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Research Article

Removal of metallic toxicant copper by phytoremediation technique from grown in industrial effluent water

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Abstract

This paper reports the removal of Copper metal from Grown in Industrial Effluent Water by using Phytoremediation technology. Effect of various process parameters such as initial metal ion concentration, p^H , Adsorbent Dose ,BOD and COD has been Studied for the removal of Copper metal ,experimental data were analyzed by Selected Macrophytes, *Eichhornia Crassipes* and Macrophytes, *Pistia stratiotes.* The characteristic parameters have determined by Copper metal uptake and Accumulation of Cadmium by macrophytes and its Translocation And removal efficiency have been studied through before and after phytoremediation technique.

Keywords: Copper metal, Phytoremediation , p^H , Adsorbent Dose ,BOD and COD analysis.

Introduction

The legacy of rapid urbanization, industrialization, fertilizer and pesticide use has resulted in major pollution problem in both terrestrial and aquatic environments. In response, conventional remediation systems based on high physical and chemical engineering approaches have been developed and applied to avert or restore polluted sites, Much as these conventional remediation systems are efficient, they are sparsely adopted because of some economical and technical limitations.

Generally, the cost of establishment and running deter their use and meeting the demand particularly in countries with a weak economy. Logical, this high cost technology can neither be applied justifiably where: (1) the discharge is abruptly high for a short time but the entire average load is relatively small, (2) the discharge is very low but long-term (entire load of medium range) nor (3) the discharge is continuously decreasing over a long duration. Thus conventional remediation approaches are best for circumstances of high pollutant discharge like in industrial, mining and domestic wastewater. Recently, it is evident that durability restoration and long-term contamination control in conventional remediation is questionable because in the long run the pollution problem is only suspended or transferring from one site to another.

Remediation technology

In view of this there has been growing interest in the search for alternative remediation technology that is effective, durable and also cost-effective. One such technology is Phytoremediation, the use of plants and associated microbes for environmental cleanup. The technology is allegedly cost-effective because it is natural energy drive and requires minimal capital and running costs. It is a non-invasive alternative or complementary technology for engineering-based remediation methods, It is a cutting edge area of research in the contemporary field of environmental and remediation technology. Earlier research in phytoremediation focused on screening plants species for phytoremediation potential. The focus is drifting towards engineering the phytoremediation systems for efficiency and responsiveness to contamination loading. Plant species with potential for phytoremediation should posses the following properties; (1) they should extract and accumulate, transform, degrade, or volatilize contaminants at levels that are toxic to ordinary plants; and (2) the plant species must have fast grown and high yield. Additionally, a good phytoremediation species should be applicable to remediate multiple pollutants simultaneously because pollution rarely occurs as a single chemical. Currently, a few plants species are known to possess these properties that qualify them to be good phytoremediation species for terrestrial and aquatic environments.

Objective of Phytoremediation

Phytoremediation, the use of plants to help clean up toxic waste sites, is not only a growing science but also a growth industry; Researchers have created an engineered *Arabidopsis* plant that safely takes up the toxic arsenic element, and hope to use it to restore soils that are too contaminated for human use. Once arsenic is concentrated in the leaves or stems of plants, the plants can be harvested cheaply and incinerated safely. Genetically engineered, deep-rooted perennial trees are well suited to remove arsenic from soil. So far no land which is capable of absorbing the arsenic from deep soil and water has been designed and proved effective outside the laboratory. Plants (trees) carrying the genes for detoxification of mercury present in polluted soil have been developed and it has been proved that these plants absorb mercury from the soil and vaporize it effectively to the atmosphere in non-toxic form

Drinking water thought the North Indian region has been contaminated by soils polluted naturally and by spills and drainage from factories. There is an urgent need to develop and apply phytoremediation technology using genetically engineered plants to decontaminate that polluted soils and water bodies in India. This will be effective in bringing new resources and technology to solve environmental problems, and in India human resource Expertise in biotechnology is not lacking.

Heavy metals in nature fresh systems

The elemental composition of uncontaminated fresh water has been calculated and is show in the second Colum (A) of Table 1. The values are of course rather imprecise, partly because of analytical error involved in estimations in the ng/g (ppb) rang and partly because of the problem of extrapolating to the entire fresh hydrosphere from a relatively small number of rivers.

Table 1. Elemental concentrations in water (µg/ml) dry weight (µg/g) for freshwater vascular plants – FVPs).

Element	A	B	C	D	E	C/A
Ag	0.003	0.06	0.15	0.12	67	500
As	0.002	0.20	2.7	1.14	1200	1350
Cd	0.0002	0.64	1.0	1.4	90	5000
Co	0.0002	0.48	0.32	0.37	350	1600
Cr	0.001	0.23	4.0	2.8	65	4000
Cu	**0.007**	**14**	**7.9**	**42**	**190**	**1128**
Hg	0.0001	0.015	0.50	0.58	1000	5000
Mn	0.007	630	370	430	8370	52,857
Mo	0.001	0.90	12	-	-	12,000
Ni	0.0003	2.7	4.2	6.1	290	14,000
Pb	0.003	2.7	6.1	27	1200	2033
Se	0.0002	0.2	1.0	0.30	21	5000
U	0.00004	0.04	0.50	0.05	1.1	12,500
V	0.0009	1.6	3.6	-	-	4000
Zn	0.02	100	52	47	7030	2600

A-Uncontaminated river water (Turekien, 1969)
B-Terrestrial plants (Bowen, 1996)
C-Median values for uncontaminated FVPs
D-Median values for contaminated FVPs
E-Maximum value for contaminated FVPs
C/A- Accumulation factor for FVPs growing in uncontaminated waters.

It will be seen from this table that in nature uncontaminated fresh waters, elemental abundances are extremely low and in most cases are in the ng/g (µg/L). Under these conditions, the FVPs appear to be invariably hyper accumulators of the heavy metals even in the uncontaminated aquatic environment.

Heavy metals in freshwater vascular plants

Aquatic plants are used in water quality studies to monitor heavy metals and other pollutants of water nod submerged soils. Their selective absorption of certain ions combined with their sedimentary nature is a reason for using hydrophytes as biological, Pollution of water and sediments can be clearly demonstrated by increased concentrations of heavy metals in aquatic plants. Aquatic plants are therefore used in water and submerged soils. Their selective absorption f certain, combined with their sedentary nature, make such plants suitable as biological monitors.

The utilization of wetland areas as natural filters for the abatement of pollutants transported by wear in river or lakes is considered to be an effective, low-cost cleanup option to ameliorate the quality of surface waters. Indeed, wetlands have been extensively utilized in last three decades to clean pollutant water almost all over the world.

The vegetation covering the wetland areas plays an important role in sequestering large quantitative of nutrients from the environment by stoking them in the roots and/or shoots. Wetland plants have high remediation potential for macronutrients because of their general fast growth and high biomass production. Wetland plants also take up heavy metals from the environment but tend mainly to accumulate these in the belowground tissues Restriction of shoot translocation is believed to be strategy of metal tolerance for non-hyper accumulators. In so doing, the plants avoid the potential effects of high metal concentrations on the photosynthetic tissue. It has been shown that the heavy metals accumulation is responsible for the decrease of total chlorophyll concentration and negatively affects the Chl a / Chl b ratio

However, the capacity to accumulate heavy metals in the aboveground plant tissues represents a central point for the suitability of the plants for metals Phytoextraction. The amount of metals accumulated in the aerial part may vary during the growing season as a consequence of the inherent growth dynamics of the plant, as well as in response to variation in the heavy metals level and availability in the surrounding water and soil.

Role of Macrophytes

Macrophytes play an important role in sediment-water trace element cycling through root uptake, excretion into water and detrital absorption of metals that may be conveyed to the sediments. Elemental toxicity experiments have shown that Ag, As, Cd, Cr, Hg and Ni are about 10 times more toxic to macrophytes than are Lead or Zinc. Copper is one of the most toxic of these elements and its effects are visible at concentration of 0.05-0.15 µg/mL. Compared with phytoplankton, macrophytes are 10-100 times less sensitive to most elements except copper to which they are equally sensitive.

Copper -contamination of soil and water is widespread which possess a serious threat to plants, animals and humans. There has been growing interest in developing remediation of Cu-contamination ecosystem. Studies were conducted to examine the uptake of Copper (II) and Copper (I) by mustard plants from water and soil. Addition of phosphate was found to inhibit the uptake and accumulation of Cu in plants. In general, roots accumulation large amount of Cu than shoots and flowers, phosphate addition was found to decrease the bioavailability of Cu, particularly, Cu (II).

Cupper - a Heavy Metal Toxicant

Cupper (Cu) is a toxic metalloid which enters terrestrial and aquatic ecosystems through both natural (geological) processes and anthropogenic (industrial and agricultural) activities. Cupper -contamination of soil and water is widespread which poses a serious threat to plants, animals and humans. Arsenic is a unique carcinogen. Therefore, there is a growing interest in developing regulatory guidelines and remediation technologies for mitigating Cu-contaminated ecosystem. A range of technologies, including bioremediation, has been applied with varying levels of success either to remove Cu from the contaminated medium or to reduce its bio-toxicity.

Plants are increasingly being used to enhance the removal of Cu. This technology is known as phytoremediation and it attracts intensive research and commercial interests. The effectiveness of this technology is, however, variable and depends on several factors associated with soil and plant characteristics and the chemistry of Cu in the environment. Several soil amendments like lime, Phosphate (P), compost etc., are used to enhance the effectiveness of phytoremediation. In the current study we examined the potential of mustard crop in hyper accumulating the Cu from soil and water and the impact of phosphate on Cu uptake by crop.

The goal of Phytoremediation

The goal of Phytoremediation is to completely mineralize organic pollutants into relatively non-toxic constituent, such as CO_2, nitrate, chlorine and ammonia Organic pollutant that are potentially important targets for Phytoremediation include polychlorinated biphenyls (PCBs) such as dioxins polycyclic aromatics hydrocarbons (PAHs) such as benzoapytene, nitro aromatics such as Tri Nitro-Toluene (TNT) and linear halogenated hydrocarbons such as trichloroethylene (TCE) Many of these compounds are not only toxic and teratogenicity but are also carcinogenic.

Inorganic pollutants occur as natural elements in the earth's crust of atmosphere, and human activities such as mining, military, agriculture, traffic and industrial activities promote their release into the environment, thereby causing toxicity Inorganics cannot be degraded but can be phytoremediated via phytostavilization, volatilization or sequestration in harvestable plant tissues. Inorganics that can be phytoremediated include macronutrients such as nitrates and phosphates and plant trace elements such as Cr, Ni, Zn, Mn, Mo, Fe and Cu non-essential elements such as Hg, Se, Cd, Pb, V, and W Polluted soils and sediments have been phytoremediated at military sites (TNT, metal), agricultural fields (pesticides and herbicides, selenium), industrial sites (metals etc.) and wood treatment sites Plants can also be used to filter air, both indoors and outdoors, from SO_2, NO_2, Ozone, CO_2, dust and soot particles and halogenated volatile hydrocarbons.

Copper- a Heavy Metal Toxicant

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Cupper poisoning

Cupper is causing a global epidemic of poisoning and the been associated with skin lesions, cancers and other symptoms. Natural contamination of freshwater by arsenic has become a crucial water quality problem in many parts of the world such as China, India, Vietnam, Bangladesh, Italy, Iran, etc One of the main causes of this widespread arsenic poisoning is the growing current trend around the world of drinking water from polluted underground and surface water, naturally and anthropogenic sources. The range of arsenic concentration found in natural waters is large, ranging from less than 0.5 to more than 5000 μgL^{-1}. Typical concentration in freshwater are less than 10 μgL^{-1} and much higher concentration are found in groundwater

Methods

Mechanism of Phytoremediation

The process of metal accumulation involves several steps, as follows:

Solubilization of the metal from the soil matrix

Many metals are found in soil-insoluble forms plants use two methods to desorb the metals from the soil matrix; acidification of rhizosphere through the action of plasma membrane proton pumps and secretion of ligands capable of chelating the metal. Plants have evolved these processes to liberate essential metals from soil, but soils with high concentration of toxic metals will release both essential and toxic metals to solution.

Uptake in to the root

Soluble metals can into the root sumplast by crossing the plasma membrane of the root endodermal cells or they can enter the root apoplast through the space between cells. While it is possible for solutes to travel up through the plant by apoplastic flow, the more efficient method of moving up the plant is through the vasculature of the plant called the xylem.

To enter the xylem, solutes must cross the casparian strip, a waxy coating, which is impermeable to solutes unless they pass through the cells of endodermis. Therefore, to enter the xylem, metals must cross a membrane probably through the action of a membrane pump (or) channel. Excluder plants survive by enhancing specificity for the essential elements (or) pumping the toxic metal back out of the plant

Transport to the leaves

Once loaded into the xylem, the flow of the xylem gap will transport the metal to the leaves. Where it must be loaded into the cells of the leaf, again crossing a membrane. The cell types where the metals are deposited vary between hyper accumulator species. For example, *Thalpsicaerulescens*was found to have more Zn in its epidermis than in its mesophyll.

Detoxification/chelation

At any point along the pathway, the metal could be converted to a less toxic from through chemical conversions or by complexion. Various oxidation states of toxic elements have very different uptake transport, sequestration or toxicity characteristics in plants. Chelation of toxins by endogenous plant compounds can have similar effects on all these properties as well. As many chelators use thiol groups as ligands, the sulfur (S) biosynthetic pathways have been shown to be critical for hyper accumulator function.

Sequestration/Volatilization

The final for the accumulation of most metals is the sequestration of the metal away from any cellular process it might disrupt. Sequestration usually occurs in the plant vacuole, where the metal/metal ligand must be transported across the vacuolar membrane. Metals may also remain in the cell well instead of crossing the plasma membrane into the cell, as the negative charge sites on the cell walls may interact with polyvalent cations. Selenium may also be volatilized the stomata.

Mechanisms of cupper uptake in aquatic macrophytes

The inorganic forms (Cu (I) and Cu (II)) and the methylated forms (MMACu(II)) and DMACu(I)) are the main species of Cupper in natural water Aquatic organisms, such as algae, reduce Cu (I) and Cu (II) and further bio transform to methylated arsenicals which results in the occurrence of thermodynamically unstable Cu(II) and methyl Cupper compounds in natural water .The bulk of the total dissolved arsenic is inorganic arsenic in seawater and in freshwater Although the predominant form of methylarsenicals is consistently DMACu(I) followed by MMACu(II), the existence of trivalent methyl Cupper species in the environment has also been reported Cupper uptake mechanisms in terrestrial hyper accumulating plants have been studied and reported in a number of literatures ,However, three mechanisms have been proposed for the uptake of Cupper species in aquatic macrophytes – (i) active uptake through phosphate uptake transporters, (ii) passive uptake through aqua glycerol prions, and (iii) physicochemical adsorption on root surfaces. Plants mainly uptake As (V) through phosphate uptake transporters, however, physicochemical adsorption on root surfaces has also been supposed to be an alternative uptake pathway for this arsenic speciesCu(I), DMACu and MMACu get into the plants by passive mechanism through the aqua glycerol prion channels

Biology of *Eichhornia crassipes*

Eichhornia crassipes, commonly known as common water Hyacinth, is an invasive species of plant which is native to the Amazon basin. This plant is also used like a medicinal plant.

Ecology

Its habitat ranges from tropical desert to subtropical or warm temperate desert to rainforest zones. It tolerates annual precipitations of 8.2 dm to 27.0 dm (mean of 8 cases =15.8), annual temperatures from 21.1°C), and its pH tolerance are killed by frost and salt water, the latter trait being reseed to kill some of it by floating rafts of the cut weed to the sea. Water hyacinths do not grow when the average salinity is greater than 15% that of sea water. In brackish water, its leaves show epinasty and chlorosis, and eventually die.

Because of E. crassipes invasiveness, several biological control agents have been released to control it, including two weevils, *Neochetina bruchi* Hustache (Coleoptera: Curculionidae) and the north *Miphograpta albigurralis* (Warren) (Lepidoptera: Pyralidae). *Neochitina eichhirniae* causes "a substantial reduction in water hyacinth production" (in Louisiana); it redices plant height, weight, root length, and makes the plant produce fewer daughter plants.
Azotobacter chroococcum, an N-fixing bacteria, is probably concentrated around the bases of the petioles. But the bacteria do not fix Nitrogen unless the plant is suffering extreme N-deficiency

Fresh plants contain prickly crystals. This plant is reported to contain HNC, alkaloid, and triterpenoid, and may induce itching. Plants sprayed with 2,4-D may accumulate lethal doses of nitrates, as various other notice elements in polluted environments.

Biology of *Pistia stratiotes*

Pistia is a genus of aquatic plant in the family Araceae, comprising a single species, *Pistia stratiotes,* often called water cabbage or water lettuce. Its native distribution is uncertain, but probably pantropical; it was first described from the Nile near Lake Victoria in Afrca. It is now present, either naturally or through human introduction, in nearly all tropical and subtropical fresh waterways.

Result and Conclusion

Table 1 Concentration of Cupper in SIPCOT industrial effluent mixed water in different experimental sets by selected macrophytes

Number of days	Eichhornia crassipes	Pistia stratiotes	Lemna gibba
Initial	0.050	0.050	0.050
5th day	0.032	0.035	0.042
10th day	0.024	0.026	0.032
20th day	0.012	0.021	0.028
30th day	0.02	0.018	0.024

Fig. 1 Concentration of Cupper in SIPCOT industrial effluent mixed water in different experimental sets by selected macrophytes

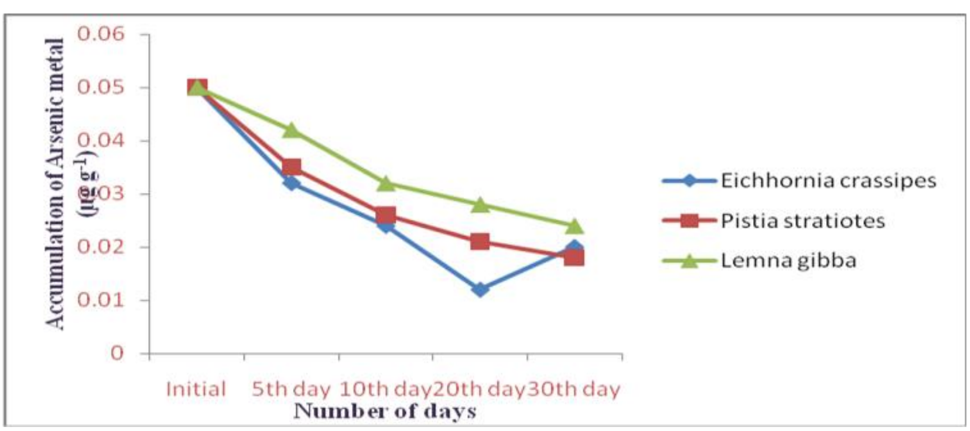


Table 2 Accumulation of Cupper metal (µg g-1) by macrophytes, *Eichhornia crassipes* grown in industrial effluent water

Macrophyte	Number of days	Tissues	
		Root	Leaves
Eichhornia crassipes	Initial	0.00	0.00
	5th day	1.18±0.02	0.62±0.20
	10th day	1.03±0.04	0.81±0.02
	20th day	1.38±0.02	0.94±0.03
	30th day	0.62±0.05	1.12±0.20
	p	0.612**	0.169

Values are significantly different the control *p<0.005, by One-way analysis of variance (ANOVA) with Tukey Kramer comparison test.

Fig. 2 Accumulation of Cupper metal (µg g-1) by macrophytes, *Eichhornia crassipes* grown in industrial effluent water

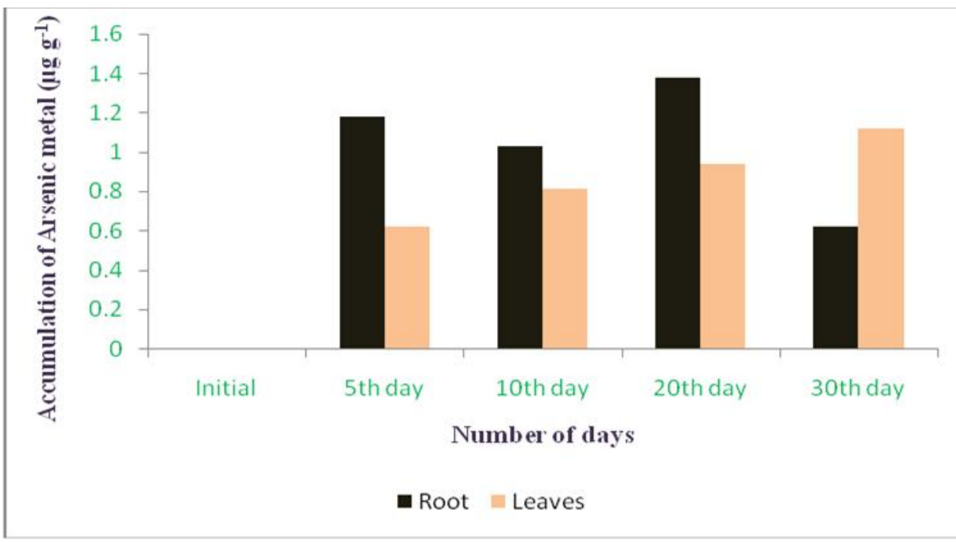


Figure 3Accumulation of Cupper metal (µg g-1) by macrophytes, *Pistia strtiotes* grown in industrial effluent water

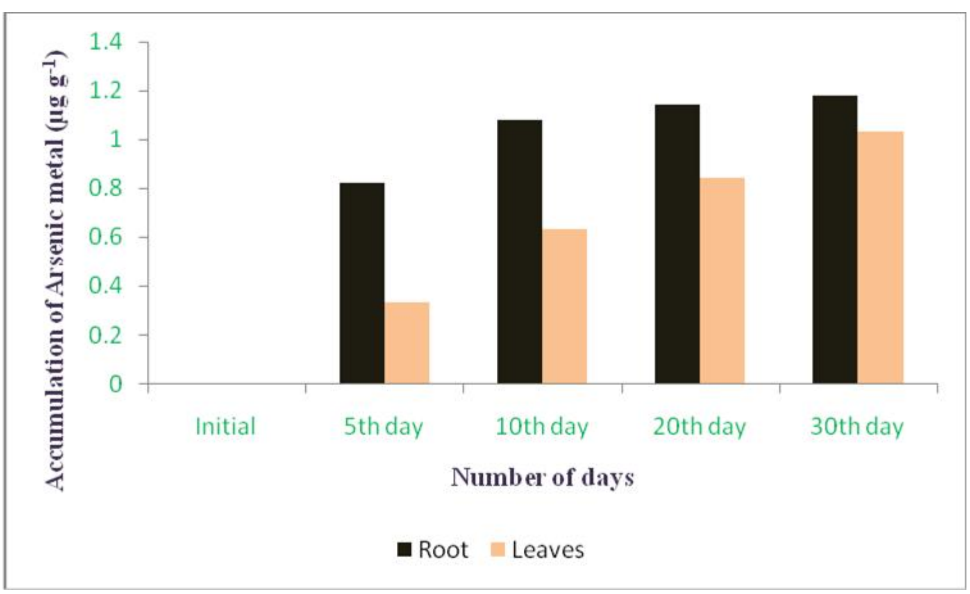


Table 3 Accumulation of Cupper metal (µg g-1) by macrophytes, *Lemna gibba* grown in industrial effluent water

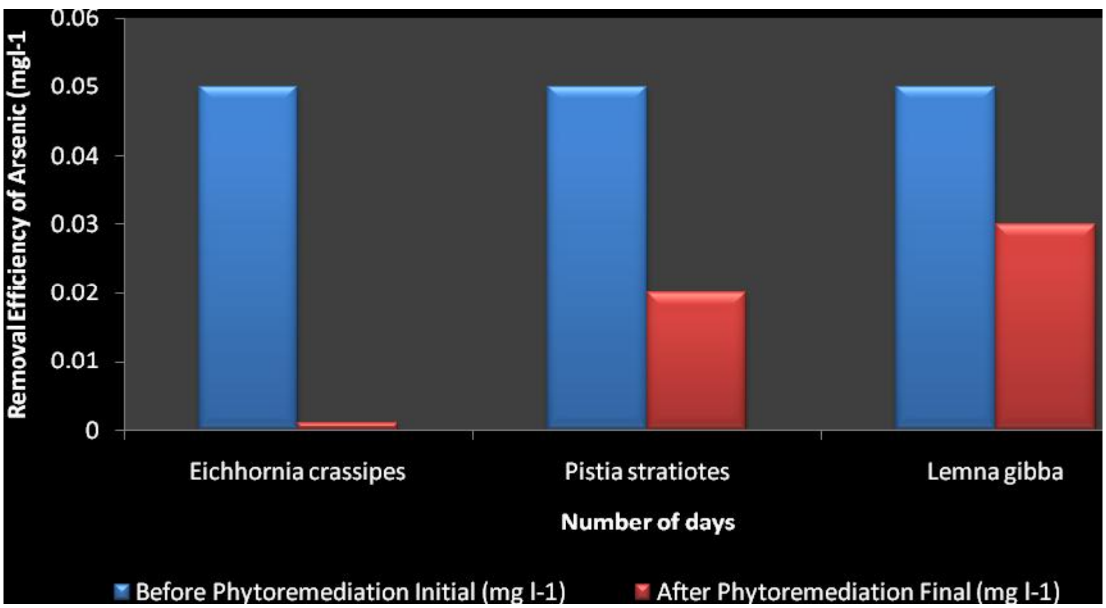
Macrophyte	Number of days	Tissues	
		Root	Leaves
Lemna gibba	Initial	0.00	0.00
	5^{th} day	0.12±0.11	0.08±0.01
	10^{th} day	0.26±0.12	0.18±0.02
	20^{th} day	0.35±0.03	0.26±0.20
	30^{th} day	0.72±0.22	0.51±0.04
	p	0.300	0.310

Values are significantly different the control *p<0.005, by One-way analysis of variance (ANOVA) with Tukey Kramer comparison test.

Table 4 Removal efficiency for Cupper metal by selected macrophytes, before and after Phytoremediation

Macrophytes	Before Phytoremediation	After Phytoremediation	Removal Efficiency (%)
	Initial (mg l^{-1})	Final (mg l^{-1})	
Eichhornia crassipes	0.05	0.001	80
Pistia stratiotes	0.05	0.02	60
Lemna gibba	0.05	0.03	50

Figure 4 Removal efficiency for Cupper metal by selected macrophytes, before and after Phytoremediation



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