccumulator plants are summarized in Table 3.

Table 3. Number of hyperaccumulator plants

reference	Plant species name	Metal removed
(32)	<i>Nerium Oleander</i>	
(33)	<i>Sesbania Drummondii</i>	
(33)	<i>Helianthus Indicus</i>	Pb
(34)	<i>Salsola Kali</i>	
(35)	<i>Zea mays</i>	
(33)	<i>Lemna Gibba</i>	
(36)	<i>Pteris Vittata</i>	As
(37)	<i>Holcus Lantus L</i>	
(33)	<i>Horedeum Vulgare</i>	
(38)	<i>Cynodon Dactylon</i>	
(39)	<i>Thlaspi Caerulescens</i>	Zn
(34)	<i>Gundelina Tourefortii</i>	
(33)	<i>Agrostis Tenuis</i>	
(33)	<i>Solanum Nigrum</i>	
(40)	<i>Greillu Pteridifolia</i>	Cd
(40)	<i>Eucalyptus Camaldulensis</i>	
(41)	<i>Amaranthus Spp</i>	
(42)	<i>Alyssum Lesbiacum</i>	Ni
(43)	<i>Sorghum Bicolor</i>	
(44)	<i>Spinacia Oleracea L</i>	

(45)	Helianthus Annus	
(46)	Prod Stachys	
(47)	Medicago Sativa	Cr
(46)	Phlomis Anisodonta Boiss	
(48)	Populus Spp	Se
(49)	Salix Spp	
(34)	Zizphoro Persica	Fe
(34)	Muscari neglactum	
(34)	Artemisia Sieberi	Cu
(50)	Brassica Napus L	
(51)	Jatropha Curcas L	Mn
(52)	Lactuca Sativa L	
(53)	Marrubium Vulgare	Hg
(54)	Pisita Stratiotes	
(55)	Nicotiana Tabacum	U
(56)	Lolium Perenne	
(57)	Nelumbo Nucifera	Co
(58)	Gmelina Arborea	Al

Phytoremediation techniques

The phytoremediation process involves different techniques, and different terms are used for each technique (Figure 1).

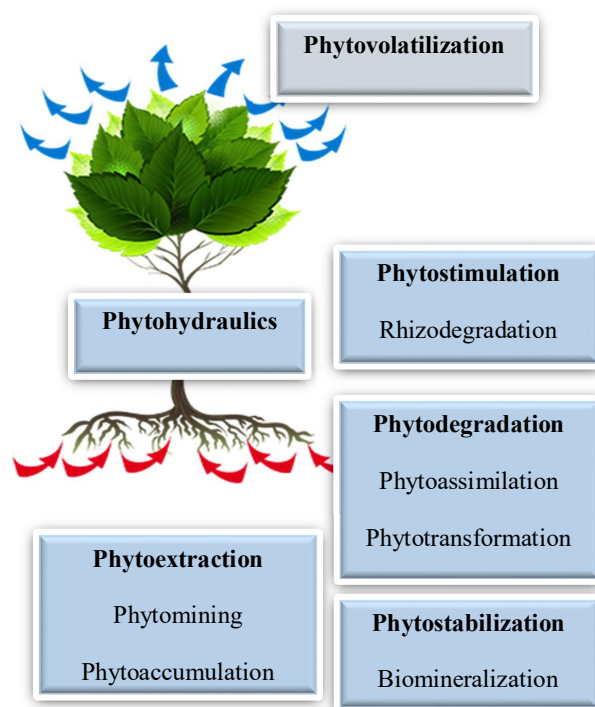


Fig 1. Phytoremediation techniques

1. Phytoextraction

In this method, heavy metals are absorbed by the plant and may be transferred to the shoots or accumulate in the roots. From practical point of view, the produced biomass from this method should be more than three tons of plant dry matter per hectare in a year, leading to remove of large amounts of pollutants from the polluted environments. To absorb contaminants by the plant, those must have a $\log K_{ow}$ between 1 and 3. The compounds with $\log K_{ow} > 3$ are hydrophobic and bind to the surface of soil particles and roots, so these compounds can not be absorbed and transferred into the plant. However, the compounds with $\log K_{ow} < 1$ are completely soluble in water, these cannot be fully absorbed by the roots, leading to limitations in their uptake through plant cell membranes (59).

As the phytoextraction term can be used to extract rare metals with high economic values (such as gold, silver, platinum and palladium), this term can be also called Phytomining. Heavy metals were extracted by plants through a special physiological mechanism from the environment (especially soil). On the other hand, by facilitating the secretion of chelated compounds by the roots, plants not only could increase the dissolution of the metal but facilitate the flow of dissolved metals to the root wall (25).

2. Phytodegradation

After the absorption of the contaminant in the phytoextraction stage, the bonds between the large and complex molecules are broken and converted into simple molecules and stored in the tissues. Plant degradation may be done in the presence of the plant or away from the plant by releasing enzymes such as oxygenase, reductase and dimalogenase, which have the unique ability to destroy and break down bonds (60-62). Plant degradation is not related to the microbial population in the area of root development and the activity of soil microorganisms, but depends on the secretions released from the plant roots (59).

Root secretion compounds are made in the plant and excreted through the roots and include sugars, amino acids, organic acids, fatty acids, sterols, nucleotides, flavonoids, growth factors and other compounds.

Bacterial population and their activity in the rhizosphere increase in the presence of these secretions (63). The destruction of heavy metals due to microbial activity at the root surface is much slower than their decomposition inside the plant tissues (64).

3. Phytohydraulics

Plant roots will be able to act as a hydraulic pump and adsorb water from surface and ground waters leading to decrease the solubility of the pollutants. Also, a percentage of contaminants enter the plant tissue with water absorption and as a result, the concentration of contaminants in the environment decreases. The natural growth of plants roots and creation of an extensive natural network with large coverage of area could be considered as positive aspect of this method. However, the instability of absorbing pollutants in different seasons is one of its disadvantages. According to Pivetz, the Populus tree can absorb 100 to 200 liters and the Salix tree can absorb 5,000 gallons of water each day (65-67).

4. Phytostimulation

Plant stimulation not only improves and increases the decomposition and degradation of contaminants in the soil in the presence of the plant but also creates favorable conditions for the decomposition and eliminate the toxicity of contaminants. The presence of plants in the soil stimulates microbial populations around the root in development area by releasing secretions into the soil, and provides coexistence between fungi and plant roots. Researchers reported the presence of arbuscular mycorrhizal fungi and the colonization of plant roots by them in soils contaminated with heavy metals. Lee *et al* (2002) stated that the root in development area (rhizosphere) has a higher and more active microbial populations than the rootless soil, because plants are able to release nutrients and their secretions into the soil and transfer oxygen to the root area stimulates and increases the activity of microbial populations (59, 68). Because microorganisms have different strategies such as bioaccumulation, biosorption, biotransformation, and mineralization to survive in contaminated environments, these can also be used to remove heavy metals called bioremediation (69).

5. Phytofiltration

Phytofiltration means the use of plants to clean and remove polluted aquatic environments. In this method, the plants roots or seedlings are used for internal or surface absorption of metal contaminants in water and wastewater sources. Root area secretions and rhizosphere pH changes cause heavy metals to deposit on the root surface. Soil or aquatic plants can be used in this method, but because soil plants have a wider root system, those are more preferred. On the other hand, aquatic plants have a higher percentage of water in their tissues, which makes them trouble to dry, burn and compost (70, 71). In fact, plants used in the Phytofiltration process should have a high tolerance to heavy metals, have low maintenance costs and produce significant root biomass. Those can also store large amounts of heavy metals in their root and leaf tissue (72). This method is highly effective for removing metals such as cadmium, copper, chromium, zinc, lead and nickel (60, 61, 73).

Low-tech natural wastewater treatment systems such as artificial wetlands can be used to treat wastewater, which could reduce economic costs. Artificial wetlands are also very cheap and easy to operate and maintain. Wetlands either do not consume energy or if those do, it will be small (74-78). Artificial wetlands are derived from the ecosystem of natural wetlands and today are considered as a potential alternative system or as a complementary system for wastewater treatment (79). This system has a high efficiency in wastewater treatment, especially for industrial wastewater (80, 81).

6. Phytostabilization

In this method, instead of removing the maximum amount of contaminants in the contaminated area and evaporating them, plants stabilize and immobilize them by absorbing metals into or on the surface of their roots. By using this method, the mobility of pollutants is reduced and their transfer into groundwater and the atmosphere is prevented (82). In-place inactivation or phytoimmobilization are other definitions (59, 83).

Plant stabilization is not possible without the presence of a dense and diffuse root system (often found

in herbaceous plants). This method is effective when current surface waters conservation and rehabilitation are required and plant biomass should not be used in the future. Remaining contaminants in the soil is the most important disadvantage of this method in which their concentrations must be constantly monitored, while the measurement of contaminants in the soil is not easy. In fact, in plant stabilization, only the migration and movement of pollutants is reduced (84).

7. Phytovolatilization

This method involves the use of plants to absorb contaminants, including heavy elements in contaminated environments and then transform them into volatile (gaseous) form by enzymes such as nitrate reductase, lacase, dihalogenase and nitrilase, which finally enters the atmosphere through plant perspiration. Plant sweat was first used to extract mercury, the metal mercury after absorption is released from the plant in the form of mercury ions, which is less toxic than the original form. One of the disadvantages of this method is that mercury re-enters the ecosystem cycle through precipitation (60, 61). The most important advantage of this method is the conversion of pollutants to a safe form or a form with less toxicity. However, some studies have shown that vinyl chloride enters the atmosphere in a toxic form (85, 86).

This method is commonly seen in tree species that absorb all kinds of organic and inorganic pollutants through irrigation water (87). Herbal perspiration is highly effective in absorbing and refining Tritium. Tritium enters the atmosphere in the form of helium volatile. Tritium is one of the hydrogen isotopes that enters the environment following nuclear activity and has a half-life of 12 years (88). Nowadays most attention is paid to the plant evaporation of selenium, because this element is one of the most serious environmental problems in parts of the world that have selenium-rich soils (89). The toxicity of selenium volatile compounds such as dimethyl selenide ((CH₃)₂Se) is $1/600$ to $1/500$ times more toxic than the original form of selenium (5).

The pores of the plant could close by deposition of dust on their leaves, which reduces the sweating of the plant. The leaves also absorb the gaseous forms of

pollutants through their surfaces. The entry of contamination into the plant body causes changes in the amount of chlorophyll, photosynthesis, these changes will reduce plant growth. Species of trees such as oak, Tehran pine, cypress simin and cypress Shiraz deposit sediments of heavy metals in the air on their leaves (90, 91).

Upgrading Hyperaccumulator plants

1. Upgrade by mushrooms

Arbuscular mycorrhizae fungi plays a significant role in the stabilization of heavy metals during the phytoremediation process and helps the resistance and tolerance of mycorrhizal plants (plants that coexist with arbuscular mycorrhizal fungi) against heavy metals. Some reports indicated an increase in the uptake of heavy metals by mycorrhizal plants, and these fungi also modulate the toxicity of heavy (92-94). In a study by Juner and Liwal (2001), Clover plants and Mycorrhizal corn have more lead in roots and aerial organ than non-mycorrhizal plants (95).

Mycorrhizal symbiosis does not always improve plant growth, in some cases negative effects on growth indices have been observed. Killham and Firstson (1982) observed that arbuscular mycorrhizal fungi increases the absorption of heavy metals, which causes some plants to absorb more heavy metals than their capacity, As a result the concentration of contaminants in the plant tissues increased and the acidity of the plant increased, eventually the plant experienced a decrease in growth (96). This coexistence is suitable for low concentration contaminated environments, For example, arbuscular mycorrhizal fungus enhance the uptake of zinc metal into aerial organ at low concentrations but decrease at high concentrations (97-100).

2. Upgrade by earthworms

Earthworms can accumulate many contaminants such as heavy metals in their bodies (101). They are naturally in contact with the soil, so in recent years these organisms have been used to remove heavy metals (102). A study by Nahmani *et al* (2007) showed that Iznia photida worm could reduce the concentration of

metals in the contaminated environment by adsorption process, in which phytoremediation method at low metal concentrations will be best done (103). But in a study by Spurgeon *et al* (1995) showed that the presence of cadmium, lead, copper, and zinc reduced the growth and increased the mortality of this type of worm (104). Subsequently, the results of studies by Zaltauskaite *et al* (2010) showed that increasing the lead concentrations increased the mortality rate of earthworms but did not occur significantly in the case of cadmium (105). Earthworms have several other effects such as increasing soil porosity, increasing oxygen delivery to plant roots and increasing organic matter. Iznia Fotida cream can also be used in the preparation of vermicompost. Vermicompost has more nutrients for plant growth than compost (106).

3. Upgrade by compost

Compost could be prepared from municipal waste under special conditions. Generally, the application of compost in the soil could maintain and increase the stability and fertility of agricultural and garden soils. (107). Organic matter in compost increases the cation exchange capacity of the soil. Depending on the type of organic matter, the amount of cation exchange capacity could be varied (108, 109). Other benefits of compost include reduced municipal waste volume and economic costs (110, 111). Compost also reduces soil acidity by increasing the pH and EC values (112, 113).

4. Upgraded by Genetic Engineering

Genetic engineering and production of transgenic plants along with plant genetic modification have created a new perspective for phytoremediation. Genetic engineering methods have been proposed by many studies to place genes with high efficiency to accumulate heavy metals in different plants. Another goal of genetic engineering is to improve the plants storage capacity of toxins and pollutants by increasing biomass production. Also, the placement of genes that can produce toxic compounds of various substances into ionic compounds and absorbable elements in plants by producing specific enzymes (114, 115). The low potential for success in genetic engineering can cause plant anatomy limitations (116).

The fate of plants used in phytoremediation

One obstacle in the phytoremediation process is the fate of infected plants after harvest. After the phytoremediation process, the concentration of heavy metals in the soil decreases, but a large amount of hazardous biomass is produced that must be addressed (9). The method of composting and compaction can be one of the preliminary steps to reduce the production volume of these plants, but it should be noted that the

leachate from compaction is completely collected (59). The best way to consume produced biomass by phytoremediation is thermochemical modification. In this method, biomass is used as an energy source. The main components of any biomasses are lignin, hemicellulose, cellulose, minerals and ash. Biomass has high amounts of moisture and volatile organic matter, which makes it has a low calorific value (7, 117). Ashing process takes less time and is more environmentally friendly than direct incineration (59).

Advantages and disadvantages of phytoremediation

Table 4 - Classification of phytoremediation benefits

reference	Advantages
(59)	Cheap
(59)	Less soil displacement
(59)	Can be used for various combinations
(59)	No need for specialized equipment and manpower
(59)	Prevents soil erosion
(59)	Prevents dust
(118)	Create a pleasant beauty
(60)	Increases the activity and diversity of soil microorganisms
(119)	Extraction of precious metals

Table 5 - Classification of phytoremediation disadvantages

reference	Disadvantages
(115)	Creating acidic conditions for better performance
(72)	Its time consuming and low speed
(59)	Restricted to shallow contaminated site
(59)	The weather conditions must be favorable
(59)	Danger of the remaining biomass
(117)	Possibility of air pollution through evaporation of pollutants
(115)	Contamination concentrations should not be high
(115)	Its success depends on soil fertilization, soil aeration and the importance of using effective organic methods
(120)	Necessity of calcification of soil after plant extraction in order to neutralize soil acidity

Conclusion and Recommendations

Because a wide range of different contaminants from industrial activities and sewage sludge disposal release to the soil, phytoremediation of soil has gained

more attentions than climat. it should be highlighted that measuring the amount of contaminants in the soil is not easy. Phytoremediation is not only used to clean heavy metals from contaminated environment, but also has a

high efficiency for cleaning oil pollutants and other pollutants. As mentioned, more than 400 species of Hyperaccumulator plants have been identified so far, and researchers can discover more by increasing studies and research in this field. Some of these 400 species may not function well in the environment, because laboratory conditions are in some cases quite different from environmental conditions. Some of the plants listed in Table 3 can be used to remove several heavy metals simultaneously.

Some environmental consequences and low nutrition value could be considered the main problem in the use of compost. Accordingly, before preparing compost fertilizer, the pollutants and salinity in municipal waste should be corrected. To prevent the atmosphere entrance of contaminants volatile, incineration of plant residues used in the phytoremediation process should be done in a special combustion chamber. The generated ash should also be disposed safely in unused highlands and lowlands where groundwater levels are low. The best landfill for ash is a place away from groundwater aquifers and not in the path of runoff, floods and valleys. Today, Gis software can be used to select the best burial site. In the end, it should be explicitly stated that just as capitalists and factory owners pollute the environment, they must also pay for its clean-up.

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Conflict of interest

The authors have no conflict of interest in this study.

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