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Review Paper

Phytoremediation: A Review Focusing on Phytoremediation Mechanisms

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Abstract: Rapid industrialization and urbanization has led to increased disposal of pollutants such as heavy metals, radio-nuclides, various types of organic and inorganic compounds into the environment. The rapid build-up of toxic pollutants in soil, surface water, and ground water affects natural resources, besides causing major strains on ecosystems and thus pose serious risks to human health. Many physico-chemical processes such as screening, coagulation, activated carbon treatment, ion-exchange electrodialysis, trickling filtration, reverse osmosis and activated sludge digestion have been employed for the treatment of polluted water. But all these methods involve high energy and large capital investments. Recently, Phytoremediation has been employed successfully to clean up ground water pollution and soil-contaminated sites because this method is aesthetically pleasing, solar energy giving and passive technique. The objective of this review paper is to present the various phytoremediation mechanisms such as Phytoextraction, Phytovolatilization, Phytostabilization, Rhizofiltration, Phytodegradation Rhizodegradation for different plant species and their potentials as phytoremediators. Although these techniques have been successfully employed for the treatment of water pollution, yet the commercial application of this technology has to be investigated.

Keywords: Phytoextraction, Rhizofiltration, Phytovolatilization, Phytostabilization, Phytodegradation, Rhizodegradation.

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Introduction

The term 'phytoremediation' has been coined from two prefixes, the Greek prefix *phyto* meaning plant and the Latin prefix meaning to correct or remove^[1]. Phytoremediation is replacing the earlier technologies used for removing water pollution which often require high capital inputs and are labour and energy intensive. Phytoremediation is an eco- friendly technology used to treat and control wastes in water, soil and air by using plants. Contamination of soil by oil spills is a huge environmental problem which requires cleaning of the sites of contamination.

Phytoremediation describe the use of plants to reduce the volume, mobility, or toxicity of contaminants in soil^[2], groundwater, or other contaminated media^[3]. In Phytoremediation the plants are used to clean up pollution in the environment.

Plants can clean many kinds of pollution including heavy metals, pesticides, explosives, petroleum-hydrocarbons and oil^[4,5]. They also help to prevent groundwater, rain, and wind from carrying pollutants away from sites to other areas.

Phytoremediation is a cost effective *in situ* technology that can be used for the clean-up of contaminated soils. The utility of phytoremediation is high in tropical climatic conditions which favors plant growth^[6].

The ability of plants that they can remove contaminants from the environment has been recognized from at least 300 years and is used in many applications such as land farming of waste. With the passage of time, this plants are used for the construction of treatment wetlands or to counteract air

pollution. During recent years, it has been recognized that huge damage occurs around the world from extensive use of chemicals in industries, therefore it creates interest in finding technologies that could remove the residual contamination. Phytoremediation is emerging technology which does not create environmental pollution. Stephenson et al. studied the evolution of phytoremediation and said that it is one step forward, but two step backward process into commercial technologies^[7].

Research activity based on application of phytoremediation has increased during the last 15 years. In the United States^[8], phytoremediation has been utilized as a remedy through plants at 18 different highly polluted sites. In Europe, phytoremediation is used in long term field experiments of trace element-contaminated soils^[9]. The International Journal of Phytoremediation is being published quarterly since 2001. International conferences have been convened many times on phytoremediation work. Sufficient amount of funds have been made available to carry out research in the laboratory, greenhouse, and field scale to understand the mechanism and the actual remediation performance of various plant species in different media and contaminants^[10].

The objective of this review paper is to present the various phytoremediation mechanisms for different plant species and their potentials as phytoremediators. Many researches are required to make this technique a commercially available technology in many parts of the world especially in the developing countries like India.

Mechanisms of Phytoremediation

The mechanism and efficiency of phytoremediation process depend on the type of contaminants, bioavailability and soil properties^[11]. There are many ways by which plants can remediate contaminated sites. The uptake of contaminants in plants occurs primarily through the root system. The root system provides sufficient surface area which absorbs and accumulates nutrients essential for growth along with other non-essential contaminants^[12].

It has been identified that there are six mechanisms by which plants can remove contaminants in soil, sediments, and water.

- Phytoextraction
- Rhizofiltration
- Phytovolatilization
- Phytostabilization
- Phytodegradation
- Rhizodegradation

Every mechanism will have an effect on the volume, mobility or toxicity of contaminants as a phytoremediation method^[13].

Phytoextraction

Phytoextraction is the focus of present research and is therefore most commonly recognized among different phytoremediation techniques. It involves the use of plants to facilitate the removal of metal contaminants from a soil^[14]. In practice, metal-accumulating plants are seeded or transplanted into metal-polluted soil and are cultivated using normal agricultural practices. The roots of established plants absorb metal elements from the soil and transfer them to the above-ground shoots where they accumulate. If metal availability in the soil insufficient for plant uptake, then chelates or acidifying agents may be added to liberate them into the soil solution^[15,16]. After sufficient plant growth and metal accumulation, the above-ground portions of the plant are harvested and removed, resulting the permanent removal of metals from the site. This is also called phytoaccumulation. Discovery of metal hyperaccumulator species demonstrates that plants have the potential to remove metals from contaminated soils^[12]. A hyperaccumulator plant like *Halianthus annuus*, *Calendula officinalis*, *Cannabis sativa*, *Solanum nigrum*, *Rorippa globosa* etc. is a plant species capable of accumulating 100 times more metal than a common non-accumulating plant^[17-19]. Metals such as nickel, zinc and copper are most conveniently removed by phytoextraction because they are preferred by a majority of plants that uptake and absorb unusually large amounts of metals.

Many factors determine the effectiveness of phytoextraction in remediating metal-polluted sites^[20]. The site selection is of primary concern. Phytoextraction is applicable only to those sites which contain low to moderate levels of metal pollution, because plant growth is not sustained in heavily polluted soils. Soil metals should also be subjected to absorption by plant roots. As a plant-based technology, the success of phytoextraction is dependent upon several plant characteristics. The two most important factors are

- (i) The ability to accumulate large quantities of biomass rapidly and
- (ii) The ability to accumulate large quantities of environmentally important metals in the shoot tissue^[21, 22].

Ebbs et al.^[23] reported that *B. juncea*, is more effective for Zn removal from soil than *T. caerulescens*, a known hyperaccumulator of Zn. This advantage is due to the fact that *B. juncea* produces ten-times more biomass than *T. caerulescens*. At present, *B. juncea*

along with few other potential members of family Brassicaceae considered among the most viable candidates for the phytoextraction of a number of heavy metals including Cd, Cr, Cs, Cu, Ni, Pb, U and Zn^[24].

Plants which are used for phytoextraction must be able to tolerate the targeted metal, or metals, and should be efficient at translocating them from roots to the harvestable above-ground portions of the plant^[20]. Other important characteristics of plant is that it should have the ability to tolerate difficult soil conditions (e.g., soil pH, soil structure, water content, salinity). It should be able to tolerate the production of a dense root system and few diseases and insect problems. Although many plants show promise for phytoextraction, but there is no plant which shows all the desirable traits. The selection of the perfect plant for phytoextraction is the focus of many plant-breeding and genetic engineering research efforts. Plants must have mechanisms to tolerate high metal concentrations in their shoots^[25]. *Calendula officinalis* is able to accumulate Cu and Zn in their roots and shoots^[26]. Other plant like *Amaranthus* sp. is able to phytoextract heavy metals like Pb, Cd, Cu, Ni and Zn^[27], whereas *Psoralea pinnata* was able to remove Cr and Cu from the contaminated soil^[28].

There are many advantages of phytoextraction. The cost of phytoextraction is inexpensive when it is compared to conventional methods. Another benefit of phytoextraction is that the contaminant is permanently removed from the soil. In addition, the amount of waste material that must be disposed of is substantially decreased (up to 95%) and in some cases, the contaminant can be recycled from the contaminated plant biomass.

The use of hyperaccumulator plant species is decreased by shallow root system, slow growth, and small biomass production. The plant biomass must also be harvested and disposed of properly, complying with standards^[12]. There are many factors which limit the extent of metal phytoextraction includes:

- Bioavailability of metals within the rhizosphere
- Proportion of metal “fixed” within the roots
- Rate of metal uptake by roots of plants
- Rate of translocation to shoots
- Cellular tolerance to toxic metals

The method is also usually limited to metals and other inorganic compounds in soil or sediment^[13]. This clean-up method can become feasible only, when the plants are able to

- (1) extract large concentrations of heavy metals into their roots,
- (2) translocate the heavy metal into the surface biomass,
- (3) produce a large quantity of plant biomass.

In addition, remediative plants must be able to detoxify and/or tolerate high metal concentrations accumulated in their shoots^[25].

Rhizofiltration

This is basically used to remediate extracted surface water, groundwater, and wastewater with low concentrations of pollutants. It is due to absorption of pollutants in the solution surrounding the roots. Rhizofiltration is typically used for removal of metals or other inorganic compounds from the groundwater, surface water, or wastewater^[9]. In this process, plants are raised hydroponically and then they are transplanted into metal-polluted waters where plants absorb and concentrate the metals in their roots and shoots^[29-32]. pH also may cause metals to precipitate onto root surfaces. The roots or whole plants are harvested for disposal, when they become saturated with the metal contaminants^[30-32].

It is believed by many investigators that plants for phytoremediation accumulate metals only in the roots^[29-31]. It has been explained that the translocation of metals to shoots would decrease the efficiency of rhizofiltration due to increase of contaminated plant residue which should have been disposed. In contrast, Zhu et al.^[32] suggest that the efficiency of the process can be increased by using plants which have a higher power to absorb and translocate metals within the plant. In spite of the different views, it is apparent that selection of proper plant is the key to ensure the success of rhizofiltration. Dushenkov and Kapulnik^[33] describe the characteristics of the ideal plant for rhizofiltration. Plants should be able to accumulate and tolerate significant amounts of the metals under consideration, besides easy handling, low cost, and minimum secondary waste disposal. It is also desirable that the plants should produce significant amounts of root biomass or root surface area. Several aquatic plants such as water hyacinth (*Eichhornia crassipes*), pennywort (*Hydrocotyle umbellata*), duckweed (*Lemna minor*), *Pistia stratiotes*, have the ability to remove heavy metals from water^[34-38].

However, these plants have limited potential for rhizofiltration, because of their low efficiency to remove metals due to their slow-growing roots^[18]. These authors also point out that the high water content of aquatic plants complicates their drying and incineration. In spite of these limitations, Zhu et al.^[32] indicated that water hyacinth is effective in removing trace elements in waste streams. Terrestrial plants are also suitable for rhizofiltration because they produce longer, more substantial, often fibrous root systems with large surface areas for metal sorption. Sunflower (*Helianthus annuus* L.) and Indian mustard (*Brassica juncea* Czern.) are the most promising terrestrial plants for metal removal in water. The roots of Indian

mustard are effective in the removal of Cd, Cr, Cu, Ni, Pb, and Zn and sun flower removes Pb, U, Cs, and Sr from hydroponic solutions^[39-41].

Rhizofiltration is a cost-effective technology in the treatment of surface water or groundwater containing low concentrations of heavy metals such as Cr, Pb, and Zn Cu, Cd, Ni, which are primarily retained within the roots^[42]. This technology has gain commercialization because of driven by economics as well as by such technical advantages as applicability to many problem metals, ability to treat high volumes, lesser need for toxic chemicals, reduced volume of secondary waste, possibility of recycling, and the likelihood of regulatory and public acceptance^[29]. However, the application of this plant-based technology may be more challenging than other methods of similar cost. The production of hydroponically grown transplants and their successful maintenance in hydroponic systems in the field will require the expertise of qualified personnel, and the facilities and specialized equipment required can increase overhead costs. Perhaps the greatest advantage of this remediation technique is related to positive public perception. The use of plants at a site where contamination exists conveys the idea of cleanliness and progress to the public in an area that would have normally been perceived as polluted.

Rhizofiltration is similar to phytoextraction, but the plants are used primarily to address contaminated ground water rather than soil. The plants to be used for cleanup are raised in greenhouses with their roots in water rather than in soil. To acclimatize the plants, once a large root system has been developed, contaminated water is collected from a waste site and brought to the plants where it is substituted for their water source. The plants are then planted in the contaminated area where the roots take up the water and the contaminants along with it. As the roots become saturated with contaminants, they are harvested. Sunflower, Indian mustard, rye, spinach, and corn have been studied for their ability to remove lead from water, with sunflower having the greatest ability. In one study, after only one hour of treatment, sunflowers reduced lead concentrations significantly^[12].

The advantage of rhizofiltration is that this technique is able to use both terrestrial and aquatic plants for either *in situ* or *ex situ* applications. Another advantage is that contaminants do not have to be translocated to the shoots. Thus, species other than hyperaccumulators may be used. Terrestrial plants are preferred over aquatic plants because they have a fibrous and much longer root system, increasing the amount of root area^[12].

Disadvantages and limitation of this method is that it requires constant need to adjust pH, plants may first need to be grown in nursery, there is periodic harvesting and plant disposal. The cost of remediation by rhizofiltration has been estimated to be \$2-\$6 per 1000 gallons of water^[3].

Phytovolatilization

Some metal contaminants such as As, Hg, and Se may exist as gaseous species in environment. In recent years, it has been established that some naturally occurring or genetically modified plants that are capable of absorbing elemental forms of these metals from the soil, biologically converting them to gaseous species within the plant, and releasing them into the atmosphere. In Phytovolatilization contaminants are taken up into the body of the plant, but then the contaminant in form of a volatile degradation product is transpired with water vapor from leaves^[9]. Phytovolatilization involves the diffusion of contaminants from the stems or other plant parts that the contaminant travels through before reaching the leaves^[12]. This process is mainly used for mercury. It is also used for volatile organic compounds like trichloroethene and inorganic chemicals such as selenium and arsenic^[13].

Mercury and Se are toxic^[43,44], But there is doubt that whether the volatilization of these elements into the atmosphere is safe^[45]. There are many areas of Se-rich soil in many parts of the world, therefore most attention has been given to selenium phytovolatilization^[46-49]. Certain members of Brassicaceae family are capable of releasing up to 40g Se ha⁻¹day⁻¹ as various gaseous compounds. Some aquatic plants like cattail (*Typha latifolia* L.) are also used for Se phytoremediation^[50]. However, Hg-phytovolatilization has been done by genetically modified plants. The genes like bacterial organomercurial lyase (*merB*) and mercuric reductase (*merA*) genes has been inserted into plants like *Arabidopsis thaliana* L. and tobacco (*Nicotiana tabacum* L.) to modify them genetically^[51,52]. These plants absorb elemental form of Hg and methyl mercury (MeHg) from the soil and release volatile form of Hg from the leaves into the atmosphere.

The advantage of phytovolatilization is that the metal contaminant like mercuric ion, may be transformed into a less toxic substance (i.e., elemental Hg). Volatile Se compounds like dimethylselenide, are 1/600 to 1/500 as toxic as inorganic forms of Se found in the soil^[53]. The volatilization of Se and Hg is also a permanent site solution, because the inorganic forms of these elements are removed and the gaseous species are not likely to be redeposited at or near the site. Furthermore, the sites that utilize this technology may not require much management after the original

planting. This remediation method has the added benefits of permanent site solution, minimal site disturbance, less erosion, and no need to dispose of contaminated plant material^[54-55].

The disadvantage of phytovolatilization is that the mercury released into the atmosphere is again recycled by precipitation and then redeposited back into lakes and oceans, repeating the production of methylmercury by anaerobic bacteria. Methylmercury, organic form of mercury, can increase the number of abnormal sperm and decrease sperm concentration and testosterone levels^[56]. However, this technique would not be wise for sites near population centers. In spite of the controversy surrounding phytovolatilization, this technique is still used for the remediation of Se and Hg contaminated soils.

Phytostabilization

Phytostabilization is a plant-based remediation technique by which metal toxicity is reduced by immobilizing or fixing metals in soil. This technique is applied to clean those metal-polluted sites, where there is no immediate effort to remove pollutants, either because the responsible companies no longer exist or because the sites are not of high priority on a remediation agenda^[57]. This technique physically and chemically immobilizes contaminants by root sorption and by chemical fixation with various soil amendments^[57-59]. This technique decreases the movement of the contaminants and prevents migration to the ground water and thereby reduces its bio-availability into the food chain. Thus it is in-place inactivation, therefore it is also known as phytoremediation.

Metal-tolerant species is used to restore vegetation at contaminated sites, thereby decreasing the potential migration of pollutants through wind erosion and transport of exposed surface soils and leaching of soil contamination to ground water. Phytostabilization can occur through the precipitation, sorption, metal valence reduction or complexation. It is useful for the removal of lead (Pb), chromium (Cr), copper (Cu), arsenic (As), cadmium (Cd), and zinc (Zn).

The up-to-date explanation of the phytostabilization process is offered by Berti and Cunningham^[57]. Before planting, the contaminated soil is plowed to prepare a seed bed and to incorporate lime, fertilizer, or other amendments for inactivating metal contaminants. Soil amendments should fix metals rapidly following incorporation, and the chemical alterations should be long-lasting if not permanent. The most promising soil amendments are phosphate fertilizers, organic matter or bio-solids, iron or manganese oxyhydroxides, natural or artificial clay

minerals, or mixtures of these amendments. Although metal migration is minimized, soils are often subject to erosion and still pose an exposure risk to humans and other animals.

Plants which are chosen for phytostabilization should be poor translocators of metal contaminants to aboveground plant tissues that could be used by humans or animals. Selected plants should be able to grow quickly and can tolerate metal contaminants and other site conditions which may limit plant growth. Plants like *Agrostis tenuis* Sibth., *Festuca rubra* L., *K. erecta*. and *Eleusine indica* are commercially used for the phytostabilization of Pb-, Zn-, and Cu-contaminated soils^[60]. Phytostabilization is most effective at sites having fine-textured soils with high organic-matter content but is suitable for treating a wide range of sites where large areas of surface contamination exist. But, Phytostabilization is not suitable for treating highly contaminated sites because plant growth and survival is not a possibility^[57]. At sites which support plant growth, site managers must be concerned with the migration of contaminated plant residue off site or disease and insect problems which limit the longevity of the plants. The plants with low shoot accumulation should be used in order to stabilize the metals and reduce the metal dispersion through grazing animals^[61].

The advantage of this technology is that the disposal of hazardous biomass is not required and it is very effective when rapid immobilization is needed to preserve ground and surface waters^[62]. The plants also decrease soil erosion and decrease the amount of water available in the system^[3]. It is less expensive, less environmentally evasive, easy to implement. However, disadvantages of this technology is that contaminant remains in soil, therefore mandatory monitoring is required.

Phytodegradation

Phytodegradation is a technique in which plants and their associated micro-organisms uptake the organic contaminants and then metabolize and degrade them. In this technique, the roots of plants are used in combination with microorganisms. They detoxify soil contaminated with organic compounds^[63]. It is referred to the degradation of organic contaminants by internal and external metabolic processes driven by the plant^[64]. It is also known as phytotransformation. This process involves the degradation of complex organic molecules to simple molecules^[65]. When the phytodegradation mechanism is at work, contaminants are broken down after they have been taken up by the plant. As with phytoextraction and phytovolatilization, the plants can uptake the contaminants only when their solubility and hydrophobicity fall into a certain acceptable range. Phytodegradation can remediate

some organic contaminants, such as chlorinated solvents, herbicides. The plants are able to decontaminate soil, sludge, sediment, ground and surface water, organic compounds, including herbicides insecticides, chlorinated solvents, and inorganic contaminants within the plant tissue^[66]. Plants produce enzymes like dehalogenase and oxygenase which help to catalyze degradation.

Rhizodegradation

Rhizodegradation involves the breakdown of contaminants within the root zone of plant. It is done by bacteria or other microorganisms. There are 100 times more microorganisms in rhizosphere soil than soil outside the rhizosphere^[3]. Thus, it is plant-assisted bioremediation in which microbes and fungi stimulate degradation by release of exudates/enzymes into the root zone (rhizosphere)^[67]. This is also referred to as phytostimulation. The roots provide additional surface area for the growth of microbes and a pathway for oxygen transfer from the environment.

The rhizodegradation is primarily useful in the treatment of contaminated soil, but it can also treat a wide variety of organic chemicals like petroleum hydrocarbons, polycyclic aromatic hydrocarbons (PAHs), chlorinated solvents, pesticides, polychlorinated biphenyls (PCBs), benzene, toluene, ethylbenzene, and xylenes^[13].

Conclusion

There are several methods by which plants can remediate contaminated sites. Plants degrade or break-down organic pollutants, stabilize inorganic contaminants to remove pollutants from soil, sediment and/or water and air. The success of phytoremediation is not only due to one of these mechanisms because a combination of mechanisms may be at work. Thus, Phytoremediation is a cost effective, eco-friendly technique which can be profitably employed for the abatement of pollution from industrial waste water. The mechanisms by which plants promote the removal of pollutants are varied, including uptake and concentration, transformation of pollutants, stabilization, and rhizosphere degradation, in which plants promote the growth of bacteria underground in the root zone that in turn break down pollutants. Phytoremediation is useful to a variety of organic and inorganic compounds and may be applied either in situ or ex situ. In situ applications decrease soil disturbance. Moreover, Phytoremediation is easy to implement and maintain, and aesthetically pleasing to the public.

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