



## Phytoremediation Mechanisms for Heavy Metal Removal in Contaminated Soils: A Comprehensive Review

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### Abstract

The rapid development of industrial sector has increased the heavy metal pollution issue recently, as the need of various metals is increasing for manufacturing purpose. These metals are the natural components that can be found in soil, but contamination happens when the concentration of these metals are high in soil due to anthropogenic activities. Several remediation techniques such as physical method, thermal desorption, chemical, and electrokinetic remediation are used to remediate the soil contaminated by heavy metals recently. As these remediation technologies have limitation on cost, effectiveness, and environmental friendly remediation issue, phytoremediation is then attracting the attention from various researchers due to its advantages of efficient, cost-effective, and eco-friendly remediation method. The mechanisms of phytoremediation are phytoextraction, phytostabilization, phytovolatilization, phytodegradation, phytodesalination, rhizofiltration, rhizodegradation, and phytoevaporation. However, these mechanisms were affected by several factors such as the plant species, properties of medium, bioavailability of metal, and the addition of chelating agent. The type of plant



utilized for phytoremediation (metallophytes) is categorized as metal indicators, metal excluders, and metal hyperaccumulators. This review article comprehensively discusses the source and effect of heavy metal on human health as well as phytoremediation techniques and mechanism during the heavy metal removal.

**Keywords:** Phytoremediation . Environmental pollutant, Toxicology, Heavy metal, Metallophytes plant

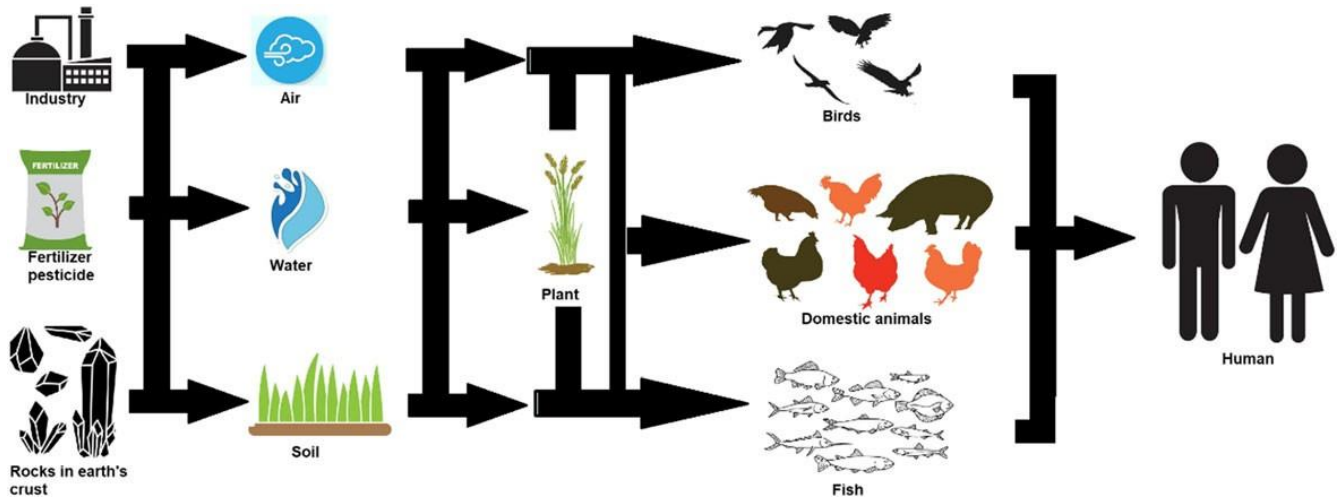
## 1. Introduction

The rapid development of the industrial sector has increased the heavy metal pollution issue recently, as the need for various metals is increasing for manufacturing purposes. Heavy metals such as copper, lead, zinc, cadmium, chromium, and arsenic are widely used by agriculture and industries and are highly toxic at very low concentrations. These metals are the natural components that can be found in soil, but contamination happens when the concentration of these metals are high in soil due to the mining and smelting activities [1]. This issue has become a worldwide concern as the heavy metal can enter the food chain and eventually cause adverse health impacts on humans. Besides, a human can also expose to the heavy metal in the soil through inhalation of particulate matter and direct contact with the contaminated soil [2]. Table 1 gives toxicity level, anthropogenic sources of heavy metals, and its effect on human health. Thus, recovery and remediation of the contaminated sites are required to prevent the health impact on humans. During the time when there is no advanced technology to carry out soil remediation, the heavy metal-contaminated soils are controlled using onsite management or being excavated and disposed of a landfill site. However, this method does not solve the heavy metal contamination issue, but only involve the migration of the heavy metal-contaminated soil from the contaminated site to landfill. With the development of remediation techniques and technologies, several chemical and physical methods have been used to remediate the contaminated site recently. However, these methods require a high cost and are technically complicated to apply [3]. These methods can also cause disturbance of native soil microflora and irreversible changes in soil properties by degrading the valuable component of soils. Moreover, the chemical technologies can produce secondary pollution problems, which a large volume of sludge will be generated and hence, increase the cost for sludge management [4]. As an effective, eco-friendly, cost-effective, and easy-to-apply remediation method, phytoremediation has gained enormous interest from the researchers for soil remediation. Phytoremediation is a treatment method that utilized plants and the associated soil microbes to remove the contaminants in the environment [5]. The plant used to remove the contaminant is not affecting the topsoil; thus, this method does not disturb the ecosystem and is environment-friendly [6]. Heavy metals can be in the form of free metal ions and soluble metal complexes in the soil. Besides, they can also precipitate hydroxides, oxides, carbonate, and embedded into a silicate mineral structure. The bioavailability of the heavy metals is important in order to let the heavy metal contaminant be absorbed by the plant roots through phytoremediation techniques. However, the solubility of the metals can affect the bioavailability of heavy metals in soil [7,8,9]. This paper aims to overview the



phytoremediation concept and discusses the use of several mechanisms to phytoremediate the heavy metal-contaminated soil. Several factors that affect the mechanisms uptake were also reviewed.

Fig. 1 Source of heavy metal and their pathway in the environment





## 2. Current Trend of Heavy Metal Remediation Techniques

With the increment of urbanization and industrialization, the cases of soil contaminated by heavy metals have increased rapidly and become a threat to food safety, ecological environment, and sustainable development of the agriculture sector [10]. Thus, soil remediation is essential to avoid the adverse impact, reduce the risk to the environment from toxic metals, and ensure a safe environment for future generations [11]. Several remediation techniques such as soil replacement method, thermal desorption, chemical leaching, and electrokinetic remediation are used to remediate the soil contaminated by heavy metals recently. Soil replacement method is a soil remediation method that dilutes the concentration of the contaminant in the soil and then increases the soil's environmental capacity. Soil spading, soil replacement, and new soil importing are the three concepts used in this method. Soil spading is a technique that carries out natural degrading of the contaminant in the soil by digging and spreading the contaminated soil to reduce the concentration of the contaminant [12,13]. Soil replacement is a method that can be applied for small area-contaminated soil by removing the contaminated soil and replacing with the new and clean soil. This method requires treatment for the replaced soil to inhibit second pollution [14,15]. New soil importing is also a method to dilute the contaminated soil by adding a large amount of clean soil, covering, and mixing with the contaminated soil. This method is decreasing the toxic effect on the environment effectively, but it is expensive, required big working volume and only appropriate for small-scale severely contaminated soil treatment. Besides, the executing of earthworks when using the soil replacement method may also disturb the ecosystem within the soil [16]. Thermal desorption is a remediation method that volatilizes the heavy metals such as mercury and metalloid arsenic by heating the contaminated soil using a microwave, steam, and infrared radiation. The vacuum negative pressure or carrier gas is then being used to collect and remove the volatilized heavy metals [17]. The two types of thermal desorption are hightemperature desorption, which carried out with temperature between 320 and 560 °C, and low-temperature desorption, which carried out with temperature between 90 and 320 °C. The advantage of this remediation technology is having a simple process to carry out soil remediation. However, the devices used to carry out thermal desorption are expensive and required long desorption time [18]. A remediation technique that leaches the contaminant from the soil is called soil washing or chemical leaching. This method uses liquids that contain chelation agents, freshwater, and other solvents to wash the contaminated soil with mechanical processes [19]. The environmental and health effects and the ability to solubilize specific contaminants are the factors to select the solvents used. By using this method, the heavy metal content in the soil is transferred from the soil to the liquid and formed leachate. The leachate is then comprising the chelation agents, surfactant, and inorganic eluent such as the heavy metals. This remediation method requires multiple mechanical processes to remove the contaminants in the soil. For example, the soil has to go through physical washing first, then only remove the contaminants through several stages of the chemical extraction process. The soil also needs to be



heated up to 200 °F by using a volume of reduction washing unit and be washed with a surfactant, water, and other solvents. Researchers have found that ethylenediaminetetraacetic acid (EDTA) is an effective chelation agent for soil washing. However, this chelation agent is expensive and bad in biological degradability [20,21,22]. Soil treatment method which uses an electric field gradient to remediate the contaminated soil is called electrokinetic remediation. This method generates a low electric field by inserting two electrodes in the contaminated soil [23]. Electromigration, electrophoresis, or electroosmotic flow is then becoming the driving force to transport the contaminants from soil to electrodes. The contaminants can then be removed when they adsorb or precipitate at the electrode. This treatment method suits for the treatment of low permeable soil has low cost and is easy to install and operate [24,25]. As the application of this treatment method does not destroy the natural ecosystem in the soil, it is considered an environmentally friendly method. Nevertheless, the treatment efficiency of this method is low and cannot control well the pH value of the soil system. Moreover, the current flow will be diverted when there are buried metal objects in the soil and thus, requires a longer time for remediation. The presence of a high amount of unknown contaminants will also affect the effectiveness of electrokinetic remediation. As these remediation technologies have a limitation on cost, effectiveness, and environmentally friendly remediation issue, phytoremediation is then attracting the attention of various researchers due to its advantages of efficient, cost-effective, and eco-friendly remediation methods [26,27].

### **3. Techniques of Phytoremediation**

Phytoremediation defines as the use of the plant to render the soil and water harmless by adsorbing or degrading the contaminants. This remediation method is a biological remediation method as the plant is the biological component used to treat the contaminated environment. Phytoremediation is a cost-effective remediation method as it involves only little manpower. Besides, the esthetically pleasant characteristic of phytoremediation method has made it be a remediation method that is well accepted by surrounding residents. Phytoremediation is classified as an environmentally friendly method as it reduces the risk of contaminant dispersion and protects the original ecotype by avoiding the excavation of the contaminated sites [28,29]. Phytoremediation is also being applied for the purpose of risk containment and phytoextraction of valuable metals such as nickel, thallium, and gold. Moreover, previous researchers have also found the economic value for applying phytoremediation on durable land as the land can be used to cultivate crops with higher market value when the soil quality is improved through phytoextraction [30]. The mechanisms of phytoremediation are phytoextraction, phytostabilization, phytovolatilization, phytodegradation, phytodesalination, rhizofiltration, rhizodegradation, and phytovolatilization.

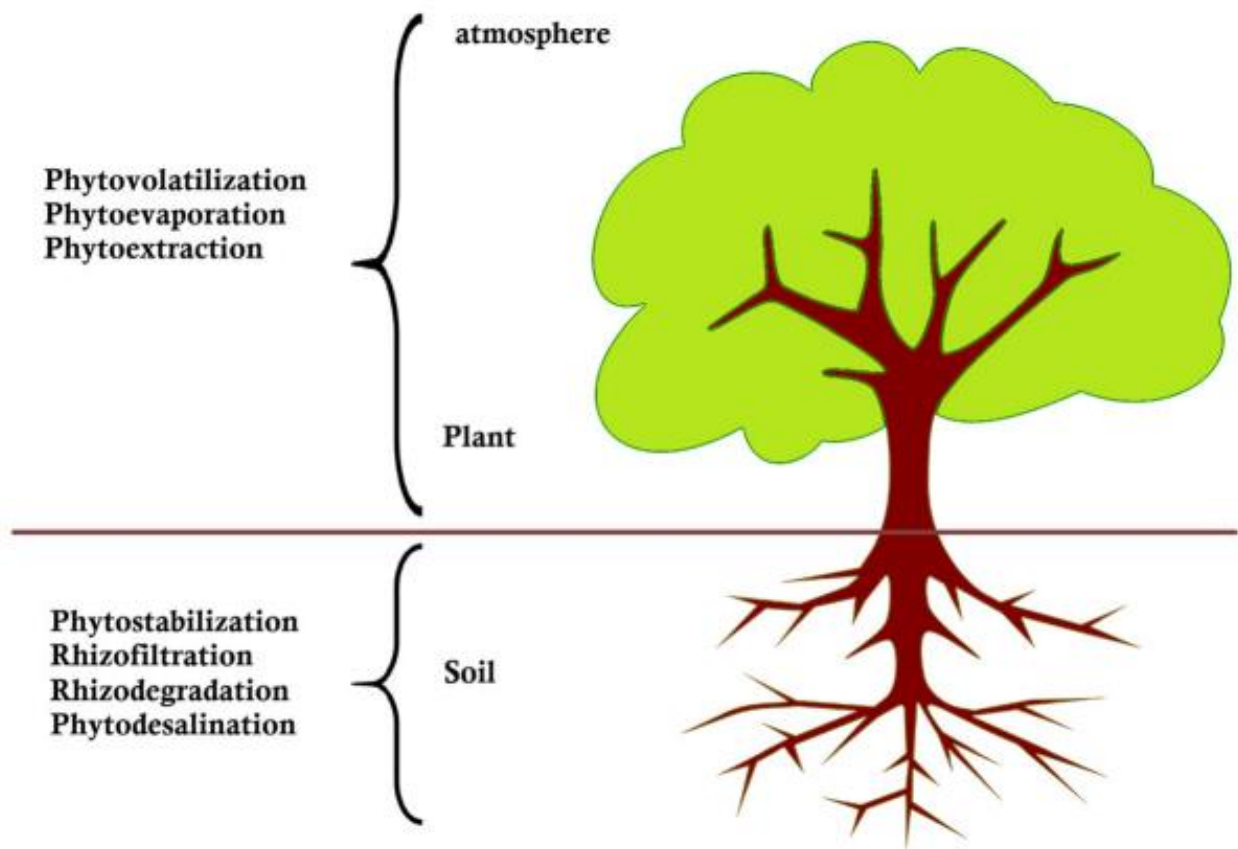
#### *3.1. Phytoextraction*

Phytoextraction or phytoaccumulation is performed by a plant when the roots of the plant absorb the contaminants from soil or water, transport, and accumulate the contaminants in the



aboveground biomass such as shoots and leaves. The plant that is used to carry out phytoextraction should have high ability in producing high biomass or accumulating the contaminants [31,32,33]. Hyperaccumulator species are the desirable plants to be used for performing phytoextraction as they have a high ability to accumulate the contaminants [34]. However, the plant species that can produce high biomass but accumulate less can also be used to execute phytoextraction [35,36]. The effectiveness of the plant species in metal phytoextraction is determined through the ratio of metal concentrations in the soil and the plant. The plants that carry out phytoextraction are then be harvested and incinerated. The ash produced from the incineration will be sent to landfill for disposal, and thus, the contaminants in the soil are removed. However, the low bioavailability of metal in soil and low absorption rate of metal will limit the performance of phytoextraction. Besides, the effectiveness of phytoextraction will also be lowered when the metals are held within the roots instead of being transported to the shoots and leaves [37,38,39,40].









### *3.2. Phytostabilization*

The absorption of heavy metals on the roots or precipitation of heavy metals within the rhizosphere that limits the mobility of the contaminants in the soil is known as phytostabilization. In this process, the plant that is being used to carry out phytostabilization alters the soil chemistry and hence, facilitates the absorption and precipitation processes of heavy metals in soil [41,42,43]. Moreover, the special redox enzymes excreted by the plants during phytostabilization process converts the heavy metals in soil into a less toxic state [44]. This method was well practiced at the metal mining–contaminated site. The phytostabilization process inhibits further percolation and mobilization of metal contaminants, and therefore prevents groundwater contamination. However, this method is only a management strategy as it inactivates and stabilizes the heavy metals, but not removing them from the soil or water [45,46].

### *3.3. Phytovolatilization*

Phytovolatilization is the process that absorbs the contaminants from soil, transports the contaminants through the xylem, converts the contaminants into less toxic and volatile form, and releases them into the atmosphere. Phytovolatilization has been widely used to remove metals like mercury and selenium, as these metals have high volatility [47,48]. Previous studies found that *Astragalus racemosus* can convert the selenium into dimethyl diselenide through phytovolatilization process, while *Arabidopsis thaliana* can convert  $\text{Hg}^{2+}$  into  $\text{Hg}^0$ , which increases the volatility of mercury. However, the surrounding temperature and light intensity can influence the ability of the leaf tissues on releasing the mercury to the atmosphere [49,50,51]. Moreover, Liphadzi et al. [52] have also found that the transpiration rate of the plant can affect the effectiveness of phytovolatilization [52]. Nevertheless, the edible product of the plant such as fruit may also contain the contaminants, as a result of accumulation and translocation when executing phytovolatilization. Another drawback of phytovolatilization is that it does not fully remove the contaminants, as the contaminants are only transformed into less toxic form and transferred from soil to atmosphere [53].

### *3.4. Rhizofiltration*

The process which plants adsorb and precipitate the organic and inorganic contaminants on the roots to remove them from the contaminated wastewater, groundwater, and surface water is known as rhizofiltration. Characteristics such as hypoxia tolerant, metal tolerant, and large absorption surface area are the main factors to choose the suitable plant to apply rhizofiltration [54,55]. As a comparison with aquatic plants, terrestrial plants are more desirable plants to perform in situ or ex situ rhizofiltration as they have a more fibrous system and developed roots that provides larger surface areas for absorption [56]. A success case of rhizofiltration is the use of *Phaseolus vulgaris* and *Helianthus annuus* to remove uranium from contaminated groundwater. The uranium removal result by the plants through rhizofiltration has an efficiency



of more than 90%, and the uranium is accumulated at the root. The necessity of first cultivation in a greenhouse and pH adjustment are the downsides of this mechanism [57]. Moreover, the plants used to carry out rhizofiltration have to be harvested and disposed of when the root adsorption capacity reaches a maximum [58,59,60].

### *3.5. Rhizodegradation*

Rhizodegradation is performed when the microorganisms in the rhizosphere degrade the organic contaminants in the soil. The examples of microorganisms that carry out rhizodegradation are fungi, bacteria, and yeasts [61,62]. There are more microorganisms present in the rhizosphere than on the ground surface. The exudates that are secreted by the plants contain amino acids, carbohydrates, and flavonoids. The nutrient-containing exudates provide nitrogen and carbon sources to the microorganisms in the rhizosphere and thus, enhance the metabolic activities of the microorganisms by 10–100 times higher [63,64]. The efficiency of extraction and removal of contaminants are then increased due to the nutrient-rich environment. Besides, the enzymes released by the plants also help in stimulating the growth of the soil microbes and degrading the organic contaminants in the soil [65,66]. Other studies found that the large surface area provided by the roots of the plant aids in the microbial growth by providing more oxygen. However, the efficiency of rhizodegradation is lowered in the deep soil of 20 cm depth onwards. Moreover, the physical structure of the soil will limit the growth of the roots towards the deeper soil [67].

## **4. Plants for Phytoremediation of Heavy Metals**

As plants require macronutrients and micronutrients for growth, plants will take up metals like copper, zinc, nickel, and iron from the soil. The plant root system takes up the metals through active mechanisms such as the transportation of protein with the cell membrane and passive mechanisms such as transpiration. The common non-accumulator plants only take up less than 10 mg/L of micronutrients, which is a sufficient amount for their metabolic needs. However, the growth of the plant will be affected when the plant is cultivated on the soil with a high concentration of heavy metals. This is because the high concentration of heavy metals in soil is phytotoxic. However, plants that can be used to carry out phytoremediation are known as metallophytes. The three types of metallophytes are metal indicators, metal excluders, and metal hyperaccumulators [68,69,70,71]. The list of metallophytes plants is shown in Table 4. Plant that takes up a high concentration of heavy metals from the soil and accumulates them in the shoots and leaves is known as metal indicators. Thus, the shoot and leaves have an uptake high concentration of heavy metals, which can reflect the heavy metal concentration in soil. The plants are eventually died-off due to the metal toxicity as a result of continuous uptake of heavy metals. As the metal indicator plants are good in the absorption of the contaminants, these plants are used to indicate the possible heavy metal presented in the soil. Metal excluders are plants that cease the transportation of the absorbed heavy metals to their aboveground tissues but accumulate the absorbed heavy metals at their roots. Previous studies confirmed that metal excluders are efficient to perform phytostabilization [72,73,74,75]. Metal hyperaccumulators are



plants that can take up and accumulate a high concentration of heavy metals in the plant foliage. The plant can only be classified as metal hyperaccumulator when it can remain healthy and not showing any signs of toxicity, after accumulating the concentrate heavy metals. The metal hyperaccumulators use the accumulated heavy metals in their tissues for ecological and physiological functions. Metal hyperaccumulators are widely used to perform phytoremediation as the metal hyperaccumulators will make the heavy metal–accumulated leaves unpalatable, and hence, evade the herbivores such as caterpillars from consuming it. This shows that the metal hyperaccumulators not only can protect themselves from consuming by predators but also aid in the prevention of heavy metals entering the food chain. The other advantage of using metal hyperaccumulators for phytoremediation is, bio-ore of some commercial value may be produced from the metal hyperaccumulators that have accumulated a high level of heavy metals, and thus, reducing some costs of soil treatment [76,77,78,79,80,81].

## 5. Factors Affect Phytoremediation

The three main mechanisms of phytoremediation for heavy metal removal are phytostabilization, phytoextraction, and phytovolatilization. Phytostabilization limits the mobility of the heavy metal from entering the food chain; phytoextraction adsorbs the heavy metal from the soil and accumulate in the plant tissues; and, phytovolatilization volatilizes the heavy metals from the soil and releases them to the atmosphere in less toxic or non-hazardous form. However, these mechanisms may affect by several factors such as the plant species, properties of a medium, the bioavailability of metal, and the addition of chelating agent [82,83,84,85,86].

### 5.1. Plant Species

Suitable plant species must be chosen before carrying out phytoremediation on heavy metal–contaminated soil. A plant that considers to have high efficiency of phytoextraction technique needs to achieve a high accumulation of heavy metals and produce large amounts of biomass. Moreover, the characteristics of the plant species also affect uptake efficiency [87,88,89].

### 5.2. Properties of Medium

Researchers have reported that agronomical practices such as pH adjustment and addition of fertilizers can improve the efficiency of phytoremediation. A few studies show that the pH, amount of organic matter, and phosphorus content in the soil can affect the plants on lead absorption. The soil pH that is adjusted to a level of 6.5 to 7.0 with lime can reduce the lead uptake by plants [90,91,92].

### 5.3. Bioavailability of Metal

The efficiency of phytoextraction is critically affected by the bioavailability of heavy metals in the soil. The phytoextraction of lead is highly affected by low bioavailability. A few parameters can affect the bioavailability of heavy metals such as the soil pH, soil redox potential, and



amount of organic matter, clay, and oxide minerals in the soil. The metal concentration in the soil solution can be reduced by the increment of soil pH, due to the complexation of metals by functional groups of organic matter and oxides. Besides, the extent of the metal complexation with organic C-based ligands in the soil is influenced by the pH control and hence, affected the solubility of heavy metals [93,94,95,96,97]. Soil redox potential is an essential factor that affects the heavy metal transformation, solubility, and uptake by plants. Research shows that metals with higher oxidation states such as iron and manganese have lower solubility. Moreover, the mobility of metals is limited when the solubilized metals undergo re-precipitation and thus, affects the absorption and uptake by plants. A high amount of organic matter, clay, or oxides can decrease the bioavailability of metals in soil, as the metal cations react with these components that have high cation exchange capacity and high specific areas. Some heavy metals will become non-exchangeable as a result of binding to the humic substances in the inner-sphere complexes [98,99,100,101].

#### *5.4. Addition of Chelating Agents*

The addition of biodegradable physicochemical factors such as chelating agents and micronutrients can increase the uptake of heavy metals by the plants and stimulate the heavy metal uptake capacity of the microbial community in and around the plant. Remediation periods through phytoremediation will be shorter when the rate of heavy metal uptake by plants increases, and thus, the cost of remediation will reduce. Chelating agents are required in alkaline soils that have a level of pH above 5.5 to 6, as the alkaline soils decrease the bioavailability of heavy metals [102,103,104,105].

### **6. Disposal of Metal-Accumulating Plant Waste**

One of the vital concerns about phytoremediation is the handling and disposal of the metal-accumulating plants. Proper management and disposal of metal-accumulating plants must be carried out to prevent potential risks. These plants must be harvested and either disposed of or recycled in compliance with applicable regulations as the metal-accumulating plants are considered hazardous waste. The metal concentrations in the plants will determine whether the plants need to be landfilled or perform metal reclamation through pyrolysis of biomass, smelting, or extraction. The value of the reclaimed metals from the biomass of the plants may offset the cost of remediation. The resulting ash from the incinerated plant must be disposed to hazardous waste landfills, while radioactively contaminated plants must be disposed of as radioactive waste. The handling of plants before disposal is significant as some species such as *Brassica juncea* become crumbly, dry, and flaky after harvesting, thus, may become a source of secondary emissions of the metals that they have adsorbed and absorbed [106,107].

### **7. Conclusion**

Effective remediation on heavy metal-contaminated soil is necessary as this environmental problem could bring serious health impact to humans. Due to the limitation of physical and

chemical remediation methods such as expensive, disturbance of native soil ecosystem, irreversible changes in soil properties, and creation of secondary pollution problems, phytoremediation becomes a better choice of technology to remediate the heavy metal-contaminated soil. The main mechanisms of phytoremediation are phytostabilization, phytoextraction, and phytovolatilization. Several factors such as a selection of plant species, properties of a medium, the bioavailability of metal, and the addition of chelating agents are important to enhance the efficiency and success rate of phytoremediation technology. Metal hyperaccumulators are usually being used to perform phytoremediation. These plants can accumulate large amount of concentrated heavy metals in their biomass and remain healthy. According to Hall [108], heavy metal-tolerant plants can also protect themselves from metal toxicity through detoxification strategies. These plants have several mechanisms such as chelation, presence at the cellular and subcellular levels that are involved in the sequestration, or detoxification of toxic heavy metals [108]. The buildup of toxic metals around the sensitive organelles in the cell is then being prevented by chelation and hence, avoiding damages to the plant cells [108]. One of the significant advantages of phytoremediation is that it can avoid the accumulated metals entering the food chain, by making the leaves unpalatable and evade the herbivorous from consuming them. Besides, metal reclamation from the metal-accumulated plants may help in offsetting the remediation cost. However, climate and hydrologic conditions such as flooding and drought will be the challenges for future research on phytoremediation [109]. Climate condition is also varying from one place to another, and thus, the plant growth and performance of phytoremediation will be affected.

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