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REVIEW ARTICLE

EFFICIENT REMOVAL OF HEAVY METALS BY PHYTOREMEDIATION TECHNIQUES

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ABSTRACT

Direct and indirect disposal of different wastes either due to some accidental spillage or due to practicing of sewage sludge to agricultural fields for diverse reasons in the water reservoirs contributes towards contamination of our ecosystem. Physical removal or immobilization is required for making soil and water contaminant-free from such kind of heavy metals. The Earth crust is mainly composed of these heavy metals and as they are non-degradable in nature, so there is a greater risk of their entrance into the food web and lead to various health hazards. Phytoremediation is an innovative, environment friendly, cost-effective, and aesthetically pleasing approach to remove/immobilize heavy metals. Processes mainly involves the detoxification, removal, or stabilization of retentive pollutants via utilization of vegetation and is a green environmental-friendly tool for cleaning polluted soils. It is a broad-spectrum remediation mechanism in which several processes are involved as mentioned here includes phyto-stabilization, rhizo-filtration, rhizo-degradation, phyto-degradation, phyto-extraction, and phyto-volatilization. Use of aromatic non-edible plants is sustainable and the best treatment approach for the elimination of toxic metals. These plants are not removed directly by humans or animals like non-aromatic edible crops such as cereals, pulses, or vegetables. This research is entirely based on qualitative analysis with descriptive approach. The crops like mustard plant, sunflower, rapeseed etc. are effectively put in an application at sites with superficial contamination of organic or inorganic contaminants via the above-mentioned six techniques. Phytoremediation is a reliable reclaiming treatment and hence the most demanding remediation technology in the world.

KEYWORDS

Phytoremediation, Heavy Metals, Remediation, Contaminants.

1. INTRODUCTION

Human evolution has led to extensive scientific and technological advancement. As development all around the globe has raised new challenges for ecosystem protection and conservation. Satirically, these developments in the agricultural, economical, and industrial fields are off times responsible for contaminating the environment. Since the industrial revolution in Europe and the USA continued industrialization has increased soil and water pollution due to anthropogenic emissions of heavy metals on a drastic level. The disposal of toxic effluvia into streams without any proper treatment creating an alarming situation for mankind (Förstner et al., 1995). The various industrial activities such as mining and metallurgical processes, smelting, refining and other manufacturing processes are exposing a great threat to human health. Heavy metal wastes are disposed of in the soils for their treatment, but this conventional remediation method is not economical and has deleterious effects on the environment. These certain heavy metals are entered into the food web (bioaccumulation) and then transferred from one trophic level to the next level within a food web (biomagnification). Continuous exposure of human body to these heavy metals leads to many health risks such as cardiovascular disease, cognitive impairment and chronic anemia (Iqbal, 2012). So, the safest way to prevent such kind of health risks by heavy metals remediation is the phytoremediation.

2. ENVIRONMENTAL ISSUE

Heavy metals are deteriorating the environment especially under groundwater. There are many case studies all around the world directing the toxicity of heavy metals. Water issues in South Africa regarding water quality more than quantity are rising day by day. Comparatively, Empangeni and Richards Bay are the most highlighted regions which are vulnerable to heavy metal pollution. According to sources, nickel, aluminum, and lead were dominant in the entire area while cadmium, boron, iron and manganese outstripped the implied limit at a few localities (Elumalai and Lakshmanan, 2017). Similarly, Yangtzekiang River & Taihu Lake are the major fresh waterbodies located in the Jiangsu Province, China. Deterioration in the water quality as per recent studies is harrying the aquatic ecosystem in the region. It was found that Mean Probable Effect Concentrations ($Q_{m\text{-}PEC}$) from Yangtze River were >0.5 indicating the high toxicity of sediments due to heavy metals.

Whereas ($Q_{m\text{-}PEC}$) from Taihu Lake were <0.5 which indicates that sediments are relatively less toxic but still hazardous for aquatic life (Fu et al., 2013). Ranipet Industrial area is one of the major exporter centers of tanned leather in India, which is badly contaminating the surface water reservoirs in the region. Asthma, chromium ulcers and skin diseases are very common diseases in the adjoining areas (Gowd and Govil, 2008). Mexico, the world's largest silver producing country is also vulnerable to heavy metals causing environmental issues. Zacatecas, the largest contributing state of Mexico in silver production is also famous to produce major staple food in Mexico which is maize. Recent studies have shown that food chain is at a greater risk due to high-level concentrations of silver

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(Hg), astatine (As) and lead (Pb) in soil and groundwater (Davila et al., 2012).

3. Inception of Metallic Pollution

Most of the heavy metals are essential ingredients for the survival of the human population as well as an aquatic ecosystem but to a certain permissible limit. Whereas certain metals have disastrous effects on both ecosystems even below hazardous level concentrations. Many of the human activities and anthropogenic processes aggregated these metals in the environment at a tremendous level. Major sources of heavy metal pollution include industrial processes like smelting & refining processes, electroplating, forging, casting etc., geogenic sources like leaching and weathering of rocks, agricultural & domestic effluents as well as pharmaceutical sources. Chromium is generally discharged into the environment by disintegration of Cr-containing rocks and by certain industrial processes like leather tanning industry, textile dyeing industry pigment production industry etc. Different anthropogenic processes release lead (Pb) into the environment such as ores and metals processing, smelting processes and lead-based battery manufacturing processes etc. Afterward, when untreated wastes containing heavy metals released through these sources are improperly and inadequately disposed into the soil and water and ultimately causes metallic pollution.

4. Categorization of Metals

The tremendous increase in the human population is creating difficulties for agricultural systems as cultivable land is consistently declining whereas human food demand is rising day by day. Synchronizing, a rise in heavy metal concentration is also causing a great threat to plants and animals. Before moving towards the remedies, it is critically important to recognize which metals are fundamental for plant or animal growth. As per recent studies, heavy metals are categorized into two groups: essential and non-essential heavy metals. Essential metals include zinc (Zn), aluminum (Al), iron (Fe), manganese (Mn), copper (Cu), cobalt (Co) and selenium (Se) are essential for various physiological functions of plants. Although several plants require these metals in minor quantity but still necessary for the growth and nourishment of plants. As, zinc (Zn) plays a key role in the splitting and amplification of cells, structural formation of nucleic acid, protein, carbohydrate, and lipid mechanisms (J.C., 1981).

Similarly, manganese is essential for enzymatic functioning activity. Identically, selenium (Se) is an integral element in hormone building as well as in antioxidant functions. On the contrary, the intake of all these essential metals above permissible limits rigorously affects the crop yield as well as introduces a potential health hazard in human beings. That's why, environmentalists are paying special attention to the concentration controlling techniques of these heavy metals. Non-essential metals include mercury (Hg), lead (Pb), chromium (Cr), cadmium (Cd) and arsenic (As). These metals are highly toxic even in small quantity can cause severe damages to human health and plants as well. Likewise, intake of cadmium (Cd) can cause several diseases in human-like degenerative bone disease, cardiovascular and neurological damages etc. It can also reduce the photosynthetic activity in plant to a catastrophic level (Dong et al., 2005).

Plants experiences stress in oxidative processes upon exposure to these non-essential metals that causes cellular damage and thus, hinder their biological functioning. Respectively, mercury (Hg) has detrimental effects on the process of photosynthesis and redox metabolic processes by obstructing electron transport in mitochondria as well as in chloroplasts (Abdullah et al., 2011). Thus, due to their toxicity levels, five elements (chromium, cadmium, mercury, arsenic, and lead) are prioritized as the major hazardous heavy metals. United States Environmental Protection Agency and International Agency for Research on Cancer (IARC) named them as "human carcinogens (known or probable)". The results are based on epidemiological and investigational studies on humans and animals (Tchounwou et al., 2014).

5. Phytoremediation

Phytoremediation offers an innovative, eco-friendly, and cost-efficient technique to clear out of recalcitrant environmental pollutants. It is the restoration or stabilization technique of contaminated sites and reservoirs. This method takes the edge of the general qualities of plants to intake, pile up and demote organic and inorganic matter. It is the integrated multidisciplinary technique by the combination of plant physiology, soil microbiology and soil chemistry to the detoxification of affected soil-water. Phytoremediation mainly deals with the removal of heavy metals but additionally, it can also detoxify the contaminants like petroleum hydrocarbons, radionuclides, chlorinated solvents, PCBs, PAHs, surfactants, explosives and organophosphate insecticides (Jadia and Fulekar, 2009). Several plant species can take part in the remediation of heavy metals. As per recent studies, 45 families have been distinguished as the most efficient hyperaccumulating plant species. Many researchers preferably selected plants that are proved to be the best accumulators on the base of their actions. These plants include seapink thrift, ragweed, Indian mustard, turnip, broccoli, sunflower, wheat, corn and pennycress (Paz-Alberto and Sigua, 2013). Sometimes, microbes are also used as growth promoters for the metal-accumulating plants.

6. Techniques

Phytoremediation involves different techniques mainly rely on the kind of contaminants and soil characteristics. These mechanisms involve phyto-stabilization, rhizo-filtration, rhizo-degradation, phyto-degradation, phyto-extraction, and phyto-volatilization.

6.1 Phyto-stabilization

It is the strategy used for the stabilizing the metals/contaminants specifically in the contaminated soil. It is a management mechanism applied to minimize the mobility of contaminants in the environment. It seizes the movement of these pollutants to the groundwater or their entry into the food chain. Practically, Indian mustard (*Brassica juncea*) is the most propitious and effective plant for the process of phyto-stabilization (Ko et al., 2008). Functionally, rhizosphere is a highly dynamically characterized region where different processes and interactions take place such as root processes, soil characteristics and soil microbial activities.

Plants roots release a special type of secretion known as root exudates, which acts as a nutrient source. It stimulates the microbial activity as well as regulates the pH in rhizosphere. Its chemo-attractant nature enables the attraction of several microbes in the rhizosphere. It can also act as a chelating agent and hence, form chelates by accumulating harmful chemicals (Bolan et al., 2011). Afterward, root exudates regulate the process of precipitation of these chelates. Rarely, precipitated chelates get absorbed by or adsorbed onto the roots respectively and come along with plants on harvesting. Moreover, these plants are incinerated, and metals are extracted for reuse, in a process called phyto-mining. This step has an advantageous impact on soil structure along with soil chemistry; it minimizes the soil erosion caused by wind and water.

6.2 Rhizo-Filtration

Rhizo-filtration is an emerging and one of the most demanding cleanup techniques. It involves the filtration of contaminated water via plant root systems. Plants that have stable root systems are efficient for this mechanism such as spinach, Indian mustard, sunflower and tobacco (Ghosh and Singh, 2005). The initialization of this process is like phyto-stabilization as it also includes the immobilization and chelation of heavy metals via root exudates. On the contrary, it involves the absorption of these accumulated heavy metals into their root biomass. Furthermore, hydroponically grown terrestrial plants can be used in rhizo-filtration systems.

As per recent studies, aquatic plants are also efficient for this technique but not more than hydroponically grown terrestrial plants. Heavy metals amenable to this technique include lead, cadmium, copper, chromium, nickel, zinc, and radionuclides (uranium, cesium, strontium). Moreover, research have shown that Indian mustard has a comparatively higher affinity for these contaminants (Dushenkov et al., 1995). This process has superiority over other techniques as it is a mobile activity; it can either be *in-situ* or *ex-situ*. But a well-engineered system is required in *ex-situ* conditions to control the factors like influent concentration and flow rate.

6.3 Rhizo-Degradation

Rhizo-degradation or phyto-stimulation is the process of transforming, breaking down, stabilizing or volatilizing of contaminating substances from soil and groundwater in the rhizosphere (root zone). In this process, contaminants are first accumulated onto the roots as it is done in the above-mentioned processes. Furthermore, these contaminants are degraded in the root zone by the microbial or enzymatic activity. It is also known as a plant-assisted *in-situ* degradation process. Root exudates act a vital part in culminating the contaminants. These exudates include different nutrients like sugars, sterols, amino acids, enzymes and some other compounds (Koo et al., 2005). Generally, microbial activity for the disintegration of contaminants is stimulated by: (1) action of the root exudate and its compounds, (2) aerobic transformations enhanced by the loosening of soil for proper aeration via root systems, (3) agile activation of non-transformable mycorrhizae fungi, (4) increasing microbial populations and their activities over the enhancement of plant metabolism

(Anderson et al., 1993). It aids the well-being of soil structure as well by enhancing soil aeration and mediating the soil moisture content. Contrarily, this process is not as beneficial due to certain limitations. Because this process only deals with the organic stuff, which is contaminating the environment like pesticides, PAHs and TPH. Moreover, there is a probability of uptake of these degraded contaminants by plant shoots that might complicate the interpretation of rhizo-degradation and elongates this process up to phyto-degradation or phyto-volatilization.

6.4 Phyto-Extraction

It is one of the most appealing sub-techniques of phytoremediation in which uptake of heavy metals by roots and transposing within the plant biomass occurs. This process is fundamentally deal with the handling of contaminated soil and sludge. This process is identical to the technique of rhizo-filtration as their initial activity is similar. In phyto-extraction, plant releases certain phyto-siderophores. It is small, high-affinity chelating compound especially for Fe or Zn deficit cases and transporter of heavy metals within in a cell membrane (Prasad et al., 2014). Afterward, these extracted heavy metals get stored in plant biomass such as leaves etc. The distinctiveness of phyto-extraction lies in this benefit that the plant biomass holding the removed pollutants can be used as a source of supply to the certain metal-deficit areas or as animal feed.

Some basic and efficient strategies must be considered during the selection of plants that are amenable to this technique. These plants should be naturally hyperaccumulators (accumulate high conc. of contaminants within biomass), rapid-growth plant species and genetically modified plants in case of the deficiency of above-mentioned conditions. Undoubtedly, hyperaccumulators are considered as the foremost species for this technique. It requires specific climatic conditions and consequently, in temperate-climate regions *Brassicaceae* family is preferred whereas *Euphorbiaceae* is an efficient group for tropics (Baker and Brooks, 1989). The certain disadvantage of this technique lies in the improper maintenance of these specific climatic conditions and as a result, it diminishes the growth and ultimately, affects the performance haphazardly.

6.5 Phyto-Degradation

It is the degrading process involves the depravation of organic contaminants by plants via certain enzymes such as dehalogenase and oxygenase etc. Phyto-degradation mainly concerns with the treatment of contaminated soils and groundwater. This technique mainly involves two mechanisms: uptake of organic pollutants & metabolism. This metabolism has further two processes. Metabolic activities can be done either internally or externally. Internally, the adsorbed contaminants are broken down and detoxified within the vacuoles or mesophyll via certain enzymatic activities. While, in external metabolism, degradation of contaminants occurs via hydrolyzing of organic compounds released by the plants. Afterwards, these degraded substances get adsorbed onto the leaf's surfaces as it is shown in figure 1.

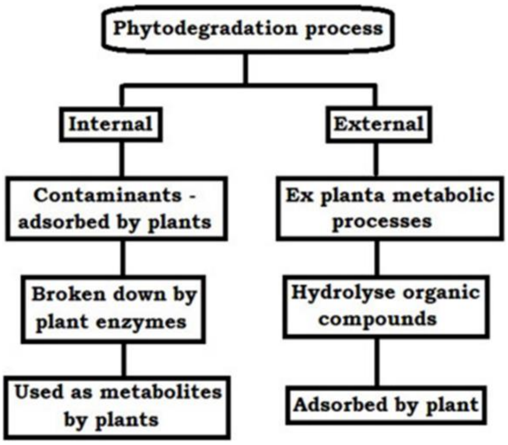

Figure 1: Phytodegradation process

Organic contaminants that can be detoxified/degraded by phyto-degradation include herbicides, chlorinated solvents, insecticides, munitions, and phenols (Jeevanantham et al., 2019). It has been identified in different case studies that *Salix nigra*, *Liriodendron tulipifera*, *Taxodium distichum*, *Quercus falcata*, *Quercus viginiana* and *Betula nigra* were able to degrade the herbicide bentazon to a great extent (Conger and Portier, 2006).

6.6 Phyto-Volatilization

Phyto-volatilization is a relatable technique to phyto-degradation as it can occur simultaneously due to their similar basic uptake and metabolic mechanism. Moreover, plant transpires these contaminants into the atmosphere after their conversion into a less toxic form. This remedial technique can be applied both to soil and groundwater. Phyto-volatilization has a remarkable advantage that it can deal with both the organic (TCE, TCA & CCl_4) and inorganic contaminants (Se or Hg). Different studies have identified suitable plants for this technique based on targeted contaminant. Researchers from the University of Washington have identified poplar tree as the best transforming specie for the removal of TCE. *Brassicaceae* family specifically includes Indian mustard and canola (*Brassica napus*) have been used for the conversion of selenium (Se) to less degree hazardous dimethyl selenite gas and subsequently, released into the atmosphere. Researchers have also identified that Kenaf (*Hibiscus cannabinus L.*) can be used as a selenium detoxifying plant but to a lower extent than canola (G.S, 2000).

6.7 Selection of Plants

The accomplishment of the aimed outcomes regarding phytoremediation mainly depends on the plant species. Thus, the selection process of plants is of vital importance to meet the goals of this technique. There are various considerations that a researcher must deal with mainly include soil conditions, climatic conditions, and the nature of targeted contaminants.

6.8 Metallophytes

The type of plants with high tolerance and high accumulating affinity for heavy metals and can thrive on excessive metal-content soils without agonizing toxicity. Plants show diversified behavior over different environmental situations. Now a day, metallophytes forged curiosity in the botanical field especially. Most of the metallophytes are concentrated in the plant family *Brassicaceae*. These plants can be used either separately or integrated with microorganisms for the achievement of goals effectively. Depending upon their heavy metal content, metallophytes are categorized into 3 main classes: excluders, accumulators & indicators (Ali et al., 2013).

6.8.1 Metal Excluders

The specified kind of plants that restricts the transfer of accumulated toxic metals into their shoots and stored them in their roots. Thus, it obstructs the chance of aeration of these heavy metals into the environment by restricting their entry into the aerial parts. These plants maintain low heavy metal content in their shoots, but they have a wide range of accumulating these metals in their roots (Baker and Walker, 1990). That's why these plants are considered as an efficient option for phyto-stabilization purposes.

6.8.2 Metal Indicators

Metal indicators are the plants that involve the basic mechanism like hyperaccumulators or metal-accumulators by taking up the toxic metals and store them in their aerial parts. Additionally, these plants unveil the metal content in the soil via their plant tissues (Sheoran et al., 2010). Furthermore, these plants die-off over the continued accumulation of metals and thus represents the tremendous toxic levels of metals in the soil. These indicator plants perform various biological and ecological functions. Therefore, metal indicators can act a vital part in relieving the environment from this metallic pollution.

6.8.3 Metal Accumulators

It is a most diversified type of plant that can thrive in highly toxic soil or water. These plants captivate these toxic metals through their root system and accumulate these toxic heavy metals to a greater extent into their plant biomass. That's why these plants are commonly called as hyperaccumulators. These plants are capable to accumulate contaminating metals far in excess to those present in the soil-water or in the ordinary plants growing nearby. There is a wide range of plants that are hyperaccumulators in nature. Several families can act as metal tolerant such as *Brassicaceae, Cyperaceae, Euphorbiaceous, Poaceae, Fabaceae* etc. Literature shows that almost 400 plant species identified as hyperaccumulators. Among all, most of the plant species are concentrated in family *Brassicaceae* (Ali et al., 2013). These stored heavy metals have beneficial effects on the functioning of plants including physiological and ecological functioning like they have a genetic advantage that they can obviate herbivores or increase the toxicity of anti-herbivorous activators due to the high concentration of toxic heavy metals in their leaves (Rascio and Navari-Izzo, 2011).

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7. Conclusions

The continuous contamination of soil and water ecosystem is a serious environmental concern, therefore restitute measures are required crucially. The extravagant and uneconomical existing clean-up and restoration methods led the researchers and experts to the exploration for new remediation techniques that can be economical and eco-friendly as well. Phytoremediation has been identified as environment-friendly & economical by many researchers. This technique has been found beneficial in soil nourishment as it increases soil fertility and improves the soil structure. It is an integrated approach with background knowledge in soil chemistry, botany, soil microbiology as well as environmental engineering. Different research are being conducted for advancement in the phytoremediation technique via genetically modification in various plant species. It is anticipated to be a commercially feasible technique in forthcoming years.

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