Review Article

PHYTOREMEDATION: AN EFFECTIVE WAY TO TREAT HEAVY METAL CONTAMINATION- A REVIEW

Abstract

Over the years there has been a drastic increase in heavy metal contamination in the soil due to a number of natural and industrial processes. As these heavy metals are non-biodegradable in nature, they remain in the environment for long periods of time and may infiltrate into the food chain through plants and eventually get accumulated in the human body *via* biomagnification. Because of their poisonous nature, they pose a major threat to human health and environment. Therefore, the process of cleaning up of this contamination from the environment is of great significance.Phytoremediation, an ecologically viable process, can be a very good mitigation strategy to rid the soil from this heavy metal pollution. Though phytoremediation is not capable of completely removing dangerous pollutants, it has no deleterious effect on the ecosystem as it is an environment friendly, cost-effective, and natural process. Different plants, the majority of which belong to the *Brassicaceae* family, that are used in the phytoremediation process are referred to as hyper accumulators. The efficacy of phytoremediation can be improved by having deeper knowledge and understanding of different mechanisms contributing to heavy metal accumulation and tolerance in plants. Different mechanisms such as phytoextraction, phytostabilization, phytovolatilization, and rhizofiltrationhave been employed to reduce contamination of heavy metals in the soil. Among these, the first and second mechanisms are the most dependable. A number of factors are taken into consideration for choosing the most appropriate phytoremediation strategy for soil decontamination. There are a number of factors that influence the phytoremediation process which include the types of contaminants, theircharacteristicsand the selection of plant species. Other factors to consider include climatic conditions, flooding and ageing, the effect of salt on the process, soil variables and the redox potential.

Keywords: Bioavailability, Heavy metals, Hyperaccumulators, Phytoremediation, Permissible limits, Toxicity

Introduction

As a result of rapid urbanization and industrialization in recent years, the concentration of heavy metals in the environment has increased significantly. This is a global concern that warrants attention and action (Ashraf *et al*., 2019). These heavy metals include cadmium (Cd), arsenic (As), mercury (Hg), lead (Pb), zinc (Zn), copper (Cu), chromium (Cr) and nickel (Ni). The accumulation of these heavy metals/metalloids in the environment results from a variety of natural and anthropogenic sources like produced water from the oil and gas industry (Pichtel, 2016), phosphate fertiliser in agriculture (Hamzah*et al*., 2016), sewage sludge (Farahat and Linderholm, 2015), metal mining and smelting (Muradoglu*et al*., 2015). Metal contamination in the environment is a worldwide problem, they are non-degradable and remain in the soil for a considerably long period of time thereby posing a great threat to the environment (Suman*et al*., 2018). They find their entry into the food chain through crops and assimilate in the human body through biomagnification, posing a serious health risk.

It was Andrea Cesalpinoin the 16th century, who discovered phytoremediation (Brooks, 1998). Phytoremediation is a process of naturally removingharmful metals from the environment *via*plants. It is environment friendly with low operating cost when compared to alternative manual procedures like electrokinetic soil remediation and acid leaching or natural methods (ion exchange, membrane filtration and adsorption) (Renu*et al*, 2017). Even at low concentration, plants,through their root system can absorb heavy metal ionic compounds from the soil. By extending their root systems into the soil matrix, plants form a rhizosphericecosystem, accumulating heavy metals and modulating their bioavailability, restoring soil fertility and thereby reclaiming polluted soil (DalCorso*et al*., 2019). Plants that can accumulate metals to a high concentration are referred as "hyperaccumulators" (Visoottiviseth*et al*. 2002).

Source, Effect and Limit of Different Harmful Metals

Heavy metals are brought into the soil environment by both geogenicand anthropogenic processes. Heavy metals from parent soil materials are released into the soil ecosystem by natural weathering processes; however they are not readily available for uptake by plants. The contamination of ground water with arsenic at a large scale in Bangladesh and West Bengal (India) is a very good example of geogenic contamination (Mahimairaja*et al*., 2005).The contribution of anthropogenic source to heavy metal pollution has risen drastically in the recent years as a result of giant strides in industrialization, urbanization,lavish lifestyles and population growth (Asati*et al*., 2016).Agricultural activities in areas on the outskirts of industrial units and peri-urban localities are being critically scrutinized due to high risk of metal pollution from sewage effluents and sludge produced from these units, which have the potential to enter the food chain through crops grown in contaminated fields, particularly vegetables. (Purakayastha, 2007, Mitra and Gupta, 1999).Chemical fertilizers also introduce into the soil a significant amount of heavy metals, for example, phosphate compounds, contain metals such as Cd. In many formulations of fungicides, such as Copper oxychloride and Bordeaux mixture, Cu is used as a trace element nutrient. It is also used as a growth promoter in poultry and piggery units in horticulture, agriculture and animal industries.

Bioavailability of these metals, on the other hand, is influenced by a variety of factors which include soil quality, exposure pathways, and animal physiological traits, and can vary from one organism to the next (Luoma*et al.*, 2005). These toxic metals can alter the water and nutrient absorption balance, interfere with their transport to aboveground plant parts and cause adverse effects on shoot growth, thereby stifle the overall plant growth (Popova*et al.*, 2009). Some metals like Cu and Zn, act as activators and cofactors of an enzyme's normal function (Mildvan, 1970). On the other hand, toxic metals like Cd, Hg, Asand leadare harmful to plants and all living things.

Toxicity of Heavy Metals

At high concentrations, all the heavy metals are toxic to crop plants. The deficiency of essential heavy metal elements is more common in agriculture than their toxicity. Heavy metals interfere withphysiological and biochemical processes, reducing growth, degrading cell organelles,and preventing photosynthesis thereby, poisoning macro- and microorganisms. Direct ingestion of contaminated soils, consumption of crops and vegetables grown on contaminated lands, or drinking water that has percolated through contaminated soils can expose humans and ecosystems to heavy metals(lead, chromium, arsenic, zinc, cadmium, copper, mercury, and nickel) (McLaughlin *et al*., 2000).For example, Chaney *et al*. (2005) concluded that lives of subsistence farmers who eat rice grown on contaminated sitesare at risk of cadmium poisoning. According to Kuzovkina*et al*. (2004), cadmium is highly phytotoxic and can result in rapid death.According to a report released by a US environmental action group, the world's most polluted places endanger the health of more than 10 million people in many countries (Chhotu*et al*. 2009).On the basis of their functionin biological systems, heavy metals are classified into two categories *viz*., essential and non-essential. The essential group comprises of Cu, Fe, Mn, Ni, and Zn. These are important for physiological and biochemical processes during the plant life cycle; however, they can be toxic, when present in excess concentrations.Pb, Cd, As, and Hg fall into non-essential categoryhaving no known function in plants and are highly toxic (Fasani*et al*., 2018). They interfere with metabolic processes and inhibit growth at higher concentrations, which can lead to plant death.They disrupt a number of physiological and biochemical processes in crop plants, resulting in reduction of agricultural productivity (Clemens, 2006). Phytotoxicity due to heavy metals can result from changes in cellular and molecular physiological processes due to deactivation of enzymes or the functional groupblocking of metabolically important molecules (Ahmadpour*et al*., 2012). Some heavy metals like Pb tend to accumulate more in the roots than in stems, because some barriers prevent them their movement from the roots to aboveground parts. However, metals like Cd, move around in plants more easily (Garbisu and Alkorta, 2001). Cadmium damages the plant's light harvesting complex II, as well as photosystems I and, which are involved in photosynthesis. Cadmium treatment reduces total chlorophyll content in the plants simultaneously increasing non-photochemical quenching in *Brassica napus*. It is likely to cause obstruction in the movement of K^+, $Ca^{2+}$and abscisic acid in guard cells, as well as stomatal opening (Shaw, 1995).

Hyperaccumulators

In order to survive in environments with high metal content, naturally growing plants use two primary tactics as part of their survival strategy.The majority of the plant species which are capable of growing in soils containing increased concentrations of hazardous trace elements have adopted the survival strategy of maximal exclusion of heavy metal (HM) ions from the plant. They are known asExcluders. Whenever an HM ion is taken up by these plants, the poisonous effect is limited to the roots, where it is detoxified, whereas the aboveground parts remain more or less unharmed. On the other hand, some plants, when exposed to higher concentration of HM, are able to collect them in their aerial parts without phytotoxic symptomsand are called hyperaccumulators (Van der Ent*et al*., 2013). Initially the term hyperaccumulator was applied when describing the New Caledonian Ni accumulating tree *Sebartiaacuminate*, the concentration of nickel in the latex on dry weight basis was determined to be 26 percent (Jaffré*et al*., 1976).

For plants to be categorized into hyperaccumulators,the concentration limitations of several metal elements in their dry biomass are10,000 mgkg^{-1} for Zn and Mn, 1,000 mgkg^{-1} for Co, Cu, Ni and Pb, and100 mgkg^{-1} for Cd and Se(Baker and Brooks, 1989). These values are up to 100–1,000 times more than for non-hyperaccumulating species under the same conditions (Rascio&Navari-Izzo, 2011). The number of recognized hyper-accumulators has been steadily rising, with over 450 HM-hyperaccumulating species known as of 2015, found in 45 angiosperm families. About 25 percent of hyperaccumulators identified so far recruit from the family *Brassicaceae*; other families rich in hyperaccumulators include *Asteraceae, Euphorbiaceae, Rubiaceae, Fabaceae, Scrophulariacea, Myrtaceae, Proteaceae, Caryophylaceae,Tiliaceae*, etc. (Rascio and Navari-Izzo, 2011).According toBrooks *et al*., (1979),some plant genera appear to feature a large proportion of hyperaccumulatorse.g., while assessing the genus Alyssum, out of 170 species tested,48 hyperaccumulated Ni. The ability to hyperaccumulatehas been discovered to vary within a species; metal specificity and accumulation can vary among different populations (Assuncao*et al*., 2008). Acoording to Milner and Kochian (2008), who evaluated the Zn, Cd and Ni model hyperaccumulator alpine pennycress (*Noccaeacaerulescens*), several essential physiological stages of heavy metal detoxification in hyperaccumulatorsare different as compared to non-hyperaccumulators. These are:

1. Increaseduptake of HM ions from the rhizosphere across the root cell plasma membrane.
2. Reduced sequestration of HM ions in root vacuoles.
3. Intensified loading of HM ions into the xylem for transportation to shoots.
4. Stimulated influx of HM ions across the plasma membrane of leaf cell.
5. Sequestration in the leaf vacuole.

Nevertheless, in the sequestration of HM ions within a plant body, a major involvement of cell wall components, especially low-methylesterifiedpectins, was also hypothesized by Krzesłowska, 2011. Thebasic mechanism for hyperaccumulation in some plants is due to improved active metal transport rather than strengthened metal complexation by some intracellular ligands like phytochelatins, glutathione, or metallathioneins(Leitenmaier and Küpper, 2013).Further, in case of extremophilic Zn- and Cd-hyperaccumulator*Arabidopsis halleri*, transcriptomic and genome-wide analysis showed an enrichment in HM-transporting P-ATPAse HMA4 gene copies and corresponding transcripts as well as other transition metal homeostasis and biotic stress function genes,as compared to the non-accumulating sister species *Arabidopsis lyrata* and closely related reference model species *Arabidopsis thaliana* (Suryawanshi*et al*., 2016). More detailed information on the various tolerance strategies of plants under HM stress and on hyperaccumulators, their taxonomic and geographical distribution, metal specificity as well as molecular mechanisms behind hyperaccumulation have been provided by Rascio and Navari-Izzo (2011);Leitenmaier and Küpper (2013) and van der Ent*et al*. (2013).

Techniques of Phytoremediation

Phytoextration

A type of phytoremediation in which the plantsextract harmful elements or compounds from the soil or water is called Phyto-extraction. It is basically the ability of some plants to absorb metals from the soil and assimilate them in the harvestable shoots. The concentration of heavy metals is higher in roots than the shoots, but there is a limit to this concentration. For example, root uptake of Pb increased inhydroponically grown plants with increase in its concentration in the solution and reached maximum, thereafter did not increase any further with increase in the concentration (Deepa, *et al*. 2006).The percentage of exchangeable Cd in the soil decreased as maize phytoextraction increased (Zhang *et al*., 2009). Phytoextraction could become a commercial technology in the future.

Phytodegradation

Phytodegradation,also knownas Phytotransformation,involves the use of plants and microorganisms for uptaking, metabolizing and degrading the organic contaminants. Plant roots in conjunction with microorganismsare used to detoxify organic contaminants in the soil (Garbisu and Alkorta, 2001). Various enzymes produced by certain plants help to metabolise contaminants that may be released into the rhizosphere, where they can persist (Singh *et al*., 2003). Some halophytes convert Cr (VI) to less toxic Cr (III) (Cacador and Duarte, 2015).Various bacterial and fungal microorganisms can also help in conversion of toxic metals into less toxic forms. By producing certain specific enzymes, some plants can decontaminate soil, sludge, sediment, and ground and surface water (Pivetz, 2001).

Phytostabilization

It is the process of reducing heavy metal mobility in the soil. The immobilization can be achieved by decreasing contaminant solubility or bioavailability in the food chain, minimizing soil erosion and reducing windblown dust. Revegetation of the sitesignificantly improves physicochemical and biological properties of the contaminated soil by increasing organic matter content, cation exchange capacity, nutrient levelsand biological activity (Arie, *et al*. 2004).Heavy metals like Cd, Cu, Zn, Cr and As can all be remedied using phytostabilization. The most important advantage of this technology is that it does not involve the disposal of hazardous materials (United States Protection Agency, 2000) and it is also very effective when quick immobilization of ground and surface waters is needed (Chhotu, *et al*. 2009).

Rhizofiltration

The technique to remediate contaminated groundwater, surface water, and wastewater with low levels of contaminants through the use of various plants is called Rhizofiltration. Ultramatic soils enriched with Cd, Ni, Zn, or Pbcan be remedied by growing *Berkheyacoddii* plants, which accumulate a significant amount of these metals. Exposed shoots as compared excised shoots in solutions containing the same heavy metals accumulate a higher amount of these metals in the leaves (Mesjasz-Przybylowicz*et al*.,2004). The ability of various plants like sunflower, rye, spinach, Indian mustard, tobacco and corn to remove lead from water has been studied, with sunflower having the greatest ability (Chhotu*et al*. 2009). Heavy metals like Pb, Cd, Cr, Zn, Cu and Ni which are primarily retained within the roots can be effectively treated with rhizofiltration(United States Protection Agency, 2000).

Phytovolatilization

This involves theusual uptake and transpiration of a contaminant by a plant, followed by the release of the contaminant or its modified form into the atmosphere. A number of these contaminants can pass through the plants to their leaves and volatilize at a low concentration into the atmosphere (Ismail, 2012). Some plants grown in high selenium media are able to transform Se into dimethylselenide and dimethyldiselenide (Banuelos, 2000). Some bacteria are capable to absorb mercury and evaporate it. In contrast to other remediation techniques, contaminants once removed byvolatilization, cannot be prevented from spreading to other areas.

Factors that Influence Heavy Metal Phytoavailability

The terms phytoavailabilityand bioavailability are used to characterise the extent to which pollutants are available for uptake or absorption by living organisms. Only the partwhichis "phytoavailable" to them causes plants to respond (Chang *et al*. 2014). Bioavailability of metals in soils is a critical element governing heavy metal uptake by plants in phytoremediation especially phytoextraction (Farid*et al*. 2013). On the other hand, metal phytoavailability, is a complex phenomenon that is affected by a number of interconnected elements.

Soil Characteristics

Soil pH

Soil pH has a direct impact on metal phytoavailability, as soil acidity determines metal solubility and their capacity to move in the soil solution. Metal cations are the most mobile under acidic soil conditions, whereas anions have the tendency to sorb to oxide minerals in this pH (Dzombak and morel, 1987). Metal bioavailability increases at low pH as more metals are liberated into the soil solution,due to competition with H^+ ions. At high pH, cationsadsorb to mineral surfaces or precipitate, causing immobilization of metal anions. Majority of the heavy metals in soil are not available to plants at neutral or alkaline pH, especially Cr and Pb, which are intrinsically immobile (Mahmood, 2010).

Soil Texture

The texture of the soil provides information regarding the concentration of particles like oxides and clay (Sherene, 2010). The particle size distribution actively affects the level of metal contamination. The reactivity and surface area of fine particles is higher than the coarser ones, resulting in greater pollution levels in the fine fraction of soil (Evanko and Dzombak, 2004). For instance,Pblevels in fine and coarse textured soils have been recorded to be 3889 $mgkg^{-1}$and 530 $mgkg^{-1}$, respectively (Sherene, 2010).

Soil Organic Matter

The behavior of heavy metals in the soil is being regulated at a large scale by the presence of organic matter in the soil. Organic matter is that fraction of the soil that may diminish the ability metals to be phytotoxic due to metal-organic complexation. Cation exchange capacity of the soil is enhanced by organic carbon,thereby allowing more nutrient retention by the plants (Yobouet*et al.*, 2010). Therefore, trace metal uptake by the plants can be reduced to a great degree by increasing the organic matter content in the soil. The soils rich in organic matter actively maintain metallic elements. The bioavailabilities of metals can be reduced in contaminated soils containing labile elements by compost amendmentsthrough sorption processes (Brown *et al*, 2003).

Redox Potential

One of the most important soil attributes that influences metal speciation variations is the redox potential. It is determined by the microbial activity that causes oxidation-reduction reactions in the soil. These redox processes convert contaminants into such forms that are non-hazardous or less toxic, more stable, less mobile, and/or inactive (Alkorta*et al*, 2004).

Conclusion

The process of phytoremediation seems to be an efficient and promising cleanup strategy for a wide variety of contaminants (organic and inorganic) and sites. It can be used both in-situ and ex-situ, depending on the situation. In-situ application is usually preferred as it limits thesoil and ecosystem disturbance and pollution spread by air and waterborne wastes. When executed properly, phytoremediation has the advantage of being ecologically beneficial and visually acceptable to the general public. It can be executed in a simple manner not requiring expensive equipment or highly qualified personnel. The main advantage of phytoremediation is that it is cost effective compared to traditional clean-up solutions. For instance, the cost of cleaning up one acre of sandy loam soil with a contamination depth of 50 cm through plants was estimated to be $60,000-$100,000 compared to $400,000 in case of traditional excavation and disposal approach (Number Ma *et al*. 1997). Therefore, the current review focuses on different phytoremediation processes and their potential as remediation techniques that take advantage of plant's inherent ability to remove contaminants from the environment, but which are still not commercially available in many regions of the world.

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