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A Case Study

Green revolution- phytoremediation of heavy metals from industrial effluent by water hyacinth

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Abstract

Heavy metals (Pb, Hg, As, Cd, Cr) present in many industrial effluents are non-biodegradable which affect the food chain and are hazardous to all living beings. Phytoremediation is a green revolution, innovative, economic, environmental friendly using metal accumulating plants to remove heavy metals. Water and plant factors such as physio-chemical characteristics, metal bioavailability, plant's ability to uptake, accumulate, translocate and detoxify metal amounts for phytoremediation efficiency. Eichhornia Crassipies, Limnobium Laevigatum are aquatic floating macrophytic plants occurring in meso and eutropic water reservoirs have natural ability of hyperaccumulator or by inducing chelating agents, phytoremediation can be achieved. The accumulation potential in aquatic plants is calculated by bioconcentration and translocation factor.

KEY WORDS : Heavy metal, Phytoremediation, Hyporaccumulatior, Eichhornia crassipies, Limnobium laevigatum

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Introduction

The quality of life on Earth is linked inextricably to the overall quality of the environment. In early times, it was believed that land, water and other natural resources have unlimited abundance but today, it is not true; in greater or lesser degree the human society has shown the carelessness and negligence in using them. The problems associated with contaminated sites now assume increasing prominence in many countries throughout the globe. Among the various environmental resources water is one of the most important commodities which require special attention. Water is a vital natural resource which forms the basis of all life. Heavy metals are among the most important sorts of contaminant in the industrial effluents that affect the environment. Heavy metals like Pb, Hg, As, Cd, Cr present in many industrial effluents are non-biodegradable and toxic pollutants. Lead and Mercury are highly poisonous metals which affect the food chain and are hazardous to all living beings. Several conventional methods used for removing heavy metals from the industrial effluents are expensive and also cause negative impact on ecosystem. The use of plants to reduce contaminant levels in waste water from industries is a cost effective method of reducing the risk to human and ecosystem health posed by contaminated water sources (Akpor and Muchie, 2010). Phytoremediation is a green revolution composed of various processes involving phytosequestration, phytostabilisation, phytoextration, rhizofiltration, phytodegradation, phytovolatilization using metal accumulating plants to remove heavy metals. Plants can degrade organic pollutants or contain and stabilize metal contaminants by acting as filters or traps. Phytoextraction, also called phytoaccumulation, refers to the plant uptake metal contaminants through the roots and moves them into the upper portion of the plant (stems and the leaves). Phytodegradation, also called phytotransformation, is the breakdown of contaminants taken up by plants through metabolic processes within the plant. The breakdown of contaminants in the soil through microbial activity and is enhanced by the presence of the rhizosphere are called enhanced rhizosphere biodegradation, phytostimulation, or plant-assisted bioremediation/degradation. Rhizofiltration is the adsorption or precipitation onto plant roots or absorption of contaminants into the roots which are in solution surrounding the root zone Phytostabilization is the process in which plants prevent contaminants from migrating by reducing runoff, surface erosion, and ground water flow rates. Phytovolatilization is the uptake and transpiration of a contaminant by a plant, with release of the contaminant or a modified form of the contaminant to the atmosphere from the plant (Ghosh and Singh, 2005).

Phytoremediation is innovative, economical and environment friendly for the treatment of environmental problems through the use of plants. Plants have natural ability of bio accumulate or metal-accumulating capacity is known as hyperaccumulator plants. Inducing of synthetic chelating substances such as EDTA (Gaikwad Rupali and Khan, 2014) increases metal uptake by plants and phytoremediation can be achieved. Phytoremediation takes the advantage of the unique and selective uptake capabilities of plant root systems, together with the translocation, bioaccumulation, and contaminant degradation abilities of the entire plant body. Eichhornia Crassipies, Limnobium Laevigatum are aquatic floating macrophytic plants occurring in meso and eutrophic water reservoirs can be used for the phytoremediation of lead and mercury from industrial effluent (Bieby *et al.*, 2011). Eichhornia Crassipies and Limnobium Laevigatum also have a high growth-rate, fibrous root system and broad leaves along with tendency to tolerate high metal concentration, it is considered as an important species to be used in phytoremediation technique. Water and plant factors such as physio-chemical characteristics, metal bioavailability, and plant's ability to uptake, accumulate, translocate and detoxify metal amounts for phytoremediation efficiency. The accumulation potential of lead and mercury in aquatic plants is calculated by bioconcentration factor and translocation factor.

Sources of lead and its effects :

Lead is a bluish-grey metal that occurs naturally in minute amounts within the Earth's crust. It has also been referred to as plumbum, lead metal, and pigment metal (Cheng, 2003). Frequent use in many industrial processes is the main reason for lead contamination of the environment. There are a variety of industrial processes that involve the use of lead such as mining, smelting, manufacture of pesticides and fertilizers, dumping of municipal sewage and the burning of fossil fuels that contain a lead additive. Many commercial products and materials also contain lead including paints, ceramic glazes, television glass, ammunition, batteries, medical equipment and electrical equipment. Proper treatment of lead from industrial effluent is very important.

Several conventional methods are used for the removal of lead from wastewater includes chemical precipitation, ion exchange and reverse osmosis, adsorption and various other process but major drawbacks with such treatments are produces large amount of sludge and may be ineffective or expensive processes. So, the search for a new, simple, effective and ecofriendly technology involving the removal of toxic heavy metal from wastewater has directed attention towards phytoremediaton. Lead has been listed as a potential carcinogen in the EPA Toxic Release Inventory. In human, it is absorbed directly into the blood stream and is stored in soft tissues, bones and teeth. It can also affect the kidney and most importantly the nervous system and brain. Thus, lead can accumulate over a lifetime and it causes diseases such as anaemia, encephalopathy, hepatitis and nephritic syndrome. Lead accumulates in the body organs, which may lead to poisoning or even death. The gastrointestinal tract, kidneys, and central nervous system are also affected by the presence of lead. Lead also affects the aquatic system. Certain communities of aquatic invertebrate's populations are more sensitive than others. However, populations of invertebrates from polluted areas can show more tolerance for lead than those from non polluted areas.

Sources of mercury and its effects :

Mercury, also a naturally-occurring element is a silver-white liquid at room temperature. Due to this property, it is also referred to as kwik, liquid silver, hydrargyrum, and metallic mercury. The most common mineral form of mercury is the non-toxic, insoluble mercuric sulfide or cinnabar a by-product obtained by the processing of complex ores that contain mixed sulfides, oxides, and chloride minerals. The problem with methyl-mercury is that it is consumed by aquatic organisms, especially fish and bioaccumulates in their tissues (Jeanna, 2000). Biomagnification of methyl-mercury poses a serious human health risk. Mercury poses such a huge threat to human health because once it enters the body the destruction that occurs is usually irreversible. Symptoms associated with mercury toxicity are tremors, ataxia, paresthesia, sensory disturbances, cardiovascular collapse, severe gastrointestinal damage, irreversible damage to the brain, kidneys, and developing fetuses, and even death. Studies conducted have shown that neurological symptoms caused by methyl-mercury can continue indefinitely even after exposure from the source has ceased.

Conventional methods for removal of heavy metals from industrial effluent :

Precipitation:

Chemical precipitation of heavy metals and metalloids as their hydroxides using lime or sodium hydroxide is widely used in this process. Lime is generally used for precipitation purpose due to its low cost and easy control pH in the range of 8-10. The efficiency of the process depends on a number of factors, which include the ease of hydrolysis of metal and metalloids ions, nature of the oxidation state, pH, and presence of complex forming ions, standing time and filtering characteristics of the precipitate (Ali and Zulkifli, 2010). This method has been used for the removal of metals and metalloids such as iron, copper, chromium, arsenic, cadmium and zinc from the effluents of the industries. The advantage of this process can be of low cost and minimum pH adjustment. The major disadvantage is large amount of sludge containing toxic compounds are produced.

Solvent extraction:

Solvent extraction is recommended a suitable method for the removal of heavy metals from the waste waters of the chemical and electronic industries. Solvent extraction involves on organic and an aqueous phase. The aqueous solution containing the metal or metalloid is mixed intimately with the appropriate organic solvent and the metal passes into the organic phase (Balasubramanian *et al.*, 2009). Liquid- liquid extraction of metals from solution on a large scale has experienced phenomenal growth in recent years due to introduction of selective complexing agents.

Reverse osmosis:

Reverse osmosis is pressure driven membrane process in which a feed stream under pressure is separated into a purified stream and a concentrated stream by selective permeation of water through a semi-permeable membrane (Applegate, 1984). Reverse osmosis enjoys wide spread popularity in the treatment of numerous diverse wastewaters. Reverse osmosis has also been successfully demonstrated for the removal of Cr, Pb, Fe, Ni, Cu and Zn from vehicle wash-rack water. The major disadvantage is high cost and clogging of membrane.

Electrodialysis:

Electrodialysis is accomplished by placing cation and anion selective membranes alternatively across the path of an electric current. The ionic component that is heavy metals are separated through the use of semi-permeable ion selective membranes. Application of an electrical potential between the two electrodes causes a migration of cations and anions towards respective electrodes. The advantage is osmotic pressure is not a factor in elctrodialysis system, so the pressure can be used for concentrating salt solutions to 20 per cent or higher (Ribeiro *et al.*, 2000). The major disadvantage of this is the formation of metal hydroxides, which clog the membrane.

Adsorption:

Adsorption is a conventional but efficient technology for the removal of toxic pollutants from wastewaters (Connell *et al.*, 2008). So, there is a need to develop low cost and easily available activated carbon adsorbents for the removal of heavy metal ions from the aqueous environment. In physical sorption, no exchange of electron is observed; rather, intermolecular attraction between favorable energy sites take place and are therefore independent of the electronic properties of the molecules involved. The biosorbate is held to the surface by relatively weak van der Waals forces and multiple layers may be formed with approximately the same heat of biosorption (Hamdi Karaoglu *et al.*, 2010). Chemical sorption involves an exchange of electron between specific surface sites and solute molecules, and as a result, a chemical bond is formed. Chemisorption is characterized by interaction energies between the surface and adsorbate comparable to the strength of chemical bonds (tens of Kcal/mol), and is consequently much stronger and more at high temperatures than physisorption. Generally, only a single molecular layer can be adsorbed. The main advantages of this technique are the reusability of material, low operating cost, improved selectivity for specific metals of interest, removal of heavy metals from effluent irrespective of toxicity, short operation time.

Ion exchange:

Ion exchange is a process in which solid material takes up charged ions from a solution and release an equivalent amount of other ions into the solution. The ability to exchange ions is due to the properties of the structure of the materials. The exchanger consists of a matrix, with positive or negative excess charge (Sahu *et al.*, 2009). This excess charge is localized in specific locations in the solid structure or in functional groups. The charge of the matrix is compensated by the counter ions, which can move within the free space of the matrix and can be replaced by other ions of equal charge sign. The pores sometimes contain not only counter ions but also solvent. When the exchanger is in contact with the liquid phase, the solvent can travel through the exchanger and cause "swelling" to an extent that depends on the kind of counter ions. Some electrolytes can also penetrate into the exchanger along with the solvent. As a result, there are additional counter ions, called co-ions, which have the same charge sign as fixed ions. Normally, exchanger has many open areas of variable size and shape that are altogether called "pores." Only a few inorganic exchangers contain pores of uniform cross section (Helfferich, 1962). The removal of anionic or cationic constituents present in water by exchange with ions of the resin. When the resin bed becomes saturated, they are regenerated using acid or alkali. Ion-exchange resins are available selectively for certain ions. However, in the presence of large quantities of competing mono and divalent ions such as sodium and calcium, efficiency of ion- exchange process decreases. Ion removal by solids could involve more phenomena, as for example in inorganic natural materials where ion uptake is attributed to ion exchange and adsorption processes or even to internal precipitation mechanism. The major disadvantage is that it permits only partial removal of certain ions.

Wastewater treatment using phytoremediation technique :

Phytoremediation is considered as green revolution and has been called as green remediation, botano-remediation, agro remediation and vegetative remediation. Phytoremediation is a novel strategy that uses various plants to degrade, extract, contain, or immobilize contaminants from soil and water (Sarma, 2011). The term phytoremediation is a combination of two words-phyto, which means plant, and remediation, which means to remedy (Salt *et al.*, 1995). The term was first coined in 1991 to describe the use of plants to accumulate metals from soil and groundwater. This technology has been receiving attention lately as an innovative, cost-effective alternative to the more established treatment methods used at hazardous waste sites. Phytoremediation efforts have focused on the use of plants to accelerate degradation of organic contaminants, usually in concert with root rhizosphere microorganisms, or remove hazardous heavy metals from waste water. Phytormediation is an attractive alternative or complementary technology that can be used along with or, in some cases in place of mechanical conventional cleanup treatments that often require high capital inputs, more labour and energy intensive. Organic substances like chlorinated solvents, explosives, pesticides and inorganic substances like heavy metals, radionuclides, can be removed by phytoremediation technique.

Mechanisms:

A relatively small group of hyperaccumulator plants is capable of sequestering heavy metals in their shoot tissues at high concentrations. In recent years, major scientific progress has been made in understanding the physiological mechanisms of metal uptake and transport in plant. The major processes involved in hyperaccumulation of heavy metals from the water to the shoots by hyperaccumulators include bioactivation of metals in the rhizosphere through root-microbe interaction (Prasad *et al.,* 2010); enhanced uptake by metal transporters in the plasma membranes; detoxification of metals by distributing to the apoplasts like binding to cell walls and chelation of metals in the cytoplasm with various ligands, such as phytochelatins, metallothioneins, metal-binding proteins; sequestration of metals into the vacuole by tonoplast-located transporters. Once the rate-limiting steps for uptake, translocation, and detoxification of metals in hyperaccumulating plants are identified, more informed construction of transgenic plants would result in improved applicability of the phytoremediation technology (Sinha *et al.,* 2004). The uptake mechanism of phytoremediation involving various processes is shown in the figure.

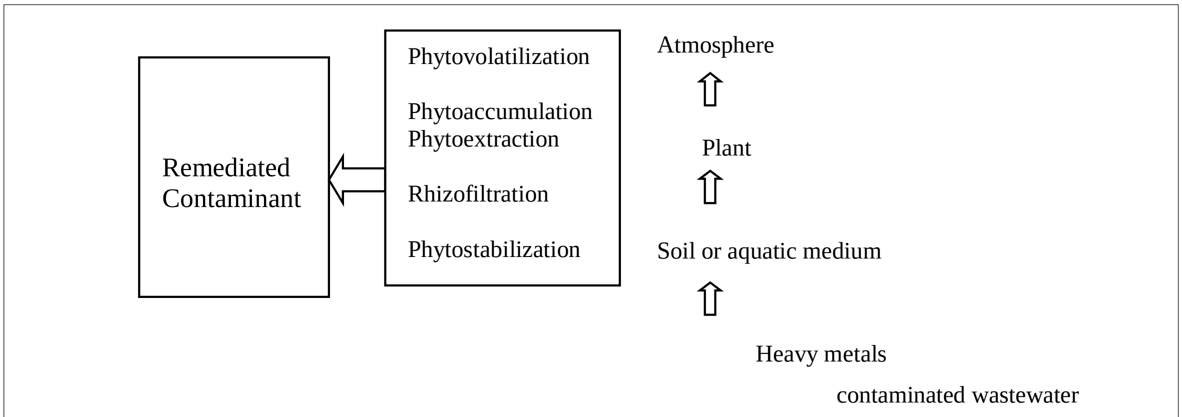

Fig. 1 : The uptake mechanism of phytoremediation

Phytoextraction:

Specific plant species can absorb and hyperaccumulate metal contaminants and/or excess nutrients in harvestable root and shoot tissue, from the growth substrate through phytoextraction process. This is for metals, metalloids, radionuclides, nonmetals, and organic contaminants in wastewater sludges medium. There are several factors limiting the extent of metal phytoextraction including, metal bioavailability within the rhizosphere, rate of metal uptake by roots, proportion of metal fixed within the roots, rate of xylem loading or translocation to shoots, cellular tolerance to toxic metal (Saraswat and Rai, 2009). The advantage of this process is inexpensive and the contaminants of heavy metals are permanently removed. The disadvantages are metal hyperaccumulators are generally slow- growing with a small biomass and shallow root systems. Plant biomass must be harvested and removed, followed by metal reclamation or proper disposal of the biomass.

Phytovolatilization:

Phytovolatilization also involves contaminants being taken up into the body of the plant, but then the contaminant, a volatile form thereof, or a volatile degradation product is transpired with water vapor from leaves (DiLonardo *et al.,* 2011). Phytovolatilization can occur with contaminants present in soil, sediment, or water. Mercury is the primary metal contaminant that this process has been used for. It has also been found to occur with volatile organic compounds, including trichloroethene, as well as inorganic chemicals that have volatile forms. The major advantages of phytovolatilization are contaminants could be transformed to less-toxic forms, such as elemental mercury and dimethyl selenite gas. Contaminants or metabolites released to the atmosphere might be subject to more effective or rapid natural degradation processes such as photodegradation. The major disadvantage is that low levels of metabolites have been found in plant tissue.

Rhizofiltration:

Rhizofiltration is primarily used to remediate extracted groundwater, surface water, and wastewater with low contaminant concentrations. Plant roots take up metal contaminants and/or excess nutrients from growth substrates through rhizofiltration process, the adsorption, or, precipitation onto plant roots or absorption into the roots of contaminants that are in solution surrounding the root zone. It is defined as the use of plants, both terrestrial and aquatic, to absorb, concentrate, and precipitate contaminants from polluted aqueous sources in their roots (Walton and Anderson, 1990). Rhizofiltration can be used for Pb, Cd, Cu, Ni, Zn, and Cr, which are primarily retained within the roots. The advantage of this method is that the contaminant, mercuric ion, may be transformed into a less toxic substance. Disadvantages and limitations include the constant need to adjust pH, plants may first need to be grown in a greenhouse or nursery; there is periodic harvesting and plant disposal; tank design must be well engineered; and a good understanding of the chemical interactions are needed.

Phytostabilization:

Phytostabilization is the process of certain plant species to immobilize contaminants in the soil and ground water through absorption and accumulation by roots, adsorption onto roots, or precipitation within the root zone of plants. This process reduces the mobility of the contaminant and prevents migration to the ground water and it reduces bio-availability of metal into the food chain (Dary *et al.*, 2010). Phytostabilization can occur through the sorption, precipitation, complexation, or metal valence reduction. It is useful for the treatment of lead as well as arsenic, cadmium, chromium, copper and zinc. Phytostabilization takes advantage of the changes that the presence of the plant induces in soil chemistry and environment. The advantage of this process is the disposal of hazardous biomass is not required. The presence of plants also reduces soil erosion and decreases the amount of water available in the system. The clean-up technology has several major disadvantages including, contaminant remaining in soil, application of extensive fertilization or soil amendments, mandatory monitoring is required, and the stabilization of the contaminants may be primarily due to the soil amendments.

Aquatic plants in phytoremediation:

Aquatic plants are known for accumulating and concentrating heavy metals and metal fluxes rough those ecosystems. Several studies have shown that aquatic plants are very effective in removing heavy metals from polluted water. Plant assimilation of nutrients and its subsequent harvesting are another mechanism for pollutant removal. Low cost and easy maintenance make the aquatic plant system attractive to use. Thus, aquatic plants are increasingly applied as a viable treatment for municipal wastewater (Alvarado *et al.*, 2008). The accumulation of metals in various parts of aquatic plants is often accompanied by an induction of a variety of cellular changes, some of which directly contribute to metal tolerance capacity of the plants. However, there are some constraints with using aquatic plants such as the requirement for large area of land, the reliability for the pathogen destruction, and the types and end-uses of aquatic plants. One reason that the aquatic plants are able to remove of the heavy metals from the water than terrestrial plants from soil is the soluble form the metals in water. Metals present in a soluble form in soils before plants can absorb them. In an aqueous solution, metals are ready in soluble form so accumulation by the plants can be achieved much easier. Recently, there has been growing interest in the use of metal-accumulating roots and rhizomes of aquatic and semi-aquatic vascular plants for the removal of heavy metal from contaminated stream.

Eichhornia crassipes also called as water hyacinth has been listed as most troublesome weed in aquatic system. It is a submerged aquatic plant, found abundantly throughout the year in very large amount and drainage channel system in and around the fields of irrigation (Singh *et al.*, 2012). The heavy metals Pb, Hg, Zn, Mn show greater affinity towards bioaccumulation. Presence of higher concentration of heavy metals in plants signifies the biomagnifications. Eichhornia crassipes is the unique property to accumulate heavy metals Cd, Cu, Pb and Zn from the root tissues of the plant. Water hyacinth is able to absorb and translocate the cadmium (Cd), lead (Pb), copper (Cu), zinc (Zn), and nickel (Ni) in the plant's tissue as a root or shoot. However, it is 3 to 15 times better to locate the elements into the roots than the shoots. Water hyacinth plants have high bioconcentration with low concentrations of the five elements. This shows that water hyacinth can be a promising candidate to remove the heavy metals. This plant also exhibited that Pb accumulated mainly in the roots and the petiole contents comparable at high concentrations than other parts and prolonged immersion. The relatively low leaf contents, until drastic conditions are used, indicated the presence of a prevention mechanism to inhibit Pb uptake (David *et al.*, 2003). Wolverton (1989); Brix (1993) and Johnston (1993) explained that reason for turbidity reduction *i.e.* the root hairs have electrical charges that attract opposite charges of colloidal particles such as suspended solids and cause them to adhere on the roots where they are slowly digested and assimilated by the plant and micro-organisms. Brix (1993) observed that Eichhornia crassipes has been used successfully in wastewater treatment system to improve the water quality by reducing the levels of organic and inorganic nutrients. Thus, the water hyacinth would probably have high tolerance and should be capable of removing large amounts of lead and mercury.

Addition of synthetic chelates :

One major factor limiting the potential for lead phytoextraction is low metal bioavailability for plant uptake. Chelators have been isolated from plants that are strongly involved in the uptake of heavy metals and their detoxification. Chelating agents like ethylenediamine tetra acetic acid (EDTA) are applied to lead and mercury contaminated water that increases the amount of bioavailable lead and mercury in the water and a greater accumulation in plants. The use of synthetic chelates in the phytoremediation process is not only to increase heavy metal uptake by plants through increasing the bioavailability of the metal, but also to increase micronutrient availability, which decreases the possibility of plant nutrient deficiencies. Increasing the mobility and bioavailability of lead in the soil through certain chelators, organic acids, or chemical compounds, allows for the hyperaccumulation of metals in some plants. For lead, a number of different chelators like EDTA (ethylene-dinitrilo- tetraacetic acid), CDTA (trans-1,2-cyclohexylene-dinitrilo-tetraacetic acid), DTPA (diethylenetrinitrilo-pentaacetic acid), EGTA (ethylebis[oxyethylenetrinitrilo]-tetraacetic acid), HEDTA (hydroxyethyl-ethylene-dinitrilo-triacetic acid), citric acid, and malic acid can be used (Van Ginneken *et al.*, 2007). Addition of the chelates results in enhanced shoot lead concentrations. Plant roots exude organic acids such as citrate and oxalate, which affect the bioavailability of metals. In chelate-assisted phytoremediation, synthetic chelating agents such as NTA and EDTA are added to enhance the phytoextraction of water-polluting heavy metals. The presence of a ligand affects the biouptake of heavy metals through the formation of metal-ligand complexes and changes the potential to leach metals below the root zone.

Translocation factor :

The accumulation potential of heavy metals in plants can be calculated by using Translocation factor and bioconcentration factor. To evaluate the potential of Eichhornia Crassipies for phytoextraction, the Translocation factor is an indication of the ability of the plant. The Translocation Factor is defined as the ratio of metal concentration in aerial parts to that of the metal concentration in roots.

Bioconcentration factor :

The bioconcentration factor is a measure of bioaccumulation of heavy metals. BCF is used to determine the quantity of heavy metal absorbed by plant from the water. It can be calculated as the ratio of concentration of the element in plant tissues to that of initial concentration of the element in the external nutrient solution. This index is used to measure the ability of the plant to accumulate a particular metal with respect to its concentration in the surrounding water medium. The higher the bioconcentration value, the more suitable is the plant for phytoaccumulation. The BCF value greater than 2 is regarded as high.

Conclusion :

Phytoremediation being a sustainable and inexpensive process is fast emerging as a viable alternative to conventional remediation methods, and will be most suitable for a developing country like India. It is easy to implement and maintain, does not require the use of expensive equipment or highly specialized personnel and is environmentally friendly and aesthetically pleasing to the public. Several factors must be considered in order to accomplish a high performance of remediation result. The most important factor is a suitable plant species which can be used to uptake the contaminant. The accumulation and translocation potential of lead and mercury from industrial effluent in aquatic plants like Eichhornia Crassipies and Limnobium Laevigatum are high comparatively to other plants. Eichhornia crassipes used in 'Eco-technology' for phytoextraction and phytofiltration are the best-developed subsets for removal of toxic metal from environment. Nutrient culture is an efficient method for screening heavy metal ions tolerant for free floating plants of Eichhornia crassipes and Limnobium laevigatum.

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