REMOVAL OF HEAVY METALS FROM WASTEWATER USING LIVING PLANTS AND LATERITE SOIL

A DISSERTATION

Submitted in partial fulfillment of the

requirements for the award of the degree

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MASTER OF TECHNOLOGY

in

CHEMICAL ENGINEERING

(With specialization in Industrial Pollution Abatement)

By

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CANDIDATE'S DECLARATION

I hereby declare that the work, which is being presented in this report entitled "**Removal of Heavy Metals from Wastewater using Living Plants and Laterite Soil**", submitted in partial fulfillment of the requirement for the award of the degree of **Master of Technology in Chemical Engineering** with specialization in **Industrial Pollution Abatement**, and submitted to the Department of Chemical Engineering, **Indian Institute of Technology Roorkee** , is an authentic record of the research done by me, under the guidance of Dr. P. Mondal**,** Assistant Professor of Chemical Engineering , Indian Institute of Technology Roorkee.

Date: June 14, 2013

Place: IIT Roorkee **VERALIKA SINGH**

CERTIFICATE

This is to certify that the above statement made by the candidate is correct to the best of my knowledge.

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Date: 14 June 2013 (VERALIKA SINGH)

ABSTRACT

Wastewater generation is a massive problem not only in India but all across the world. Wastewater is generated from industrial and domestic sources. One of the major constituent of the industrial wastewater is heavy metals. Heavy metals are extremely hazardous and pose great threat to the environment. Many of the conventional physico-chemical techniques used for heavy metal removal have their inherent advantages and disadvantages, the cost being a major factor along with the generation and disposal of sludge.

The need of the hour is the viable usage of low cost, eco-friendly techniques for the heavy metal removal from wastewater. Two such techniques have been examined in the present study; they are phytoremediation and adsorption by using laterite soil.

Phytoremediation is basically a technique that utilizes plants to remediate the contaminated sites. In the present study, a lab scale experiment for the removal of lead and chromium from synthetic wastewater using the plant Vetiver Zizanioides was performed. The experiment was performed in a setup made of Perspex which was specifically designed for this study using the floating platform technique. Since the metal contaminants are generally present in groups and are rarely present as single ions both Pb and Cr were added simultaneously in the water samples in a 1:1 ratio.

The metal removal capacity of the plant was studied for a specified time of 15 days. Three studies were carried out, in the first study the initial concentration of the metal ions were varied and their uptake was checked with respect to time, in the second study the concentration of the metal ions was kept constant and the pH was varied thus scrutinizing the effect of pH on metal removal and in the third study the metal uptake in various parts of the plant was investigated. The vetiver grass was able to remove about 98% of Pb and about 84% of Cr. It performed well for the pH range of 6 to 9.

The laterite soil was chosen for the adsorption study due to its low cost and its wide availability. In the present study the metal uptake ability of laterite soil was tested in batch mode. Surface modification of laterite soil was carried out by treatment with acid, base and iron chloride solution to examine their effect on metal uptake and compare their removal ability to that of natural laterite soil. The Raw laterite soil was chosen as the best adsorbent and was further studied. The various process parameters such as contact time, adsorbent dose, pH and the effect of initial concentration were optimized and examined.

The laterite soil showed the best adsorption capabilities at the adsorbent dose 10g/l, at the contact time of 4 hr and at pH 6, the temperature was kept constant at 305K and the rpm at 150. The regenerative and reuse capability of laterite soil was also investigated. The equilibrium and kinetic studies were performed for the better understanding of the various design parameters. The adsorptive study followed a pseudo-second order model and The Freundlich isotherm was found to fit best to the data generated.

LIST OF TABLES

LIST OF FIGURES

CONTENTS

CHAPTER 1- INTRODUCTION

CHAPTER 2- LITERATURE REVIEW

CHAPTER 3-EXPERIMENTAL SETUP AND INSTRUMENTATION

CHAPTER 4-EXPERIMENTAL PROCEDURE

CHAPTER 5-RESULTS AND DISCUSSION

CHAPTER 6-CONCLUSION AND RECOMMENDATIONS

CHAPTER 1

INTRODUCTION

1.1 General

The industrial sector has experienced an unprecedented progress in the 21st century not only in India but across the globe. On the flipside this global advancement introduces new obstacles particularly in the area of environmental safeguard and preservation. The economic, agricultural and industrial expansions are mostly accountable for the pollution caused to the ecosystem (Jadia and Fulekar, 2009).They introduce harmful pollutants into the soil and water; consisting of a variety of inorganic and organic compounds.

1.2 Heavy Metals

Heavy metals are the constituents of an inaccurately defined class of components showcasing metallic properties, this group comprises of metalloids, transition metals, actinides and lanthanides. They have been defined by many variable definitions that are related to density, atomic weight and chemical properties (Web 1).

Heavy metals are exceedingly hazardous because of their non-decomposable nature, long half-lives and their capability to accumulate in different body parts of various living beings like plants, humans and animals. Presence of heavy metals in low concentrations also has destructive effects as there are no concrete methods for their eradication (Chen et al., 2005; Singh et al., 2004).

Living organisms like plants, animals and humans require varying amounts of essential heavy metals such as cobalt, copper, Iron, manganese etc. for endurance; but high levels can be harmful. Other non-essential heavy metals such as chromium, mercury and lead are lethal and their accumulation over time causes serious illness (Kunze et al., 2001;Web 1).

Heavy metals pose serious risk to human health and disrupt the human metabolic functions; this is generally done in two ways (Singh et al., 2011; Singh 2007):

a) The heavy metals get accumulated in the human body and thereby disrupt the functional efficiencyof the vital organs and glands.
b) They dislocate the essential nourishing minerals from their original positions thereby putting a stopper on their biological functioning

Heavy metal exposure on plants, leads to extensive cellular damage and disturbance. Over the years in order to diminish the harmful effects of heavy metal exposure, many plants have developed an evolved cleansing mechanisms mainly based on chelation and secular segregation (Singh et al.,2011; Yadav, 2010). These types of plants are being utilized in the process of phytoremediation for heavy metal removal.

1.2.1 Sources of Heavy metals

The pollution occurring in the ecosystem is due to the presence of hazardous metals arising from natural and man-made sources. Natural sources consist of seepage from rocks into the rivers and lakes, volcanic activity, forest fires etc. The anthropogenic sources of pollution are smelting of metallic ores, electroplating, production of fuel and energy, excessive utilization of fertilizers and industrial manufacturing. (Sekomo et al., 2012;Chen et al., 2011; Ali et al., 2004)

With rapidly growing industrialization and consumerism, the anthropogenic sources of pollution have augmented alarmingly. (Sahni,2011) The metal specific industrial sources of heavy metals are summarised in Table 1.1 whereas Table 1.2 lists the key Indian sites contaminated with heavy metals.

Table 1.1 Sources of heavy metals (Web 2)

Metal	**Industry**	**Surface water(mg/l)**	**Ground water (mg/l)**
Chromium (Cr)	Mining, industrial coolants, chromium salts manufacturing, leather tanning	2.0	0.1
Lead (Pb)	Lead acid batteries, paints, E-waste, Smelting operations, coal- based thermalpower plants, ceramics, bangle industry	0.1	0.015
Mercury (Hg)	Chlor-alkali plants, thermal power plants, fluorescent lamps, hospital waste (damaged thermometers, barometers, sphygmomanometers), electrical appliances etc.	0.01	0.002
Arsenic (As)	Geogenic/natural processes, smelting operations, thermal power plants, fuelburning	0.20	0.01
Copper (Cu)	Mining, electroplating, smelting operations	3.0	0.06
Vanadium (Va)	Spent catalyst, sulphuric acid plant	0.1	0.006
Nickel (Ni)	Smelting operations, thermal power plants, battery industry	3	3
Cadmium (Cd)	Zinc smelting, waste batteries, e-waste, paint sludge, incinerations & fuel combustion	0.20	0.005
Molybdenum (Mo)	Spent catalyst	0.05	0.01
Zinc (ZN)	Smelting, electroplating	5	0.4

Table 1.2Major heavy metal contaminated sites in India (Sahni, 2011)

Metals				
Chromium	**Lead**	**Mercury**	**Arsenic**	**Copper**
Ranipet, Tamil Nadu	Ratlam, Madhya Pradesh	Kodaikanal, Tamil Nadu	Tuticorin, Tamil Nadu	Tuticorin, Tamil Nadu
Kanpur, Uttar Pradesh	Bandalamottu Mines, Andhra Pradesh	Ganjam, Orissa	West Bengal	Singbhum Mines, Jharkhand
Vadodara, Gujarat	Vadodara, Gujarat	Singrauli, Madhya Pradesh	Ballia and other districts, UP	Malanjkahnd, Madhya Pradesh
Talcher, Orissa	Korba, Chattisgarh			

1.2.2 Toxicity due to Metals

Humans, plants and animals are adversely affected due to heavy metal poisoning.In general; heavy metal toxicity can cause long lasting effects. Symptoms generally include: short-term memory loss, headache, Stomach upsets, allergies, vision problems etc. Some of the very well documented heavy metals health hazards are summarized in Table 1.3.

Table 1.3 Health impact of heavy metals [Martin and Griswold, 2009; Singh et al., 2011]

Heavy Metals	**Health Impact** (Due touptake of high quantities)
Arsenic (As)	Skin damage or problems with circulatory systems, bronchitis and increases risk of getting cancer
Cadmium (Cd)	Kidney damage,renal dysfunction, lung disease, lung cancer and bone disease such as Itai-Itai
Chromium (Cr)	Kidney damage, liver damage, nerve tissue damage, causes fatigue and irritability
Copper (Cu)	Stomach upset, kidney damage and anemia
Lead (Pb)	Deficiency in fine motor functions in children, kidney problems, high blood pressure, congenital paralysis, sensor neural deafness
Mercury (Hg)	Tremors, kidney damage, neurological damage, acrodynia characterized by pink hands and feet, spontaneous abortion
Zinc (Zn)	Stomach cramps, skin irritations, vomiting, nausea and anemia, fumes of zinc have corrosive effect on skin and cause damage to nervous system
Nickel(Ni)	Cancer, Respiratory failure, Birth defects, Allergies, and Heart failure
Manganese (Mn)	Inhalation and contact causes damage to central nervous system
Barium (Ba)	Contact may cause vomiting, high blood pressure, abdominal cramps, diarrhea and difficulty in breathing

1.2.2.1 Lead

Lead is an extremely dangerous element; it causes a lot of damage even in small quantities. Due to numerous human activities, such as mining, manufacturing and fossil fuel burning, lead and lead based compounds are found all over the earth, in the atmosphere, lithosphere and hydrosphere. Lead can be utilized in many ways; it is used to produce shells and bullets, for X-ray shielding devices, batteries andmetal products like pipes. Nowadays the major sources of lead exposure are water pipes in older homes, lead-based paint, household dust, contaminated soil, lead-glazed pottery and lead in certain cosmetics and toys (Salem et al.,2000; Martin and Griswold, 2009).

In grown-ups there is 20-30% chance of lead poisoning and in children it is almost 50%, lead is generally absorbed through the gastrointestinal tract or it can also enter through lungs. Since lead is chemically similar to calcium due to its size and charge similarities the body treats its uptake like that of calcium. (Web 3)

This is the main reason for the presence of lead throughout the body inteeth, lungs,bones, spleen and brain with bones being the one that are most affected. This Lead storage in bones becomes hazardous when calcium consumption increases; it is then that the lead present in the bones is replaced by calcium setting it free to mobilize in various parts of the body (Salem et al., 2000).

Deficiency of iron leads to increased Pb toxicity, thereby making pregnant women and young children highly susceptible (Flora et al., 2006). Table1.4 states the general indications of lead toxicity.

Table 1.4 Symptoms of leadtoxicity (Sahni, 2011)

- Seizures
- Tremor
- Encephalopathy
- Coma
- Motor neuropathy
- Cerebral edema
- Renal failure
- Abdominal cramping
- Lethargy
- Myalgias
- Constipation
- Abdominal pain
- Headache
- Vomiting
- Weight loss

1.2.2.2 Chromium

Chromium is released into the earth’s environment from both natural as well as anthropogenic sources, with the industrial sector being the largest contributor. These industries include metal treating, tannery facilities, stainless steel, welding, and ferro-chrome and pigment production industries.(Web 4)

Chromium has the ability to be present in all three forms; as a liquid, solid, or gas. Chromium is utilized in metal alloys such as stainless steel, magnetic tapes, as pigments for paints, cement, paper, composition floor covering, rubber, in wood preservatives and for protective coatings on metal surface by electroplating. Electroplating can release chromic acid spray and air-borne chromium trioxide, which results in the direct damage of skin and lungs. Also chromium dust is considered as a potential cause of lung cancer.(Martin and Griswold, 2009; Salem et al., 2000)

There are many factors that determine whether the exposure to chromium is harmful or not. These are the dose of chromium contact, the duration, the form of chromium (chromium VI as opposed to chromium III).

Chromium can be ingested in body through breathing of air containing chromium. Small percentage chromium can also enter the body through the digestive tract or through dermal contact. Table 1.5 lists the general signs and symptoms of chromium toxicity.

Table 1.5 Symptoms of Chromium toxicity

• Irritation on the lining of the nose • Runny nose • Asthma • Shortness of breath • Wheezing • Irritation and ulcer caused in stomach • Anemia	• Tumours • Damage to intestinal tract • Lung cancer • Damage to the reproductive system

1.3 Wastewater

Out of the total percentage of the world's resources, India accounts for about 2.4% of landmass and for about 4% of water. The entire usable water reserves in the country are predicted to be around 1123 BCM (Kaur et al, 2012). India's water predicament is an artificially created crisis due to misuse by humans, as India has a favorable climate with enough rainfall and presence of many lakes, rivers and groundwater resources.One of the foremost reasons for water shortages are exceedingly poor management, vague and unclear laws, corruption of government, industrial and human wastes. (Mehta, 2012)

Multi-sectorial demands for water due to the continuous economic growth of Indiacombined with the amplified energy usage is one of the major reasons for the increased requirement. Another reason for the enhanced water demand isgrowth in population and agricultural utilization, due to these reasons India's limited water resources are diminishing at an alarming rate and this may cause the per capita availability of water to reduce under 1000 cubic metersin the coming decade. (Web 5)

An estimated 22900 MLD of residential wastewater is being generated from metropolitan areas on a daily basis while 13500 MLD of wastewater is being introduced from the industrial sector; whereas the treatment capacity available for domestic sewage is around 5900 MLD and it is around 8000 MLD for industrial sewage. Thereis an enormous gap between the treatment and the generation of wastewater which needs to be rectified immediately to avoid future problems (Web 5; Kaur et al, 2012).

There is a crucial need for effectual water management through recycling and improved usage efficiency (Kaur et al,2012). The Indian government must strive to achieve a balance between the conflicting requirements of the urban and the rural masses, the economy and the environment, in addition to avoiding a water stress situation by incorporating its statewide water management programs at a national level.(Mehta, 2012)

Wastewater consists of a mixture of agricultural runoffs, sewage water, industrial waste discharges and hospitals wastes. In order to curtail the environmental and health risks posed by these pollutants, the quantities of the pollutants generated need to be brought down to permitted limits for safe disposal and reuse of wastewater.(Kushwah et al., 2011)

Management of wastewater in India has become a tremendously important sphere of focus due to growing consideration of health norms and also due to the alarming growth in population. Despite the increased recycle of wastewater in the last few years, due to the increased government backingand private partaking, wastewater generation is still a huge problem (Web 5). The current sewage generation and treatment capacity status of various metropolitan cities is listed in Table 1.6, also the total percentage of generated and treated wastewater is listed in Fig. 1.1.

Table 1.6 Wastewater generation and treatment capacity of metropolitan cities (CPCB 2005)

S. No.	Name of the City	Sewage generation (in MLD)	Sewage Treatment Capacity (in MLD)	Percent of treatment capacity
1	Hyderabad	426	593	100
2	Vishakhapatnam	135	-	-
3	Vijayawada	128	-	-
4	Patna	279	105	37
5	Delhi	3800	2330	61
6	Ahmadabad	472	488	96
7	Surat	432	202	46
8	Rajkot	108	44.5	40
9	Vadodara	180	206	100
10	Bangalore	772	-	-
11	Indore	204	78	38
12	Bhopal	335	22	6
13	Jabalpur	143	-	-
14	Mumbai	2671	2130	80
15	Pune	474	305	64
16	Nagpur	380	100	26
17	Nasik	227	108	47
18	Ludhiana	235	311	100
19	Amritsar	192	-	-
20	Jaipur	451	54	11
21	Chennai	158	264	100
22	Kanpur	417	171	41
23	Lucknow	364	42	11
24	Agra	260	88	33
25	Kolkata	706	172	24
26	Faridabad	164	65	39
27	Jamshedpur	199	-	-
28	Asansol	147	-	-

29	Coimbatore	120	-	-
30	Madurai	98	-	-
31	Meerut	177	-	-
32	Varanasi	230	102	44
33	Allahabad	176	60	34
34	Kochi	188	-	-
35	Dhanbad	192	-	-
Total		**15644**	**8040**	**51**

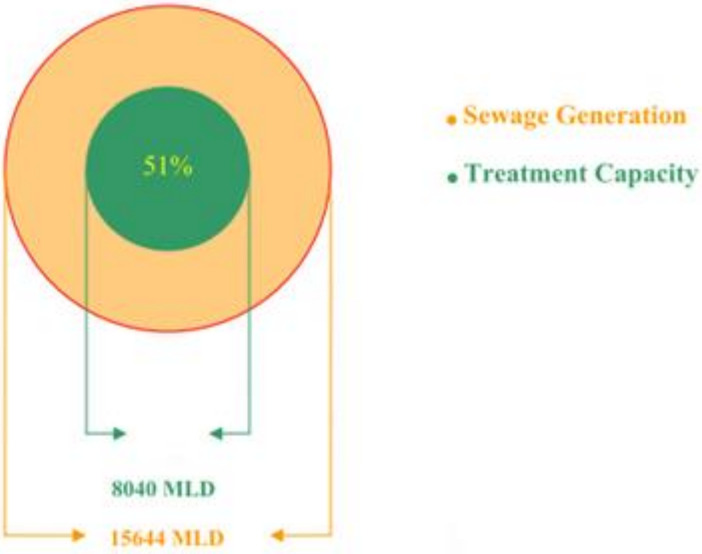


Fig 1.1 Sewage generation and treatment capacity in Metropolitan Cities (CPCB, 2009-10)

1.3.1 Wastewater treatment methods

Wastewater treatment is the procedure of removing the various pollutants and toxins from industrial and residentialwastewaters. It includes various processes (such as physical, chemical, and biological) to remove different types of impurities. The objective of the various wastewater treatment methods is to generate an ecologically harmless liquid stream or a treated sludge; having the contaminants up to the prescribed limits, suitable for disposal or reuse (Web 6).

Wastewater treatment generally involves three stages, called primary, secondary and tertiary, a stage that precedes these three steps is the pretreatment stage; this step deals with the removal ofthe easily collectable large sized materials that may otherwise damage or choke the pumps of the primary treatment tanks. The various methods used are sieving, screening, sand and gravel removal, flow equalization (Web 6). Primary treatment step deals with the physical treatment, secondary treatment step deals with the biological treatment and the tertiary treatment is performed when the prescribed limits are not met by the secondary treatment (Web 6, Web 7). The various types of methods used in each type of treatment are listed in Table 1.7 and the various step of wastewater treatment are shown in Fig 1.2:

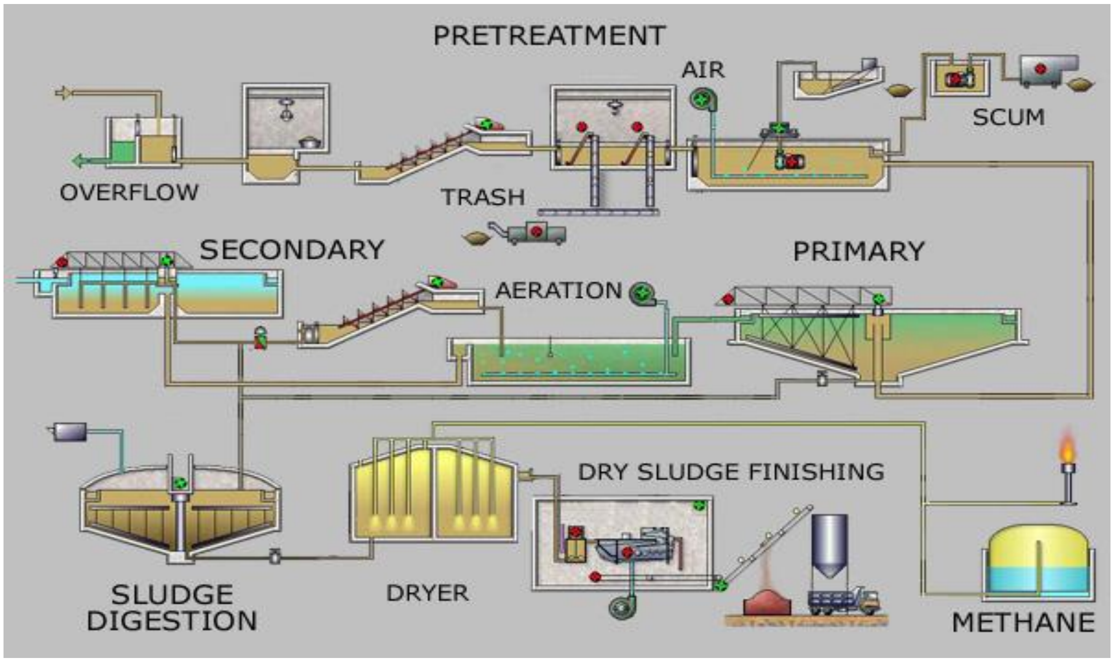


Fig 1.2 Different steps involved in wastewater treatment(Web 6)

Table 1.7 Methods used for waste water treatment (Sekomo et al., 2012)

Primary Methods (Physico-chemical methods)	**Secondary Methods (Biological methods)**	**Tertiary methods**
Adsorption Coagulation-flocculation Precipitation Floatation Chemical oxidation Membrane separation Sedimentation Sand filtration	Lagoon Aerated Lagoon Activated Sludge Trickling Filter SBRs and MBRs Anaerobic treatment	Electrodialysis Foam Separation Ozone oxidation Ion Exchange

The orthodox wastewater treatment procedures mentioned in Table 1.7 are expensive and include intricate operations and a lot of maintenance. The other drawbacks of the conventional techniques are sludge generation and disposal, high requirement of chemicals and membrane fouling. The economics through different levels of treatment have been summarized in Table 1.8.

Table 1.8 Cost of different levels of treatment of wastewaters(Kaur et al., 2012)

Specifications	**Primary treatment system**	**Simultaneous Primary and Ultra-filtration system**	**Simultaneous Primary, ultra-filtration and reverse osmosis system**
Capital cost (Rs lakhs)	30	91	145
Annualized capital cost (@15% p.a. interest & depreciation	6	18	30
Operation and maintenance cost (lakhs/annum)	6	7	13
Annual burden (Annualized cost +O&M cost) Rs. Lakhs	12	27	43
Treatment cost Rs./kl (Without interest and depreciation)	34	52	73

Taking into consideration, the needs of a developing country like India. It is very difficult for the government to come up with the budget to utilize these techniques on nationwide bases. The need of the hour is the usage of techniques which are not costly and are environment friendly atthe same time, one such type of technique is phytoremediation which uses plants to remove the contaminants such as heavy metals. Another technique that can be used is adsorption by using low cost and readily available adsorbents.

1.4 Phytoremediation

In the past decade, a promising, affordable and ecologically-harmless substitute to the conventional remediation techniques has garnered attention both in the public and private quarters. This technique is known as phytoremediation, it utilizes plants to clean the environment, as plants can absorb, accumulate and decontaminant the pollutants from soil, water and air through physical, chemical or biological processes (Jabeen et al., 2009). It was Dr. Ilya Raskin who came up with the idea of using different types of plants for remediation andwho is also responsible for coining the name of this technique. The various plants being utilised for uptake of different metals are listed in Table 1.9.

Table 1.9 Summary of plants being utilised for phytoremediation (Prasad, 2003)

S no.	**Plant name**	**Role in Phytoremediation**
1	Alyssum	Nickel accumulator
2	Amaranthusretroflexus	Accumulator of ^{137}Cs
3	Armoraciarustica	Hairy-root cultures remove heavy metals
4	Armeriamaritima	Lead accumulator
5	Atriplexprostrata	Removes salt from soil
6	Azollapinnata	Accumulator of lead, copper, cadmium, and iron
7	Brassica canola	Remediates ^{137}Cs-contaminated soil
8	B. juncea	Hyperaccumulator of metals
9	Cannabis sativa	Hyperaccumulator of metals
10	Cardamonopsishallerii	Hyperaccumulator of metals
11	Ceratophyllumdemersum	Metal accumulator
12	Daturainnoxia	Barium accumulator
13	Eucalyptus sp.	Removes sodium and arsenic
14	Eichhorniacrassipes	Accumulator of lead, copper, cadmium, and iron
15	Helianthus annus	Accumulator of lead and uranium. Removes ^{137}Cs and ^{90}Sr in hydroponic reactors
16	Hydrocotyleumbellata	Accumulator of lead, copper, cadmium, and iron
17	Kochiascoparia	Removes ^{137}Cs and other radio- nuclides
18	Lemna minor	Accumulator of lead, copper, cadmium, and iron
19	Phaseolusacutifolius	Accumulator of ^{137}Cs
20	Pterisvittata	Arsenic hyperaccumulator
21	Salix sp.	Phytoextraction of heavy metals, waste water, and leachate

1.4.1 Phytoremediation Technology and its mechanisms

Generally plants can act both as an accumulator (uptake contaminants to their aerial parts) and as an excluder (restrict contaminants into their biomass) (Sinha et al., 2004). They have highly advanced precise mechanisms for translocation and storage of micronutrients. These mechanisms are responsible for the plants being able to uptake and store the toxic elements in various parts (Tangahu, 2011). The description of the various mechanisms used in the phytoremediation technology are summarised in Table 1.10 and the pictorial representation is shown in Fig. 1.3. The advantages and drawbacks of phytoremediation are listed in Table 1.11.

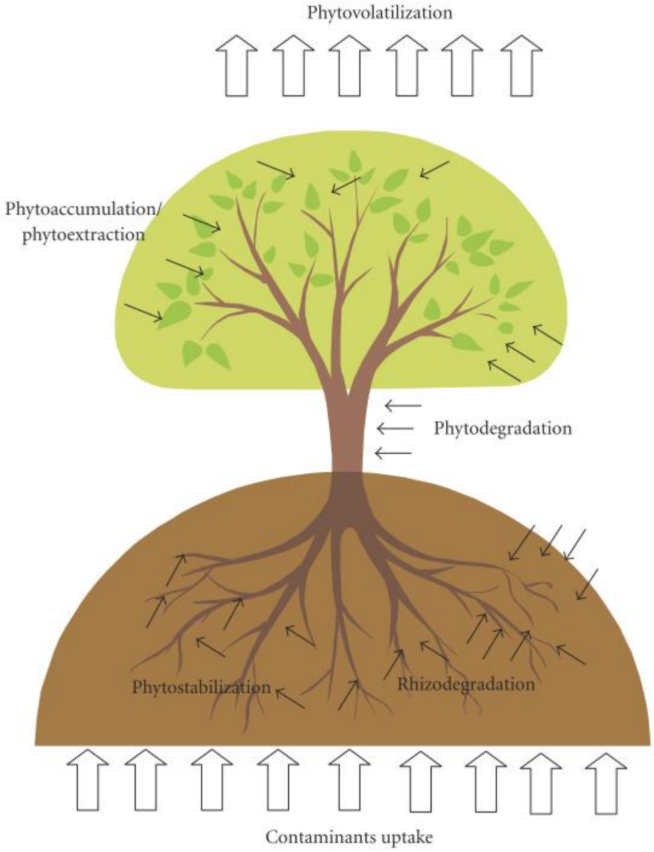


Fig 1.3 Heavy metal uptake mechanisms

Table 1.10 Applications of phytoremediation (Nagendra et al, 2006,Gosh and Singh, 2005)

S no.	Application	Description	Contaminants	Types of plants
Soil				
1	Phytotransformation	Adsorption, transformation and subsequent liberation of contaminants	Organics and chlorinated Aliphatic compounds	Different types of grasses and trees
2	Phytodegradation	Degradation or breakdown of complex substance into simpler forms by plants	Organics, hydrocarbons, TNT and pesticides	Grasses, alfalfa and trees
3	Phytostabilization	Contaminants Stabilization by absorption in root. Thus preventing their movement in soil.	Metals, organics	Plants having dense and deep root systems
4	Phytoextraction	Adsorption of pollutants from soil into roots or harvestable shoots	Metals and radionuclides	Plants such as Thalaspi, Alyssum, Brassica
Water/Groundwater				
5	Rhizofiltration	Uptake and removal of contaminants from water streams into the root system	Metals, radionuclides, hydrophobic organics	Aquatic plants and also sunflower
6	Phytotransformation	Large amount of water removal by trees from aquifers	Inorganics, nutrients, chlorinated solvents	Poplar, willow trees
7	Phytovolatilization	Adsorption and volatilization of contaminants from wastewater streams	organic compounds	Trees, Brassica, grasses, wetlands plants
8	Vegetative Caps	Plants usage to slowdown leaching of harmful components from landfills	Organics and inorganics	Trees, plants and grasses
9	Constructed wetlands	Usage of plants as part of an artificially constructed system for contaminant removal from wastewater streams	Metals, acid mine drainage, industrial and municipal wastewater	Free-floating, emergent, or Submerged plants, reeds, cattails

Table 1.11 Advantages and disadvantages of Phytoremediation (Belz,1997;Tangahu, 2011)

Advantages	Disadvantages
Aesthetically pleasing	Can take a lot of time(different growing seasons) for cleaning of a site
Environmentally friendly technique	Limited to regions having low pollutant levels within root zone of plants.
Wide range applicability for different types contaminants, including organic pollutants	Used for remediating medium levels of contamination
Uses solar energy	Cannot Remediate dense non aqueous liquids
Can be used to stimulate microorganisms by the release of nutrients and oxygen transport from roots	Poses the danger of contaminates entering the food chain
Low Cost	Liberation of contaminants through phytovolatilization converts a ground problem to an air problem
Helps to reduce soil erosion	Less effectual for extremely hydrophobic pollutants
Less disruptive than current techniques	Dependence on the climatic conditions for growth
Dual possibility of in-situ and ex-situ treatment	Plantation of a foreign species may affect biosphere
In-Situ treatment decreases the extent of spreading of contaminant.	Proper disposal for the harvested plant biomass is a requisite

There are two ways in which the mechanisms mentioned for the treatment of water in Table 1.10 can be used they are:

a) **Floating Platform:** as the name suggests in this type of technique a lightweight floating structure is used on top of seas, rivers, lakes, industrial runoffs and natural wetlands that are contaminated. The floating platform can be made be made from any material that can float on water and has a sturdy nature like from bamboos, plastic bottles, sacks used for storing cement and other recyclable materials. The biggest advantage of the floating platforms technique is that it enables terrestrial plants which have deeper and denser root systems as compared to the aquatic plants to grow directly into the contaminated sites andas a result remove the pollutants from the water systems more effectively.

b) **Constructed Wetland:** a constructed wetland system is an artificial or man-made created structure generally for the treatment of wastewaters discharged from various sources.

They are designed to simulate the structure and function of the natural wetlands. The establishment of the constructed wetland system is easier and less costly than establishing a water treatment plant. Combination of the constructed wetland with various technologies like phytoextraction and rhizofiltration proves to be extremely beneficial. The soil layering of the wetland can be done with some with laterite soil.

1.5 Adsorptive removal of heavy metals using Laterite Soil

The Lateritic soil structure varies from a loose grainy material to a massive rock type formation. It is generally dusty red in colour due to the occurrence of large quantities of iron. This soil is found in the tropical and sub-tropical regions as it requires extreme temperatures and large quantities of rainfall for its development (Maji, 2007). The term laterite was first introduced into the geological terminology by Francis Buchanan in 1807; he discovered the formations in southern India and coined the name laterite originating from the Latin term ‘later’ meaning brick. (Chowdhury et al., 1965)

Laterite occupies a place of enormous importance in the Indian geology. It has massive economic potential as it is the source of various industrial minerals such as bauxite, manganese ore, iron ore etc. (Chowdhury et al., 1965)

Laterites are the by-products of acute and long lasting tropical rock weathering. To properly appreciate the formation of laterite, emphasis must be put on the chemical reactions happening between the uncovered rocks at the earth’s surface and the penetrated rain water. The factors affecting these reactions are the extent of lateritization, the mineral constitution and porosity of the rocks, properties of the interacting water such as dissolved elements, temperature, pH-Eh which are ultimately regulated by the climate, foliage and the structure of the land.(Web 9; Maiti, 2012)

Heavy rainfall on interacting with rocks, washes out the bases, silicic acid and other soluble components of the soil and in the process enriching it by leaving behind the clay minerals such as kaolinite, gibbsite, iron, silicates, aluminum and goethite leading to the formation of laterite concrete (coarse grained vermicular material) or laterite soil (soft rocks and fine grained soil with lower concentration of Fe and Al). It is due to this iron and aluminum existence that laterite soilcan be used as an adsorbent for the uptake of heavy metals.(Maiti, 2012; Maji,2007)

The extent of lateritization (Tropical weathering) can be described by the silica-sesquioxide (S-S) ratio (Maiti, 2012):

- A ratio of 1.33 or lesser depicts is laterite concretion
- A ratio of 1.33 to 2.00 depicts laterite soil
- A ratio of 2.00 or more depicts the soil to be non-lateritic tropical soil

Laterite soils have generally been used as bricks for buildings, for layering of roads, used for layering in aquifers due to its porous nature, in cement industry for reducing the temperature of clinker and subsequently supplying both aluminium and iron, for wastewater treatment, for recovery of ores such as bauxite, iron, nickel, aluminium.(Web 10, 11)

Laterite is abundantly available not only in India but all around the world.It has been found out that laterites cover about 1/3rd of the entire earth's continental landmass. In the world they are particularly found in Australia, Brazil, Nigeria, Colombia, Central Europe, Burma, Guatemala, Cuba, Indonesia and Philippines (Web 10). In India they are well developed on Eastern Ghats, Rajmahal hills, Sahyadris and Vindhyas.

They also occur at lower levels and in the valleys. Important areas include Kerala, Bangalore, Mysore, Karnataka, Maharashtra, Andhra Pradesh, Orissa, West Bengal, Assam, Meghalaya, Jharkhand and Uttar Pradesh. (Web 11,12). Due to its abundant availability, low cost, porous nature and other morphological features, laterite soil is a good prospective adsorbent for the removal of contaminants from water.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

There are many different physical and chemical technologies for treatment of wastewaters bearing heavy metals, but the use of these techniques is a double edged sword as each technique has its inherent advantages and disadvantages. The biggest drawback of these techniques is that they are very expensive and also harm the environment by further generation of sludge.

The need of the hour is to employ a technique which has low cost and is environmentally friendly at the same time, one such technique is phytoremediation. Another technique that has been used in this study is the use of naturally available laterite soil as an adsorbent, adsorption as such is a good heavy metal removal technique as compared to some other conventional methods, it is when the cost of the adsorbent is taken into account that it becomes expensive as a result the usage of laterite soil has an inherent advantage, that it's a low cost material available abundantly all over India, thereby making adsorption by its utilization a lucrative option. Table 2.1 and 2.2 represent some of the work done on phytoremediation and laterite soil.

2.2 Work done on Phytoremediation of Heavy metals

Sekomo et al., 2012 performed two lab scale experiments; both the systems consisted of three ponds connected in series seeded with algae and duckweed. In this research paper ability of algae and duckweed ponds to be used as a post treatment option for textile wastewaters has been studied. The effect of pH, redox potential and dissolved oxygen on heavy metal removal has also been studied. The experiments were performed under two light regimes (photoperiod of 16/8 hr and 24 hr) and two different metal loadings. The hydraulic retention time was seven days. The heavy metals studied were Cd (0.05mg/l), Cr (1.5mg/l), Cu (0.1mg/l), Pb (0.25mg/l) and Zn (1.25mg/l). The experiments were performed for 3 weeks. The experiments showed good results for both Cr (94% and 98%) and Zn (70% and 80%), it showed similar removal efficiencies for Pb, Cd and Cu ranging from 20 to 30%

Pandey, 2012 examined the heavy metal removal ability of *Azolla caroliniana*. The study area was a Fly ash pond of NTPC Unchahar located in Umran village. Random samples of plants and FA effluent was collected and analysed for the presence of heavy metals. The presence of Pb, Fe, Mn, Zn, Cd, Ni, Cr and Cu was detected. Presence of a large amount of Azolla caroliniana on the metal rich fly ash pond exposes its toxicity tolerant capability. The ability of A. caroliniana to remove the heavy metals from the fly ash pond is due toits high bio-concentrationfactor.

Liu et al., 2011 examined the Cr uptake capability of Leersia hexandra Swartz for Cr (III). They collected the plant seedlings from the riverside; the seedlings were properly washed and placed in pots filled with 1.5 L of 20% Hoagland's solution. The uptake of Cr under different conditions such as introduction of metabolic inhibitor, at low temperatures (2^{o}C), introduction of ion channel blockers and effect of Fe on Cr uptake was studied. The results showed presence of DNP and low temperature limited the chromium uptake (verifying the fact that Cr uptake is dependent on metabolic activities) whereas there was no effect observed on the uptake of Cr due to the addition of ion channel blockers.

Chen et al., 2011 performed both hydroponic and pot experiments using the plant species vetiver zizanioides. They tested the plant species on its uptake capacity of lead, copper and zinc. The effect of additions of different chelators such as EDTA, EDDS, citric acid has also been examined on the heavy metal removal. The hydroponic experiments were performed in 2L experimental tanks filled with 1.5L of nutrient solution (Hoagland), the concentration of heavy metals was kept constant at 5 mg/l and concentration of the three chelators was kept at 5mM. For the pot experiments the soil was also spiked with Cu, Zn and Pb respectively. It was well mixed and air dried for 5 days in order to mimic local contaminated soils. In the hydroponic experiments, EDTA caused the most significant toxic signs on vetiver as compared to EDDS and citric acid.In the pot experiment, the major finding was that vetiver perceived to act as a hyperaccumulator during treatment for Cu with EDDS; Zn with all the three chelators and for Pb with EDTA and EDDS.

Hoang Ha et al., 2011 studied the metal accumulating ability of *Eleocharis acicularis*. They exposed the plant to In, Ag, Pb, Cu, Cd, and Zn under laboratory conditions. The experiments were performed in a hydroponic setup with the plants being allowed to grow directly in 2L beakers. The experiment was conducted for fifteen days. After the experimental run on the analysis of the results it was found out that the plant is a good species for both remediation and phytominig.

Khan et al., 2009 studied the effective metal removing ability of constructed wetlands has been investigated. The area of study chosen was the Swabi district of Pakistan, a free flow surface wetland having 7 cells was constructed in the Gadoon Amazai industrial estate (GAIE). Variety of native plant seedlings (such as Typha latifolia, Phragmites australis, Juncus articulates, Lemna gibba etc.) were transported and cultivated on the CW, plants were chosen on the bases of their growing ability and heavy metal tolerance. The experimental study was conducted for about one year in which samples of wastewater from the inlet, outlet and all the cells of CW was collected along with the samples of sediments and plants.

Mishra and Tripathi, 2009 studied the metal (Cr and Zn) uptake capability of *Eichhornia crassipes* (water hyacinth). The plants were grown in 15L tanks filled with water up to 10 L. The metal concentration used was 5, 10, 15, 20 mg/l. The solutions added in each tank consisted of single metal ions. The experiments were performed for 11 days. The plant performed extremely well in removal of both Zn and Cr, it safely removed Zn for all concentrations without showing any toxicity but in case of chromium plants showed some morphological toxicity for 15, 20 mg/l of concentration. During the 11 days a total of 95% of Zn and 84% of chromium were removed.

Natarajan et al., 2008 investigated the effect of plant density and nutrient concentration on the uptake of arsenic. The plant species used was Chinese brake fern. The experiment done was a hydroponic field experiment where the contaminated ground water was brought from the site and the plants were made to grow in 30L of contaminated water. The remediation treatment comprised of different number of plant species per chamber, two types of nitrogen dilutionsand two phosphorous dilutions. Low levels of phosphorus showed good As removal whereas change in nitrogen levels showed no affect.

Rai, 2008 examined the phytoremediation ability of a small free floating plant *Azolla pinnata*. This plant species was used to remove concentrations of 0.5, 1 and 3 mg/lfor both Cd and Hg.The fern was grown in twenty four aquariums having capacity of forty litres. The experiment study was carried out for 13 days. At the end of the experiment, metal contents in the solution were reduced up to a range of 70% to 94%.

Meyers et al., 2008 examined the effect of Pb on Brassica juncea. The plant species was grown in a hydroponic setup, it was given a growth time of 14 days after plant growth it was exposed to Pb for 3 days at concentrations of 3.2, 32 and 217 µm. It was found out that the lead ions were restricted to the root tissues by performing Atomic absorption spectroscopy (AAS) on the plant samples. Other different kinds of testing such as STEM and EDS were done to discern the effect of Pb on the plant and also to find more about its uptake mechanism.

Zhang et al., 2007 utilized various ornamental hydrophytes such as *R. carnea*, *A. gramineus*, *A. orientale*, *A. calamus*, *I. pseudacorus*, *L. salicaria* in a constructed wetland experiment to investigate the treatment capacity of each ornamental hydrophyte for domestic or rural wastewaters. All the hydrophytes used in the study adapted well to the wastewater, the initial concentration of heavy metals (Cr, Cu, Mn, Pb, Cd and Fe) was 0.201, 2.031, 2.024, 0.211, 0.021and 2.015 respectively. The experiment was performed for about 15 days. Most of the hydrophytes were fairly efficient in reducing the amount of BOD, COD, TN, TP and heavy metals from the wastewater. Out of all the hydrophytes *A. gramineus* was the best in removing all the pollutants from the wastewater. The heavy metal removal ranged from 76.9% to 99.1% The highest removal for heavy metals was by *I. pseudacorus*, the heavy metal removal followed the trend, Cr >Pb> Cd> Fe > Cu >Mn.

January et al., 2007 exposed the Sundance Sunflowers to different kinds of heavy metals. The metals wereintroduced at a constant concentration of 30mg/l. There were three sets of experiments performed. The experimental setup consisted of two chambers being utilised simultaneously, 7 Sundance sunflowers were used per compartment. The first run examined the influence of EDTA on Cd, Cr, and Ni. The run examined the influence of As. The thirdrun examined the effect of fifth metal addition and chelators on the Sundance sunflowers.

Bragato et al., 2006 investigated the effective metal removing ability of constructed wetland. The study area was a pre-existing wetland named Ca di Mezzo which was constructed in 2000. This study was carried out to examine growth structure and heavy metal accumulating ability of the two plants: Phragmites australis and Bolboschoenus maritimus present in the region. The sampling was done from three sites of the basin. The sampling was done for six months. The presence of Cu, Cr, Zn and Ni were detected in the wetland.

Ali et al., 2004 conducted two experimental runs under hydroponic conditions. The effect of Cd and the combined effect of Cd, Cu and Zn were also examined on the growth, tolerance and mineral composition of the plant species *Phragmites australis.* In the first run the plant was exposed to the individual metal ion cadmium, the concentration was kept at 0.5, 1, 2 mg/l. neither the root nor shoot were affected by the concentration of 0.5 and 1 but the concentration of 2 mg/l significantly decreased the root number and the shoot length. In the second run the plant was exposed to a combined mixture of metal ions having different ratios, in each case at leastone ion was present in high concentration (0.5:2:5; 2:2:2; 0.5:5:2 mg/l for Cd,Cu and Zn). The combined metal exposure significantly decreased the root and shoot length and the plant fresh weight.

Maine et al., 2004 studied the Cr (III) uptake ability of two free floating plants Salvinia herzogii and Pistia stratiotes. These were grown outdoors in plastic aquariums containing water taken from the lake; the plants needed about 30 to 35 days to reach full maturity. In this study three types of experiments were performed. First, the cleansing capacity of both the plants were determined at different Cr concentrations (1, 2, 4and 6 mg/l). Second, the Cr distribution in the various parts of the plants was evaluated with time. Third, the reason ofincrease of Cr in the aerial parts was examined whether it was due to the translocation from roots ordirect contact between leaves and the solution containing metals. Both macrophytes effectively eliminated Cr from water at all the concentrations. Larger the initial concentration,larger theaccumulation was observed.

Kamal et al., 2004 examined the metal removal ability free floating plants (parrot feather, creeping primrose, and water mint)from contaminated water. The plants were grown hydroponically and were given 2 weeks to acclimatize before the addition of the contaminants. The experiment was performed in 55L tanks with a photoperiod of 16/8 hr. All the three plants were able to remove metals from the contaminated water. The average removal efficiency for the three plant species was 99.8% of Hg, 76.7% of Fe, 41.62% of Cu and 33.9% of Zn.

Axtell et al., 2003 examined the uptake ability of aqueous Pb and Ni of *Lemna Minor* (an aquatic plant) and the Pb uptake ability of Microspora (a micro-algae). Batch experiments were performed for L. Minor and both batch and semi-Batch experiments were performed for microspora. In the batch study the biomass was exposed to a single addition of metal whereas Semi-Batch study consisted of adding similar amount of metal but in small additions over the course of the study. The experiment was conducted for 10 days. The initial concentration of Pb added was 0,5,10 mg/l and of Ni was 0, 2.5, 5.0 mg/l. The removal of lead for microspora was 97% (Batch study) and 95% (Semi-Batch study). The removal of Pb and Ni for L. minor was 76% and 82% respectively.

Table 2.1 Summary of some work done on phytoremediation

Reference	**Type of water**	**Metals**	**Plant species**	**Techniques used**	**Remarks**
Pandey, 2012	Fly ash pond	Fe, Mn, Zn, Cd, Ni, Cu, Pb, Cr	Azolla caroliniana	Constructed wetland	Maximum accumulation of Fe and Zn might be the reasons responsible for lowest accumulation of Cd, in both parts of the fern.
Sekomo et al.,2012	Textile wastewater	Cd, Cr, Cu, Pb, Zn	Duckweed and algae	Free floating	Both plants are suitable for heavy metal removal, especially Cr and Zn atlower concentration.
Liu et al.,2011	Water containing $CrCl_3$	Cr	Leersia hexandra	Pot-culture experiment	Uptake of Cr by roots of L. hexandra was significantly decreased by metabolic inhibitors and low temperature.
Chen et al.,2011	Water	Cr, Zn, Pb	Vetiveria zizanioides	Floating platform	Chelator-assisted phytoremediation with vetiver can be a green alternate to the conventional, physio-chemical techniques

Hoang Ha et al., 2010	Water	In, Ag, Pb, Cu, Cd, Zn	Eleocharis acicularis	Floating platform	Eleocharis acicularis is a good option for phytoremediation and phytomining
Khan et al.,2009	Wastewater	Cd, Cr, Cu, Ni, Fe,Pb	Typha latifolia, Juncus articulatus, Lemna gibba	Constructed wetlands	Cd> Cr> Fe>Pb> Cu> Ni trend of removal was observed
Natarajan et al., 2008	Groundwater collected from South Florida	As	Pteris vittata	Floating platform	Low levels of phosphorus showed good As removal
Rai, 2008	Water	Hg, Cd	Azolla pinnata	Floating platform	Azolla pinnata growth was inhibited
Mishra and Tripathi, 2008	Water	Cr,Zn	Eichhornia crassipes	Free Floating	E. crassipes is a good accumulator of Cr and Zn.
January et al,2007	Water	Cd, Cr, Ni, As, Fe	Sundance sunflowers	Hydroponic greenhouse experiment	EDTA caused a reductionin metal uptake
Meyers et al.,2007	Water	Pb	Brassica juncea	Floating platform	B. Juncea has significant potential for use in removing toxic ions fromWater.
Zhang et al.,2007	Wastewater	Cr, Pb, Cd	R. carnea, A. gramineus	Constructed wetlands	Iris pseudacorus and Acorus gramineus are outstanding either in adapting or cleaning urban sewage in comparison to other plants.
Bragato et al., 2006	Lagoon watershed	Cr, Ni, Cu, Zn	Phragmites australis	Constructed Wetland	The heavy metal content in plants is highest in late autumn after senescence (field study)
Maine et al., 2004	Water	Cr	Salvinia herzogii, Pistia stratiotes	Floating platform	Cr uptake occurred mainly during the first 24 h
Kamal et al, 2004	Contaminated water	Fe, Zn, Cu,Hg	Parrot feather, creeping primrose,	Floating platform	Creeping primrose has the leasttolerance to heavy metal toxicity

			water mint		
Ali et al.,2004	Water	Cd,Cu, Zn	*Phragmites australis*	Hydroponic study	Combined metal conc. Decreased root, shoot length
Axtell et al.,2003	Water	Pb, Ni	L. Minor, Microspora	Free floating	Both showed good removal

2.3 Work done on adsorptive removal of heavy metals using Laterite soil

Maiti et al., 2012 conducted three studies in which the Arsenic adsorption capacity of treated laterite was investigated under different conditions in a batch study, firstly by using a single arsenic species and then in the second study using a mix of both As(III) and As(V) species and then in the third case, study of real arsenic bearing contaminated water was done. The raw laterite was brought from Midnapore. This raw laterite was then treated with acid (0.5 N HCl) followed by treatment with a base (4 N NaOH). In the batch study the concentration of arsenic was kept in range of 0.2 to 20 mg/l and was agitated in a shaker for 24 h at a fixed adsorbent loading of 0.5 g/L at 305 K.The Fixed bed column experiment was done using contaminated groundwater spiked with arsenic collected from Kharagpur and real contaminated groundwater collected from Dhabdhobi.

Maiti et al., 2012 conducted a two part study, in the first part laterite samples collected from four different sites (Kharagpur, Bankura, Manbazar, Purulia) having different compositions were compared and analysed on their arsenic removal ability. In the second part the soil samples were treated with acid followed by base and used as filter medium in a typical household column. In the first case batch study was performed keeping dose as 20g/l, rpm as 150, contact time as 24 hr, temperature as 305K, pH as 7.0 and arsenic concentration was varied from 0.1 to 5 mg/l. after the analysis it was established that the soil from Kharagpur showed the maximum removal percentage. Two household filters using the treated laterite are installed in arsenic affected area of Barasat in West Bengal, and their performance was monitored.

Aminah and Izaat., 2011 investigated the Zn removal potential of laterite soil. The laterite soil used in this experiment was brought from Berseri, Perlis. In this experiment batch study was conducted and various parameters such as the effects of adsorbent dose, initial pH, contact time and initial Zn concentration were studied. Based on the experimental results, zinc removal improved with rise in contact time and concentration, also high acidic pH favoured Zn uptake, but zinc removal decreased with higher dosage of lateritic soil.

Jahan et al., 2011 studied As (III) removal ability of natural laterite soil. The soil used in this study was collected from three locations of South Australia (Proctor Road, Range Road and Kangaroo Island). Two batch experiments were conducted, in the first experiment the comparison of the three soil samples was done on the basis of their removal capabilities and also for different doses. In the second experiment the effect of pH was examined on As(III). In the first experiment the temperature was kept at 294K, contact time was 24 hr, concentration of As(III) was kept at 50 mg/l and an rpm of 15 was maintained. Two concentrations of dose were taken 1000g/l and 200g/l. The laterites removed more than 97% and 87–97%, for the two doses respectively.Out of all the laterite samples the Kangaroo Island sampleshowed the best removal capability,the presenceof high contentof gibbsite may be one of the reasons for this.

Maiti et al., 2010 studied the effect of treated laterite for arsenic removal from water. The raw laterite used was brought from kharagpur. It was then treated with acid (2N HCl) followed by base treatment (4N NaOH). In this study three types of experiments were done a batch study, a column study and a household filter medium was designed. Arsenic removal from both synthetic water and contaminated groundwater was done. Arsenic adsorption on the treated laterite followed pseudo second order kinetics. Different characterisation tests such as FTIR, XRD, SEM-EDAX and HRTEM were done to get a detailed description and classification of the treated laterite.

Maiti et al., 2010 investigated the arsenic removal ability of acid activated laterite soil. The raw laterite was treated with 0.1N HCl to convert it to acid activated soil. The batch experiments for arsenic are performed for both synthetic and natural groundwater. Comparison of the removal ability and characteristics has also been done between the raw laterite and acid activated laterite.

As(III) and As(V) adsorption on AAL were inspected under different process parameters such as dose of adsorbent, time of contact, temperature, size of particle,concentration, and competitive ions.The arsenic concentration was altered from 0.5 to 10 mg/l and a fixed adsorbent loading of 5g/l was taken, the temperature was kept at 304K, rpm at 150 rpm and the contact time was kept at 24 hr. AAL showed better removal capability as compared to raw laterite. Column study using AAL as adsorbent bed has been done, it was used to treat arsenic-polluted ground water collected from Dhabdhobi.

Nemade et al., 2009 investigated the As uptake ability of laterite soil. The laterite soil used in the study was brought from Tambati village, for preparation of adsorbent, soil was crushed and washed with tap water and then it was dried at 100^oC. Batch experiments were performed to test the effect of various process parameters on the removal of arsenite. The concentration of As(III) was varied from 0.25 to 4 mg/l. After optimisation studies it was found that maximum uptake of As(III) occurred at a dose of 25 g/l (around 95%). The Temperature was maintained at 304 K, pH was 7.1, Contact time was 24 hr and the rpm was maintained at 130. Rapid colorimetric method was used for sample analysis.

Maiti et al., 2008 studied the removal of As(V)ions. Both the equilibrium and kinetic studies were done over a varied ranges of operating conditions to assess the removal of As(V). The laterite soil used in this study was collected from the Midnapore district. In this study both batch and column study was carried out. The optimum dose was 20g/l, particle size was 0.38mm, the effective pH was maintained in the range of 5.5 to 7.5 and the contact time was 4hr. One of the main reasons for performing the column study was to see how much effluent can be treated before regeneration of bed is required, the Adams-Bohart model was used for estimating the breakthrough curve.

Rahman et al., 2008 investigated the As removal ability of heat treated laterite. The laterite soil used was brought from Ogasawara Island in Japan. Batch experiments were performed and various parameters like dose of laterite soil, arsenic concentration and different rpm speeds were studied. The optimum dose observed was 5g/l, the optimum rpm was 400 and the initial arsenic concentration was varied as 0.3163, 0.5654, 0.8484, 1.0086 mg/L. Adsorption equilibrium data indicated both Langmuir and Freundlich models to be satisfactory.

Yu et al., 2008 studied the Hg(II) removal ability of natural laterite soil. The soil used in this study was collected for the Guizhou Province in China, different soil samples were collected from different weathered zones, in total about 10 samples were collected. The experiments were performed under batch conditions with a dose of 1g/20ml, mercury concentration was 150µg/ml, contact time was 2hr and the pH was maintained in the range of 7 to 9. After the experiment the sample was spun in a centrifuge at 3000rpm for 5 min and then the samples were analysed for Hg by the Plasma emission spectrograph. Sample 1 showed the best removal capacity of 67.88% because of the elevated presence of illite and non-crystalloids in the laterite soil. The adsorption isotherm that was followed was the Langmuir isotherm.

Maiti et al., 2007 examined the arsenite removal capacity of natural laterite. Batch experiments were carried out to test the various process parameters. The concentration of As(III) was varied from 0.3 to 5 mg/l. After optimisation studies it was found that maximum uptake of As(III) occurred at a dose of 20 g/l. the temperature was maintained at 314K, pH was 7.2, contact time was 16 hr and rpm was maintained at 150. From the kinetic analysis it was perceived that the maximum adsorption occurs within two hours of the process.

Maji et al., 2007 examined the As(III) and As(V) removal capacity of natural laterite soil. The soil crushed, washed and dried. The temperature was maintained at 298K, rpm at 170, concentration of both the arsenic compounds was taken as 0.5 mg/l. the particle size of the laterite was taken as 0.164 mm and the optimum time of contact was 4 hr, the optimum dose was 10g/l for As(III) showing a removal of 98% and 20g/l for As(V) showing a removal of 95%. The adsorption follows Langmuir, Freundlich and D-R isotherms. By the calculation of the E-valued of the D-R isotherm it was found out that As(III) adsorption follows the mechanism of physisorption whereas for As(V) it is both physisorption and ion exchange.

Maji et al., 2007 studied the arsenic removal by laterite soil. In this experimental study batch experiments were performed on both synthetic and real wastewater samples. The experimental conditions for both were kept same, temperature was maintained at 298K, rpm at 170, the pH was kept at 5.7 and the contact time was 4 hr (synthetic samples) and 30 min (real groundwater). Also the effect of various ions (Cl^-, NO^{3-} , SO_4^{2-}, Ca^{2+},Sio_3^{2+},HPO_4^{2-},Fe^{2+} and EDTA) and organic compounds (Humic acid, atrazine and 2,4-dichlorphenoxyacetic acid) on laterite were examined. Laterite showed good removal ability for both synthetic (95% to 98%) and real groundwater samples (85% to 99%).

Table 2.2 Summary of work done on adsorptive removal of heavy metals using laterite soil

Reference	**Type of water**	**Metal Removed**	**Type of Adsorbent Used**	**Type of Study**	**Process Parameters**
Maiti et al., 2012	Synthetic and Contamined water	As(III) and As(V)	Treated laterite (Acid followed by base treatment)	Batch and column	Concentration: 0.2 to 20mg/l, dose: 5g/l, contact time: 24 hr, temperature: 305K
Maiti et al., 2012	Synthetic wastewater	As(III) and As(V)	Raw laterite and treated laterite	Batch and column	Concentration: 0.1 to 5mg/l,dose:20g/l, contact time:24hr, temperature:305K, pH:7
Aminah and Izaat., 2011	Synthetic wastewater	Zn(II)	Raw laterite	Batch	Concentration: 50 to 250ppm,dose: 5g/l Contact time: 10 min, pH: 8
Jahan et al., 2011	Synthetic wastewater	As(III)	Raw laterite	Batch	Concentration:50mg/l Dose:1000g/l,200g/l Contact time:24 hr Temperature:298K pH: 4.7 to 10
Maiti et al., 2010	Synthetic and Contamined water	As(III) and As(V)	Treated laterite	Batch and column	Concentration:0.2 to 20mg/l, Dose:0.5g/l Contact time:24hr Temperature:305K pH:7.0
Maiti et al., 2010	Synthetic and Contamined water	As(III) and As(V)	acid activated laterite soil	Batch and column	Concentration:0.5 to 10mg/l,Dose:5g/l Contact time:24 hr Temperature: 304K
Nemade et al.,	Synthetic wastewater	As(III)	Raw laterite	Batch	Concentration:0.24 to 4 mg/l,Dose: 25g/l

2009					Contact time:24hr Temperature:304K pH:7.1
Maiti et al., 2008	Synthetic wastewater	As(V)	Raw laterite	Batch and column	Concentration:0.2 to 20 mg/l, Dose: 20g/l Contact time:4 hr Temperature: 302K pH: 5.0 to 7.5
Rahman et al., 2008	Synthetic wastewater	As(III)	Raw laterite	Batch	Concentration:0.31 to1.0086mg/l,Dose:5g/l, Contact time:24hr Rpm:400
Yu et al., 2008	Synthetic wastewater	Hg(II)	Raw laterite	Batch	Concentration:150µg/ml, Dose: 1g/20ml Contact time:2hr Temperature: 304K pH:7 to 9
Maiti et al., 2007	Synthetic wastewater	As(III)	Raw laterite	Batch	Concentration:0.3 to 5mg/l,Dose:20g/l Contact time:16hr Temperature:314K pH:7.2
Maji et al., 2007	Synthetic wastewater	As(III) and As(V)	Raw laterite	Batch	Concentration:0.5mg/l,Dose:10g/l,20g/l Contact time:4hr Temperature:298K
Maji et al., 2007	Synthetic wastewater and Contamined water	As(III) and As(V)	Raw laterite	Batch	Concentration:0.5mg/l,Dose:10g/l,20g/l Contact time:4hr Temperature:298 pH:5to7

2.4 Objective of the present study

Present work aims at developing a technique for the effective removal of Pb and Cr from synthetic wastewater by utilizing living plants and laterite soil. Based on the extensive literature review the following objectives have been formulated:

- Optimization of process conditions for phytoremediation of Pb and Cr using Vetiver Zizanioides
- Assessment of the heavy metal removal capacity of the plant species.
- To Study the distribution of metals in various parts of the plant body.
- Preparation of adsorbents by surface modification of laterite soil and the selection of the best adsorbent.
- Assessment of the heavy metal removal capacity of the laterite soil.
- Kinetics and equilibrium study of the adsorption process.

CHAPTER 3

EXPERIMENTAL SETUP ANDINSTRUMENTATION

3.1 Introduction

In the present study living plants and laterite soil have been used for the heavy metal removal from synthetic wastewater. Both the studies have been carried out in batch mode. In this chapter the detailed design of the experimental setup, the type of plant species and soil species used for the experiment and the various analytical and auxiliary instruments used during the study have been discussed.

3.2 Phytoremediation Study

This study was done by using the rhizofiltration mechanism of the phytoremediation technology. The plant species chosen for this study was Vetiver Zizanioides, which was brought from the Punjab Forest Department in Mohali (Punjab). The reason for the selection of Vetiver Zizanioides for the present study was that there are many papers on the uptake ability of vetiver from soil by using the phytoextraction mechanism, but there have been very few researches on its uptake ability from water thus laying down the foundation for this study.

Vetiver grass has some inherent advantages that make it a suitable plant for phytoremediation they are, it has a dense, deep and well developed root system which enables it to readily uptake metals from water and soil, it is a fast growing species and can endure different types of temperature and nutrient conditions.

3.2.1 Experimental setup

The study was carried out in tanks made of Perspex; having a capacity of 50 L (dimensions 50X29X35). This tank was equivalently divided into two halves and then these two halves were further divided into three compartments each of about 8.3 L. Four compartments were used to carry out the experiments and two compartments were used as control. A sheet made of Perspex was placed on top of the tank; holes were made on this sheet; on which plastic cups (having holes in them to provide space for the roots) were mounted and on these cups sapling of V. Zizanioides were planted.

The experiment was carried out under hydroponic conditions i.e. the plants were directly grown in water without the use of soil. One sapling of the plant was planted per compartment. Continuous aeration was provided to the plants by the use of aquarium pumps in order to provide adequate oxygen to the plants. The artificial lighting provided to the plants was in the form of CFL bulbs. The schematic diagram and the picture of the real setup is shown in Fig 3.1 and 3.2

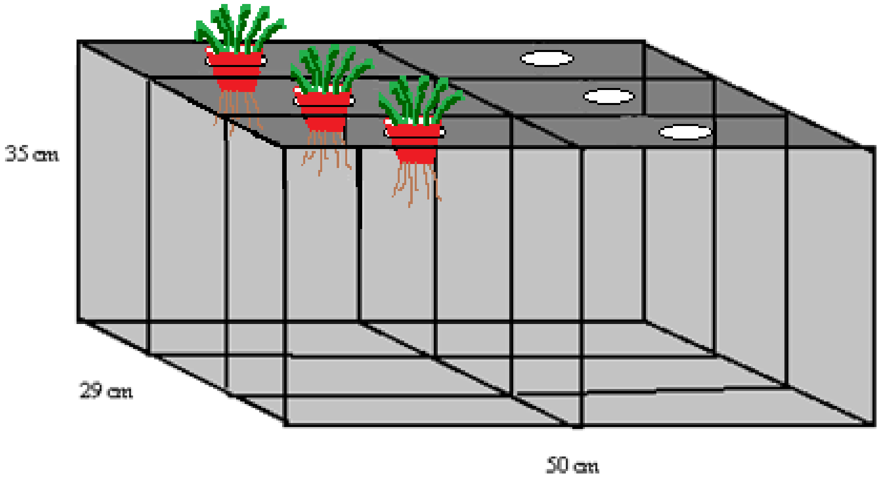


Fig 3.1 Schematic diagram of Experimental setup

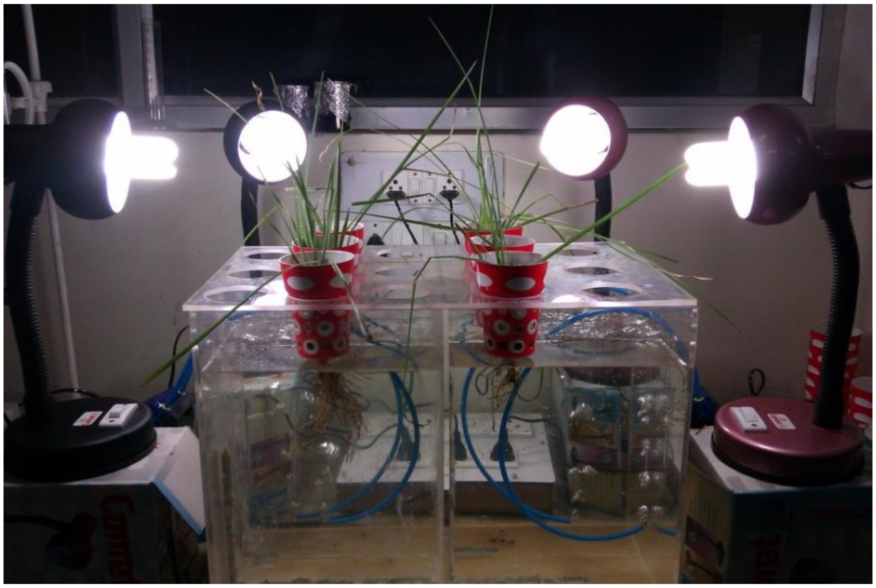


Fig 3.2 Experimental Setup

3.3 Adsorptive removal of heavy metals using Laterite Soil

The adsorption study using the laterite soil was carried out in batch mode in an orbital shaker. The laterite soil used in the present study was brought from the Bardhaman district of West Bengal. The effect ofvarious parameters such as adsorbent dose, time of contact, pH and initial Cr and Pb concentrations was studied on the laterite soil. The studies were carried out in batch mode in an orbital shaker.

3.4 Instruments and Chemicals

All the chemicals used in the present study were brought from SD Fine-Chemicals Limited and they were of analytical grade. All the stock solutions were prepared by using distilled water. The instruments used in present study were, Field emission scanning electron microscopy (FE-SEM), Fourier transform infrared spectroscopy (FTIR), Flame atomic absorption spectrometry (AAS), Brunauer-Emmett-Teller isotherm (BET) and XRD. FTIR (FTIR, Nicolet 6700, USA) spectrometer was used to find out the type of functional groups present in the soil. FE-SEM (FE-SEM QUANTA 200 FEG) study was conducted to observe the surface before and after the metal uptake in case of both plants and soil.

AAS (GBC Avanta M) study was done find out the concentration of metals in the water samples. BET(ASAP 2020 V3.05 H Micromeritics system) analysis of the soil samples was done to find out the surface area, pore size and pore volume of the sample and the XRD (BRUKER D8 ADVANCE) study was done to find out about the crystal structure, chemical configuration and physical properties of the soil.

The supplementary instruments used in the present study werepH meter (CL 54+ pH meter), muffle furnace, centrifuge, water bath, Sand bath, weighing balance, orbital shaker, distilled water plant and hot air oven.

CHAPTER 4

EXPERIMENTAL PROCEDURE

4.1 Phytoremediation Study

In this study the experimental method and technique utilized for the heavy metal removal from synthetic wastewater by using Vetiver Zizanioides has been described. The experiments were performed in a batch process, in an experimental setup that was specifically designed for this process.

4.1.1 Preparation of nutrient solution

In this study the plants were grown in a hydroponic system. As a result the nutrient solution used plays an essential role in plant growth. The nutrient solution for a hydroponic system is equivalent to the fertilizer given to the soil for plant growth. In this study Hoagland's half strength nutrient solution was used. Vetiver Zizanioides acclimatized well to the nutrient solution and showed an increased growth in roots as well as shoots as shown in Fig 4.1. The preparation of Hoagland's half strength nutrient solution is as follows:

KH_2PO_4 = 0.068 g/l

KNO_3 = 0.253 g/l

$Ca(NO_3)_2$ = 0.59 g/l

$MgCl_2.6H_2O$ = 0.20 g/l

H_3BO_3 = 0.00142 g/l

$MnCl_2$ = 0.000578 g/l

Fe-EDTA = 1 to 3 ml

The above mentioned chemicals are then mixed in 1 L of distilled water. This solution is then used as the nutrient solution.

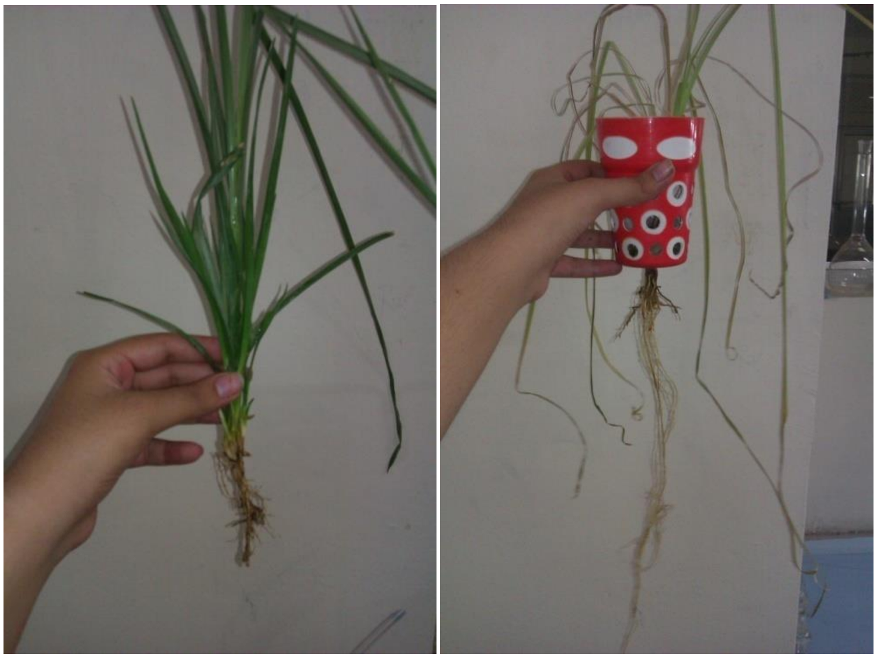


Fig 4.1Plant sapling before and after being acclimatized to nutrient solution

4.1.2 Preparation of stock solution

The metal solutions were prepared by using Distilled water. The metals Pb and Cr were introduced as metallic salts of lead nitrate and potassium dichromate respectively. They were introduced in a quantity of 5, 10, 15 and 20 mg/l respectively into the different compartments of the setup. Both these metals were added simultaneously i.e. one compartment contained both metals in a 1:1 ratio.

4.1.3 Experimental Procedure

The water present in the experimental setup consisted of half quantity of 50% Hoagland’s solution and half quantity of tap water. *Vetiver Zizanioids* was given an acclimatization period of 4 weeks into this solution. The artificial lighting was provided by four 23watt CFL grow blubs stationed on each side of the setup, the photoperiod was 14/10 hr. Aquarium pumps were used to give constant aeration to the plants in order to avoid the algae build up in the tank and also to provide adequate oxygen to the plant roots.

The study was conducted under room temperature. After the acclimatization period; the metals were introduced into the four compartments. For the first study the natural pH of each compartment i.e. 7.3± 0.1 was maintained. In the second study the concentration of metals were kept constant at 20mg/l and the pH was varied as 3, 6, 9and 12. This was done in order to see the kind of environment that promotes adequate uptake of metals. Both the studies were carried out for a period of 15 days. The sampling in case of both the studies was done at every 24 hrs by making the use of a burette.

4.1.4 Analytical methods

The samples collected were analyzed by Flame atomic absorption spectroscopy (Instrument: GBC Avanta M, Flame: air-acetylene, Wavelength: for Cr: 357.9; for Pb: 217.0 nm, Slit Width: for Cr: 0.2 nm; for Pb: 1nm, Detection limit: for Cr: 0.050 ppm; for Pb: 0.060 pm) in order to check the concentration of Pb and Cr ions present in the water samples. Before analysis of samples AAS was calibrated using standard solutions of lead and chromium. The calibration curves obtained are represented in Fig 4.2 and 4.3. The pH of the water was checked daily (Instrument: CL 54+ pH meter). After the completion of the experimental run; the plant samples were separated into three parts i.e. roots, stems and leaves.

All the parts were then oven dried at $80^{o}C$ for 48 hr.,the oven dried plant samples were grinded to fine powder using a mortar and a pestle. Plant samples (2 g) were digested in 10 ml HNO_3 and heated at $150^{o}C$for 1.5 hr. After heating, 5 ml of 30% H_2O_2 was added to the beaker, and samples were further heated at 150°C for 1 h. Samples were allowed to cool and were then diluted to 100 ml by addition of distilled water. The concentration of Pb and Cr were determined in the digests by AAS. This was done to find out the concentration of metals accumulated in the different parts of the plant.

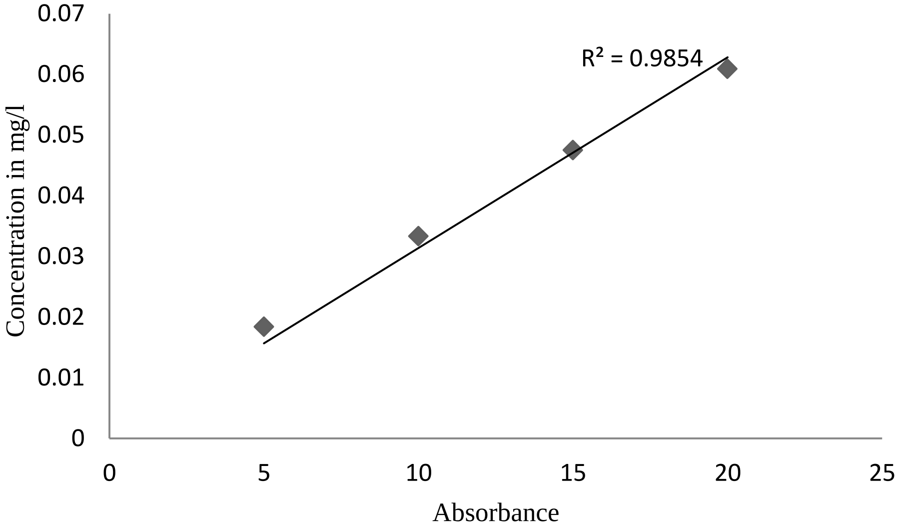


Fig 4.2 Calibration Curve for Cr

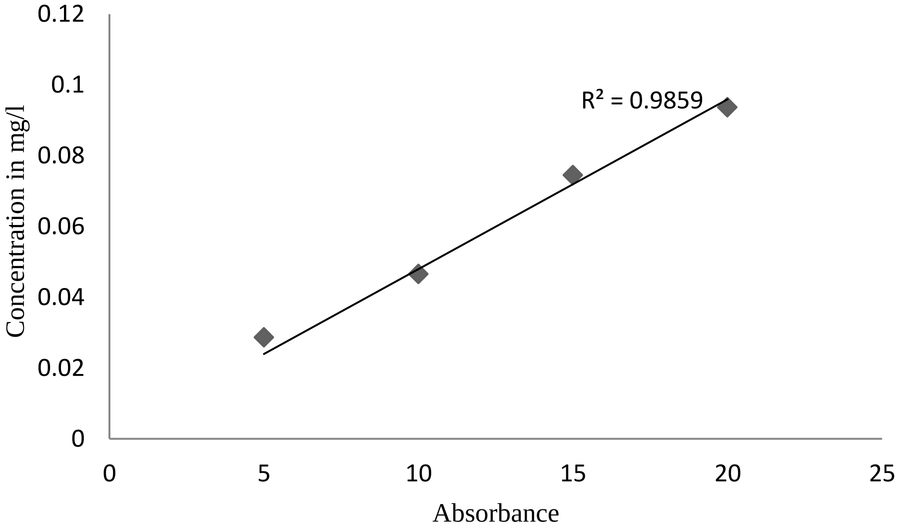


Fig 4.3 Calibration curve for Pb

4.3 Adsorptive removal of heavy metals using Laterite soil

In this study the experimental method and technique utilized for the heavy metal removal from synthetic wastewater by using Laterite Soil has been described. The adsorbent used in the current study is laterite soil of Bardhaman district; it is a low cost adsorbent and is readily available in India. Generally most of the studies relating to the laterite soils that have been carried out are based on the single component removal and the soil used is either from the Kharagpur district or the West Midnapore district. The present study is a unique study in which multi-component removal is attempted.The pictorial representation of the laterite soil used in the present study is shown in Fig 4.4.

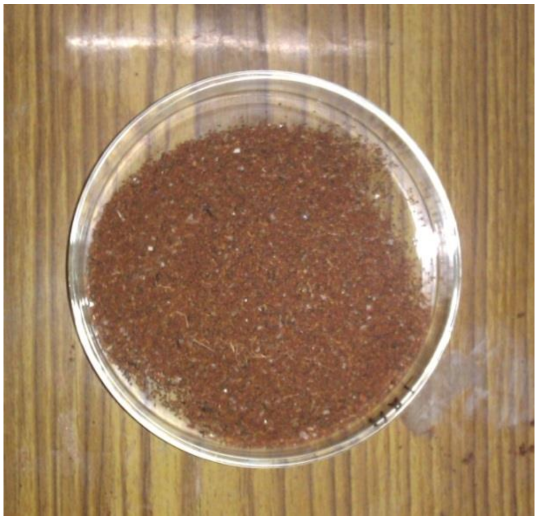


Fig. 4.4 laterite soil

4.3.1 Preparation of adsorbents

In this study surface modification of laterite soil was carried out to prepare six types of adsorbents, The various adsorbent prepared were Heat treated laterite, Heat treated+$FeCl_3$treated, Acid treated, $FeCl_3$ treated , Acid+$FeCl_3$ treated and Base treated in order to compare their Pb and Cr uptake ability with the natural or raw laterite.

4.3.1.1 Preparation of Raw laterite

Natural laterite was sun dried for two days to remove the moisture, it was then grinded and rinsedwith tap water until the lightly attached fragments were removed and the wash water showed no color. After oven drying at 100^{o}C, the particles were sieved through various mesh sizes. Particle sizes in the range of 0.5-0.7 mm were selected based on literature. Screened material was then stored in a covered beaker. This was then used as an adsorbent. (Maji et al, 2007).

4.3.1.2 Preparation of Heat treated laterite

The raw laterite prepared earlier was given heat treatment by being kept in the oven at 500^{o}C for 2 hrs. It was then allowed to cool for 30 min and was used as such as an adsorbent.

4.3.1.3 Preparation of $FeCl_3$ treated laterite

11g of the dried laterite soil was treated with 26.4 ml of $FeCl_3$ solution (having 2.5% Fe^{3+}) the natural pH of this solution was observed to be around 6.8 which elevated to 12 by the addition of NaOH solution. pH was kept high for impregnation process so as to create maximum surface charge on soil surface. This iron chloride treatment was performed at 70^{o}C in a water bath till the complete vaporization; it was then dried at 100^{o}C for 24 h.The dried material was washed with distilled water till it was free from iron.The change in the color of wash water was tested by the addition of KSCN solution. (Mondal et al, 2008)

4.3.1.4 Preparation of Heat treated + $FeCl_3$ treated laterite

The raw laterite was subjected to heat treatment as explained in 4.3.1.2; this was followed by treatment with $FeCl_3$ as explained in 4.3.1.3. The laterite soil modified in this way was then used as an adsorbent.

4.3.1.5 Preparation of Acid treated laterite

22 g of raw laterite was mixed with 44 mL of 0.2 N HCl solution and put in a conical flask. This mixture was shook at 200rpm for 1hr in an orbital shaker. The acidic supernatant was then discarded and the treated soil was kept at room temperature for 24 h. After this time the mixture wasrinsed with tap water. The soil sample was washed until the wash water displayed neutral pH.AAL was then dried and used as an adsorbent. (Maiti et al 2010)

4.3.1.6 Preparation of acid + $FeCl_3$ treated laterite

The raw laterite was subjected to acid treatment as explained in 4.3.1.5; this was followed by treatment with $FeCl_3$ as explained in 4.3.1.3. The laterite soil modified in this way was then used as an adsorbent.

4.3.1.7 Preparation of Base treated laterite

5 g of laterite soil was made to react with 75 ml of 5M NaOH. This mixturewas then boiled for 1 hr on a sand bath and after cooling it was transferred to centrifuge tubes. The sample was spunfor 10 minutes at 8000rpm, the supernatant was cast-off, after that the samplewas washed once with 0.5 M HC1to dissolve sodalite, twice with1 N $(NH_4)_2CO_3$ to remove NaCl and then with tap water to remove excess of ammonia and carbonate ions. The sample wasthen put ina petri-dish and dried at 110^{o}Cfor 12 hr, in order to volatilize the remaining $(NH_4)_2CO_3$ (Kampf and Schwertmann,1982). Three successive hot NaOH treatments were performed before the soil was used as an adsorbent.

4.3.2 Experimental procedure

Initially a preliminary adsorption run was carried out for all the seven adsorbents prepared; in a batch process under equilibrium conditions taken from literature to test which out of the sevenadsorbents showed maximum removal capacity. The adsorption was carried out using an adsorbent dose of 10 g/l; an rpm of 150 and the temperature was set at 305 K.

The contact time was set at 4 hr and the metals to be adsorbed were Chromium and Lead whose concentration was taken as 20 ppm. Cr and Pb were put simultaneously in the conical flask along with the adsorbent in the ratio of 1:1.The adsorbent that was good at adsorbing both Cr and Pb was raw laterite. Not much difference in the uptake studies of acidic and basic conditions was observed. Selecting natural or raw laterite as adsorbent various optimization studies were carried out, in which various parameters such as dose of adsorbent, time of contact, effect of pH and initial concentration of chromium and lead were studied.

The experiments were carried out in batch mode in 100 ml conical flasks; at a temperature of 305 K, the particle size was taken in the range of 0.5 to 0.7 mm and an rpm of 150 was maintained. The metals were added in a 1:1 ratio, in the conical flask i.e. if 25 ml of lead was present then at the same time 25 ml of chromium was also present.

Firstly the optimization study of time (from 0 to 8 hr) was carried out using a fixed adsorbent dose from literature, then the dose was optimized by varying in the range of 5g/l to 40g/l and then the pH optimization study was carried out. After all the parameters were optimized then the uptake ability of laterite soil for different concentrations of heavy metals was analyzed.

4.3.3 Desorption Study

In this study the reusability potential of used laterite was investigated. After the adsorption studies the laterite soil in which the metals were adsorbed was separated from the supernatant and dried at 100°C in an oven. This used and dried adsorbent was mixed with 50 ml of 1M NaOH solution and was shaken for 4hr at 150 rpm and 305K temperature. The liquid was filtered and analyzed for the metal content. After the treatment with NaOH the adsorbent was thoroughly washed with tap water and then finally with distill water until the pH of the wash water was neutral. This adsorbent was then dried and reused for the adsorption study. (Maji et al., 2007)

CHAPTER 5

RESULTS AND DISCUSSION

5.1 Phytoremediation study

The experiments were performed under laboratory conditions during the period of December-May; hence the plants were exposed to both winter and summer conditions. The plant sapling responded well to both conditions and showed good growth of the root system. In the present study the removal capability of V. Zizanioides with respect to different concentrations of heavy metals has been investigated for a certain period of time (15 days), the effect of pH on the metal uptake by plants has been examined and the different concentrations of heavy metals on the different parts of the plant body has also been investigated.

5.1.1 Effect of initial heavy metal concentration

The initial concentration of chromium and lead in the first experimental run was 5, 10, 15, 20 mg/l in various compartments and pH was maintained at 7.3; these concentrations were reduced by the Vetiver Zizanioides to 1.061, 2.206, 4.401, 4.591 mg/l for Cr and to 1.125, 2.003, 2.143, 0.876 mg/l for lead. The percentage removal of chromium for all the four concentrations was identical, in the range of 77 to 78 %. Chromium was efficiently depleted from the water and the greatest decrease was observed during the first 24 hr in all the experimental runs carried out. This follows the trend that has been reported by Maine et al. (2004).

The trend observed in the uptake of lead was totally opposite to that of chromium. While for chromium the majority of the uptake happened in the first 24 hr, in case of lead the uptake proceeded in a more gradual pace and happened all throughout the 15 days of the experiment. Also during the chromium uptake the metal removal was almost equivalent for all the concentrations whereas in case of lead the metal accumulation by the plant increased with increase in the concentration of the metal added with the highest removal being shown for 20 ppm concentration. The percentage removal for lead was in the range of 80 to 98%. The graphs depicting the difference in the concentration with respect to time for both Cr and Pb are shown in Fig 5.1and 5.2, the overall percentage removal for different initial concentrations has been shown in Fig. 5.3.

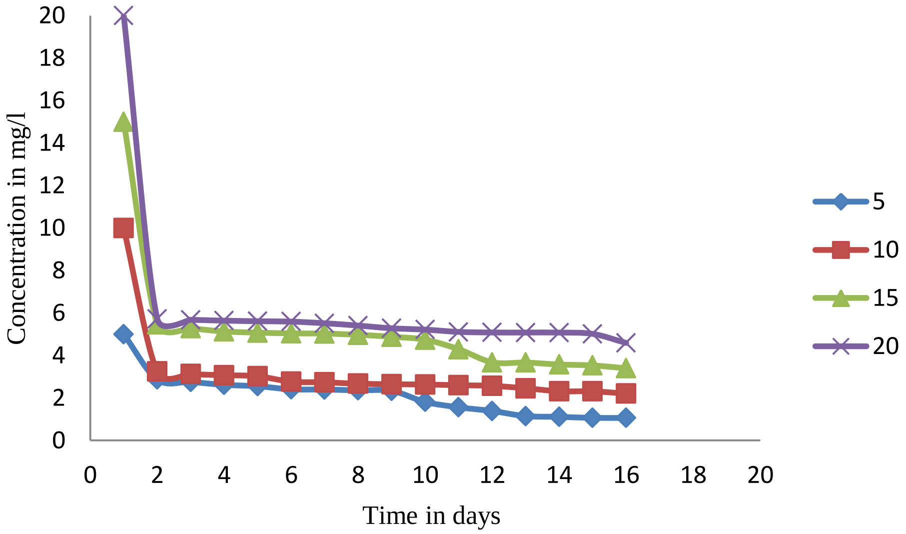


Fig 5.1Study of concentration with respect to time for Cr having constant pH

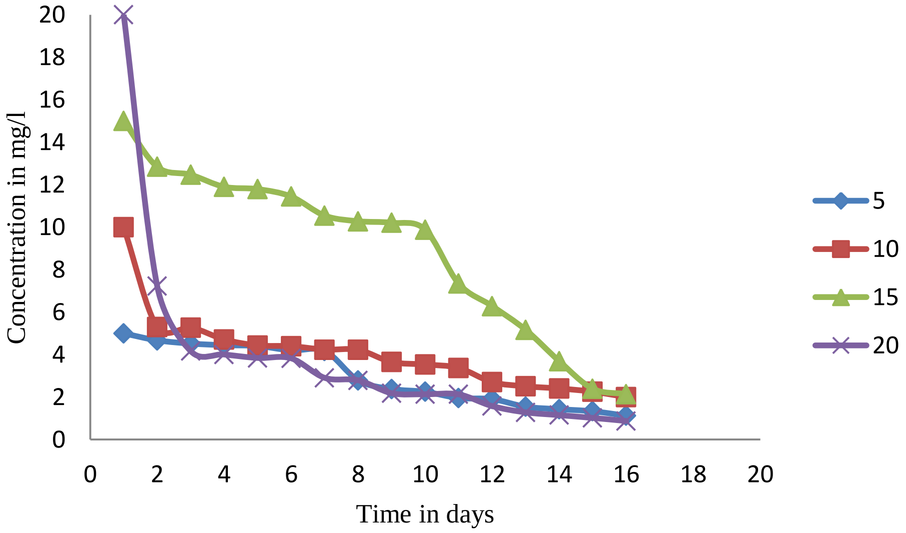


Fig 5.2 Study of concentration with respect to time for Pb having constant pH

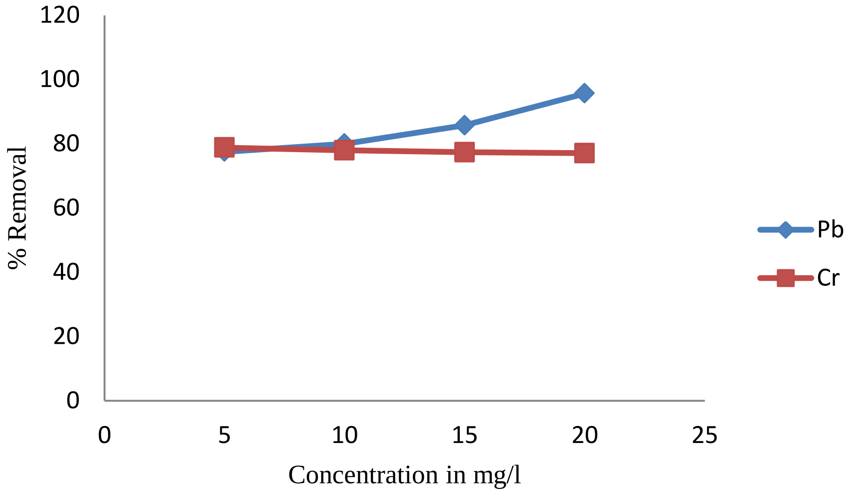


Fig 5.3Overall percentage removal of Pb and Cr for different initial concentration

5.1.2 Effect of pH

In the second experimental run the concentration was kept constant at 20 mg/l and the pH was varied as 3, 6, 9 and 12. In other words the plant sapling was subjected to extreme conditions such as high metal concentration, ultra acidic and basic conditions. The plant sapling began to disintegrate after the first five days of exposure due to it being subjected to extreme conditions as a result the removal percentage was almost constant after the 10th day.

The plant sapling showed minutely better results than when the experiment was performed for neutral pH in case of chromium but this was not the case for lead. The final concentrations at the end of the experiment were 3.901, 3.483, 3.021 and 5.098 mg/l respectively for chromium and for lead it was 10.233, 8.169, 9.386 and 12.254 mg/l respectively. The Study of concentration with respect to time for Cr and Pb having different pH are shown in Fig. 5.4 and 5.5.

The reason that Vetiver showed good potential for removal of Cr and not of Pb in these conditions was that the plant could not survive these extreme conditions and was almost dead after ten days. Since maximum Cr uptake happens in the first 24 hr and then there is gradual uptake but on the other hand Pb uptake happens gradually, as seen from the first study, the lead uptake happened gradually over the course of the entire 15 days.

The plant could uptake Cr but could not be sustained to uptake lead simultaneously. Maybe if the same conditions were kept for single metal ion then uptake observed would have been better for lead. The overall percentage removal of lead and chromium for different pH concentrations are depicted in Fig 5.6.

Vetiver Zizanioides showed good uptake ability of chromium as compared to lead for different values of pH. The removal percentage of chromium was identical for the pH values of 3,6 and 9 it was in the range of 80 to 84% respectively.

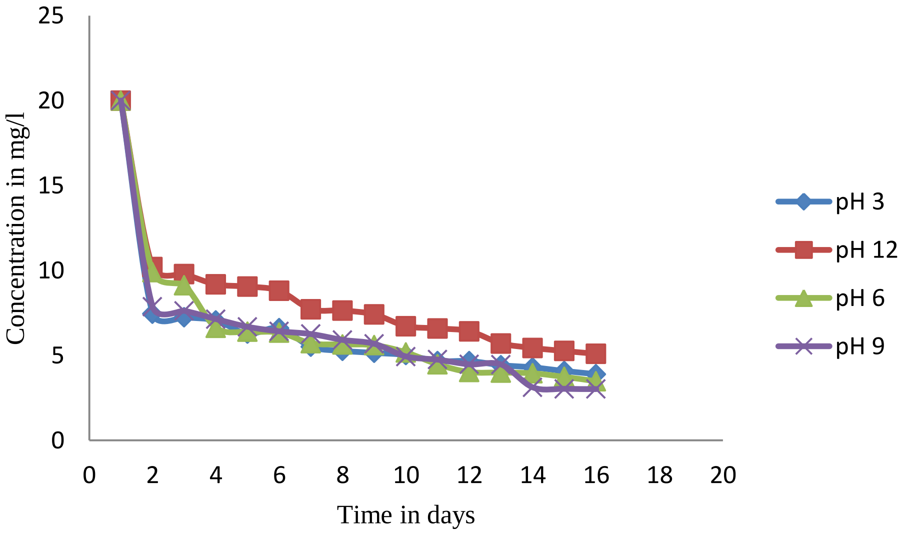


Fig 5.4 Concentration vs Time for Chromium having different pH

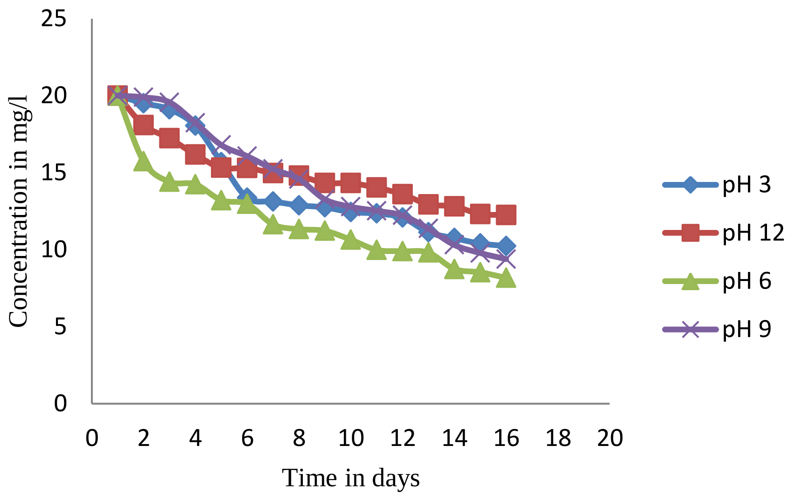


Fig 5.5 Concentration vs Time for Lead having different pH

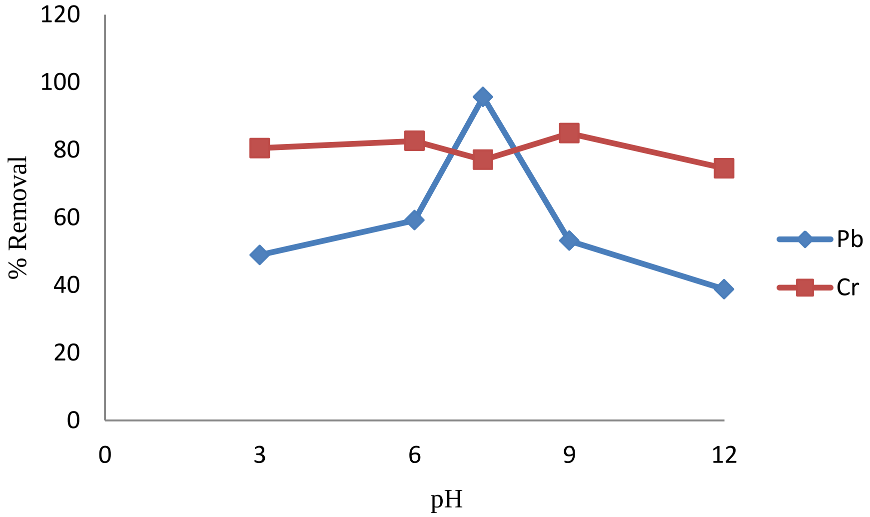


Fig 5.6 Removal percentage of Cr and Pb for different pH conditions at constant Concentration (20ppm)

5.1.3 Mechanism of heavy metal uptake by Vetiver grass

The measured Chromium concentration in the plant roots, stems and leaves obtained from the contaminated tanks was 58.3, 363.05, 332.3 g/kg respectively (dry basis). Most of the chromium was accumulated in the stems and leaves of the plant sapling. The plant translocated the metal absorbed in the roots up to the plant shoots

The measured lead concentration in the plant roots, stems and leaves obtained from the contaminated tanks was 610.15, 283.9, 48.45g/kg respectively (dry basis).This trend was also different then that observed for chromium. The majority of lead was accumulated in the roots and stem of the plant and a minor amount was accumulated in the leaves. This finding is similar to that observed by Minh and Khoa (2009) and Chen et al. (2012).

There are two processes related to the metal uptake from water using hydrophytes. They are a fast and a slow metabolism(Axtell et al., 2003; Cho et al., 1994). The fast uptake process is independent of surface reactions and generally consists of a diffusion process that ends when metal ions get adsorbed to the plant biomass. The slow uptake process relies on cellular uptake in which the process of mass transfer is involved occurring from the outside of the cell to the internal cell wall. The first process has the ability to remove large amount of metals in a few hours, this is a process that was followed by chromium in the present study, whereas the second step takes a lot more time, it may take anywhere between several hours to several days.(Axtell et al., 2003)

The ability of plants to transfer the adsorbed metal from roots to shoots has been explained by Jean et al. (2008) they reported that the transfer of metals from root to stem was related to metal chelation which enhanced the transport from roots to shoots by reducing the affinity for the binding site present in the cell walls. As a result the Metal complex is difficult to retain by ion exchange as compared to free metal ions. In this study the chelating agent used was EDTA. The mechanism of metal complex transportation enables the understanding of uptake effectiveness. The passive apoplastic transportation has been proposed as a possible mechanism (Komarek et al., 2010). This mechanism explains the uptake of both Cr and Pb. Chelator addition has generally prevented metal precipitation and is responsible for metal complex formation. The free diffusion space outside ofthe plasma membrane is known as apoplast, it has high content of carboxylic groups and acts as an efficient cation exchanger.

The chelator addition prevents the metal complex from being bound to the cell wall of roots and allowed the metal complex to enter the cells as a result they were subsequently transferred to the aerial parts of the plants through passive apoplastic pathway. (Chen et al 2012). The amounts of metals adsorbed in various parts of the plant are shown in Fig 5.7 and 5.8.

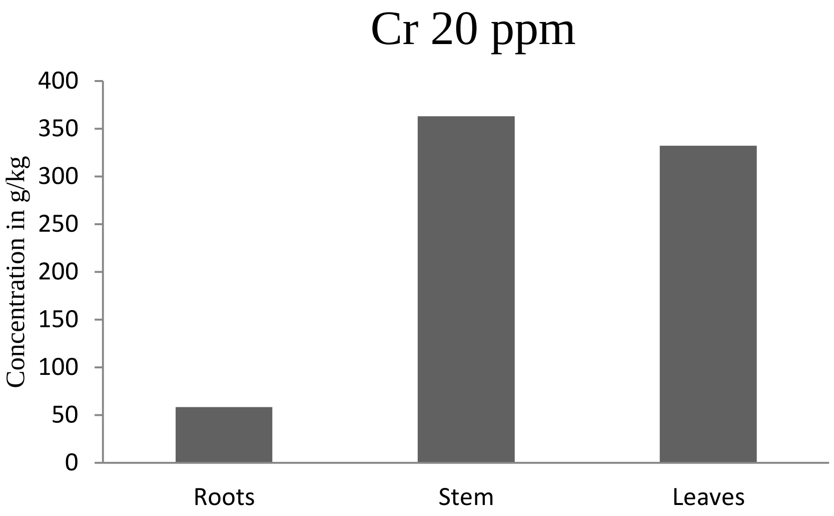


Fig 5.7 Concentration in the various parts of the plant for Cr (20ppm)

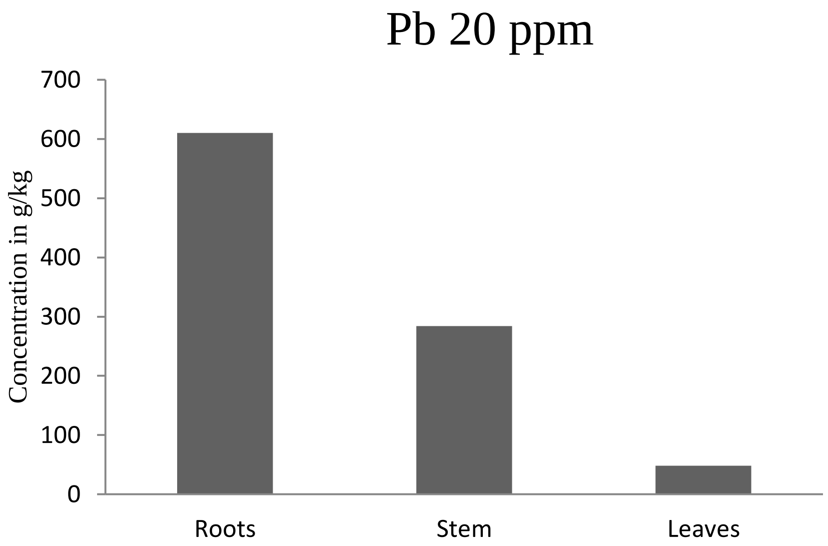


Fig 5.8 Concentration of in various parts of the plant for Pb (20 ppm)

5.1.4 Impact of heavy metal uptake on Vetiver grass

The effect of metals on the surface of vetiver grass has been examined by both macro and micro studies. The micro studies were performed by conducting the Field emission scanning electron microscopy, the FE-SEM study is basically a surface phenomenon i.e. it gives an understanding of the adsorption happening on the surface of the adsorbent but in case of plants since the uptake is happening inside the plant cell wall and all the translocation of metals happen inside the plant. The FE-SEM basically shows the outer damage suffered by the roots and leaves.

It also shows that not all the metal gets translocated inside the plant biomass and some gets precipitated on the root and shoot surface. As can be seen from the images presented in Fig 5.9 and 5.10, there is a marked difference in the appearance of both the roots and shoots before and after the metal exposure. There is an apparent distortion and appearance of metal precipitates on the surfaceof both roots and shoots.

The macro studies were performed by visually seeing the deterioration of vetiver grass when it was exposed to a high concentration of 20 ppm and ultra-acidic and basic conditions. The pictorial representation of the deteriorated grass species is depicted in Fig 5.11

a) b)

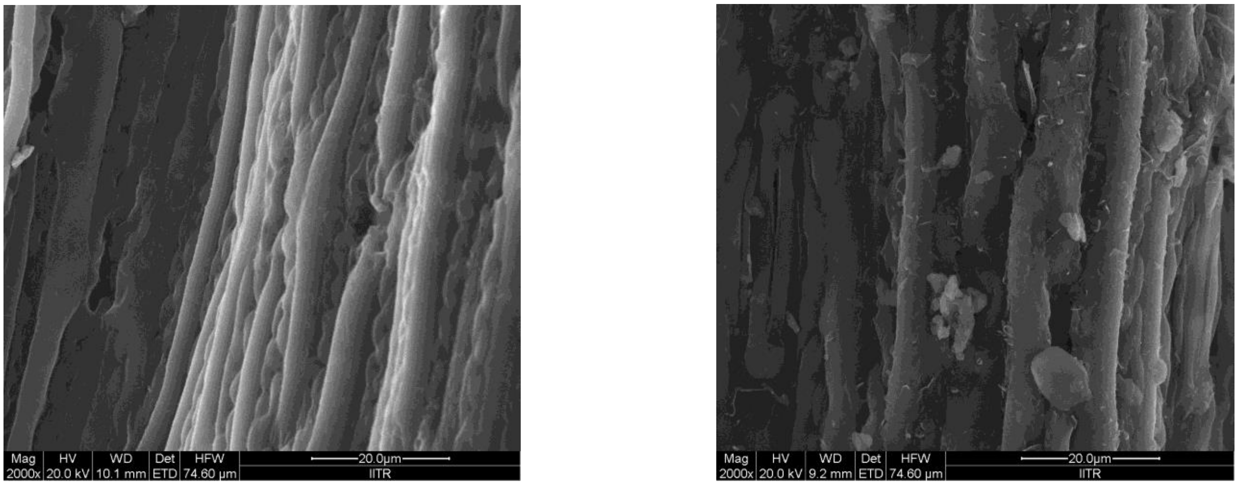


Fig 5.9 FE-SEM pictures of Leaves a) Before exposure, b) After exposure

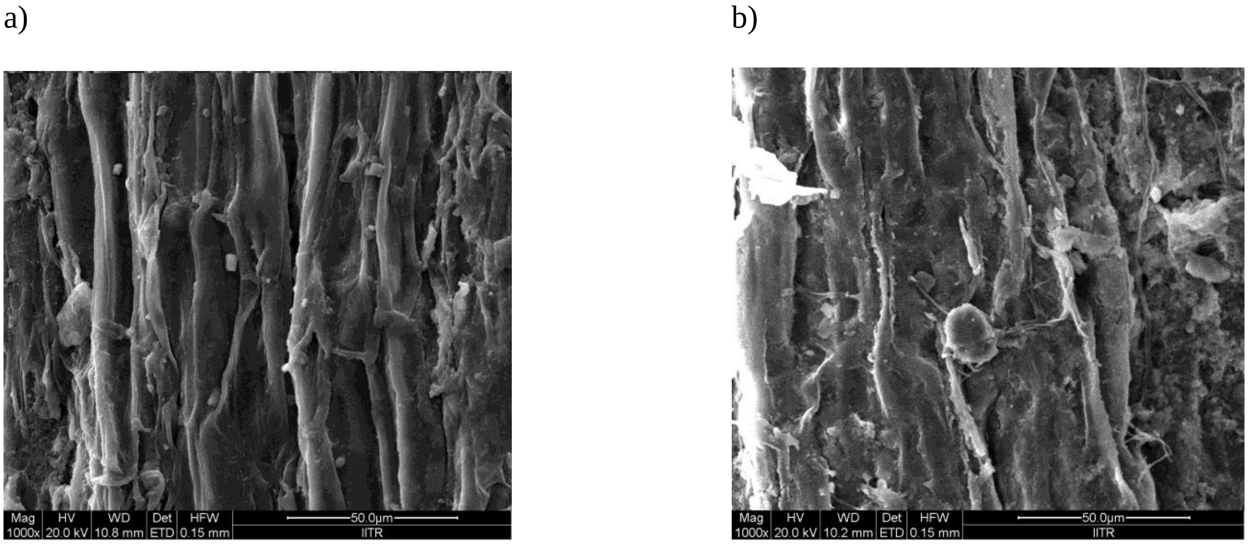


Fig 5.10 FE-SEM pictures of Roots a) Before exposure, b) After exposure

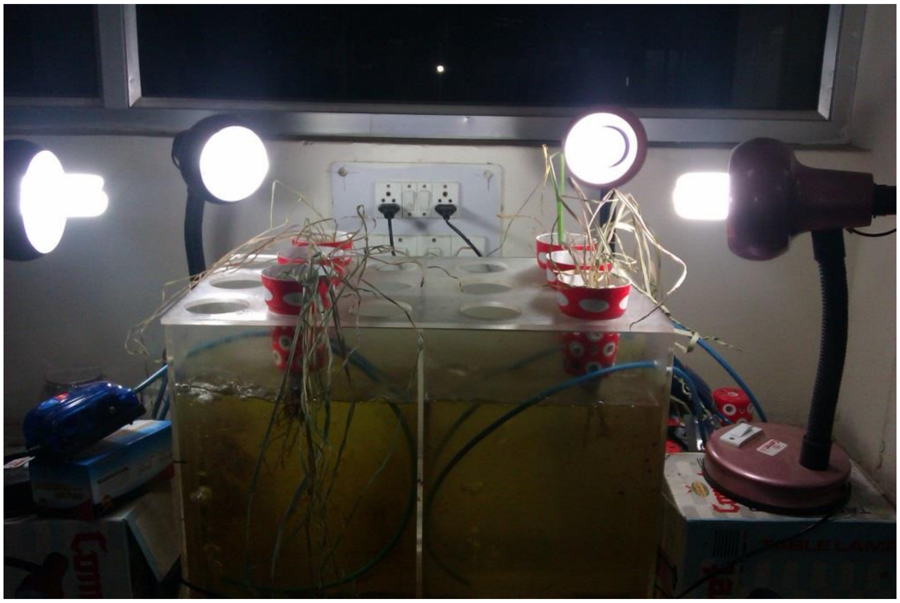


Fig 5.11 Effect of high metal concentration along with ultra pH conditions

5.2 Adsorptive removal by using Laterite soil

Initially in this study surface modification of laterite soil was carried out to prepare six types of adsorbents. These adsorbents were studied to find out if they performed better than the raw laterite for the uptake of Cr and Pb. The results of these preliminary experiments carried out under equilibrium condition are shown in Fig. 5.12 and 5.13.Almost all the surface modified laterites showed good results for Pb and a few such as AAL, NaOH treated and raw laterite showed good results for chromium.

A notable feature in these preliminary runs was that acidic conditions promoted the uptake of chromium. One of the reasons for this may be that the Cr^{6+} ion gets converted to the Cr^{3+} ion under acidic conditions which promotes its uptake. This fact has also been stated by Lukaman et al (2013). Another point of note is that the treatment with NaOH didn't drastically increase the metal uptake.

Theoretically speaking when the soil was treated with NaOH it was imparted a negative charge as a result it should have been able to adsorb the positively charged ions, but this was not the case the uptake shown by the NaOH treated laterite was similar to the acid treated and the raw laterite, a reason for this may be that treatment with NaOH stabilizes the soil and decreases the aluminum and silica content of the soil (Kampf and Schwertmann, 1982) and as result does not exhibit the kind of uptake that was expected.

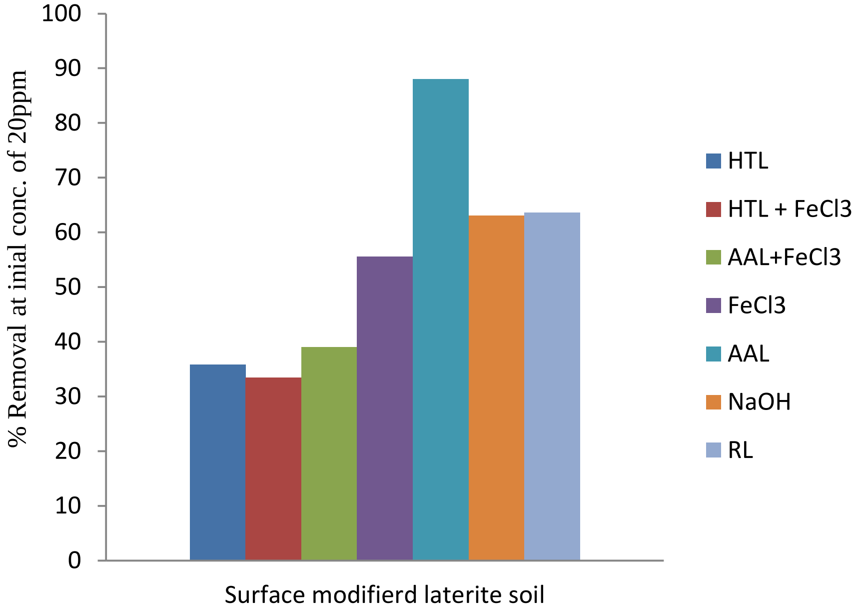


Fig 5.12 % Removal of Cr with respect to differenttreated adsorbents

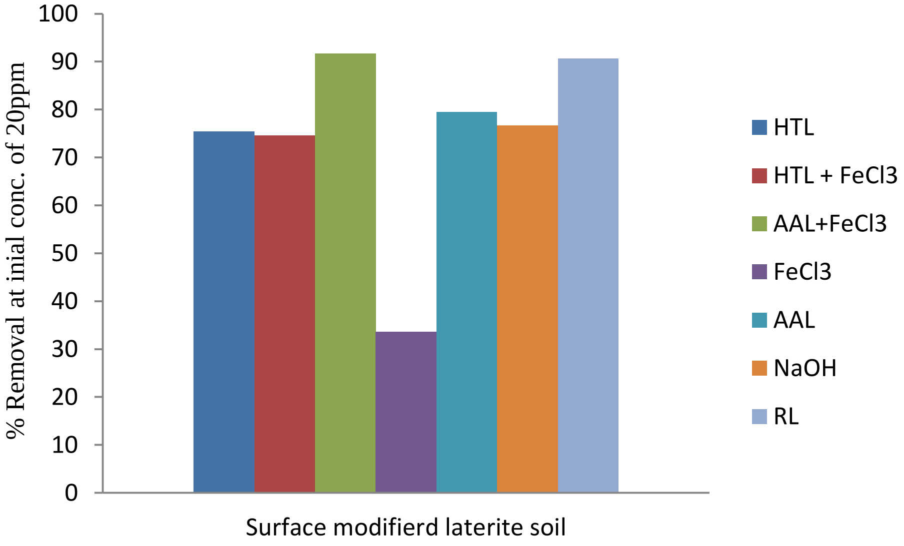


Fig 5.13 % Removal of Pb with respect to differenttreated adsorbents

Since the aim of the present study is the removal of both Pb and Cr simultaneously, since raw laterite showed good removal ability of both Pb and Cr hence it was selected as the adsorbent. Another factor that favored the selection of raw laterite over the treated laterite was the that treatment of soil with acid and base adds expenses to the overall process thus making it costly but if only raw laterite is used then there are no added expenses as it is cheap and readily available.

5.2.1 Soil Characterization

The characterization of the raw laterite has been done by subjecting it to X-ray diffraction studies, BET surface area studies, FTIR studies, FE-SEM and EDX Studies.

5.2.1.1 XRD Pattern of Laterite soil

The XRD patterns of RL are presented in Fig. 5.14, when compared with literature (Maiti et al., 2007; Nemade et al., 2009) the peaks of raw laterite show the presence of goethite, hematite, magnetite, quartz, iron oxide, silicon and aluminum oxide. The XRD pattern also suggests a crystalline structure of the laterite soil.

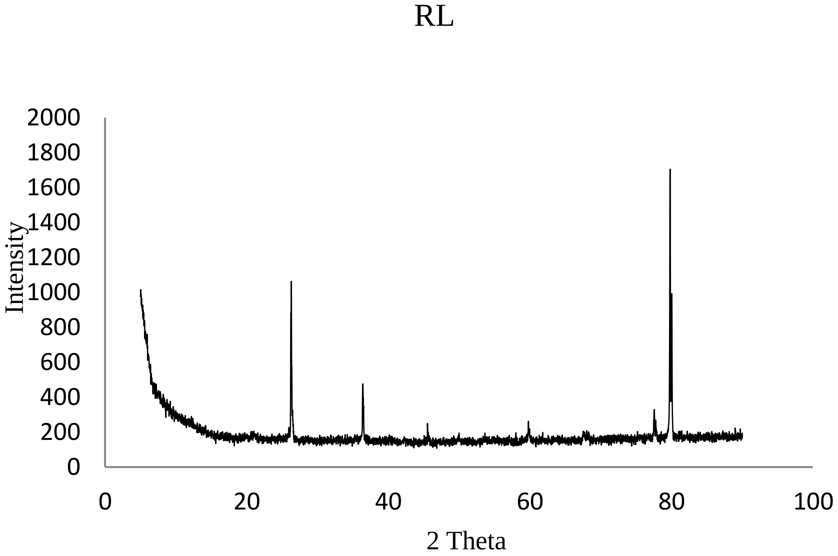


Fig 5.14 XRD Data for Raw Laterite

5.2.1.2 BET and EDX Characterization

The point of zero charge was estimated by using different quantities of laterite soil and shaking it with 10 ml of 0.1 M NaCl solution for 14 hr at an rpm of 150 and a temperature of 305 K, the pH of the resulting solutions was measured and the average pH was taken as the point of zero charge. For the bulk density measurement of the soil sample, a beaker of known volume was taken; soil was filled in the beaker and weighed. The soil sample was then dried in an oven for about one hour, after that the soil was weighed again. The difference between the weight of soil before drying and weight of soil after drying divided by the volume of the beaker gave the bulk density of the soil sample.

The S-S ratio has been calculated from the chemical composition obtained by the EDX analysis; this ratio signifies the extent of lateritization. The surface area, pore volume etc. were found by the BET analysis and the percentage of iron, silica and aluminum was found by the EDX analysis. The results of the adsorbent have been compiled in Table 5.1.

Table 5.1 Characteristics of RL

Properties	**Raw Laterite**
Particle size (spherical) (mm)	0.5-0.7
Surface area (m^2/g)	21.7252
Point of zero charge (pH_{pzc})	6.56
Pore volume (cm^3/g)	0.02399
Micropore Volume (cm^3/g)	0.000831
Average Pore diameter (nm)	4.4171
Bulk density (g/ml)	1.42
Inorganic composition (as metal oxide: wt %)	
Fe-oxide	34.17
SiO_2	19.89
Al-oxide	5.09
S-S Ratio	0.51

5.2.1.3 FTIR Characterization

The FTIR spectra patterns for the raw laterite are shown in Fig 5.15. The presence of iron, aluminum and silica oxides or hydroxides gets confirmed by studying these patterns. The bands at 3619.52 and 3424.36 signify the presence of OH group of Si, Al and Fe. The band at 1626.12 represents the presence of inner layer water molecules. The bands at 1037.37, 914.15 and 789.80 are due to the presence of Si-O-Fe, Al-OH, Fe-OH and Si-O vibrations. The bands at 530.98, 470.85 and 445.77 signify the presence of Hematite (Fe-O bond stretching). These bands have also been reported with slight variation by Maiti et al., 2012.

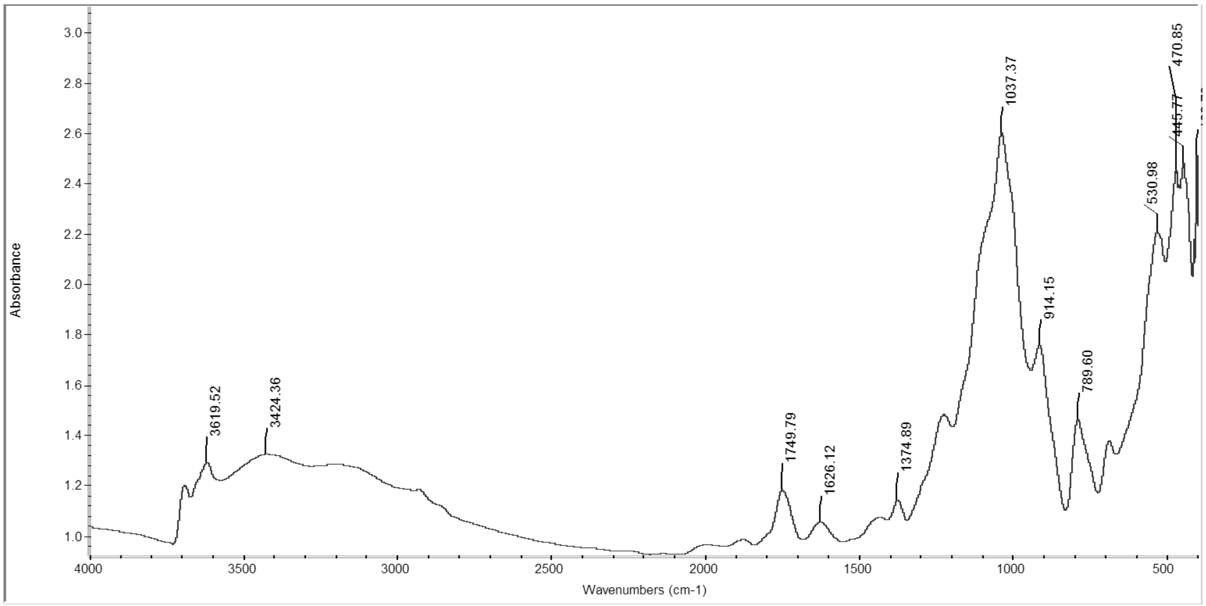
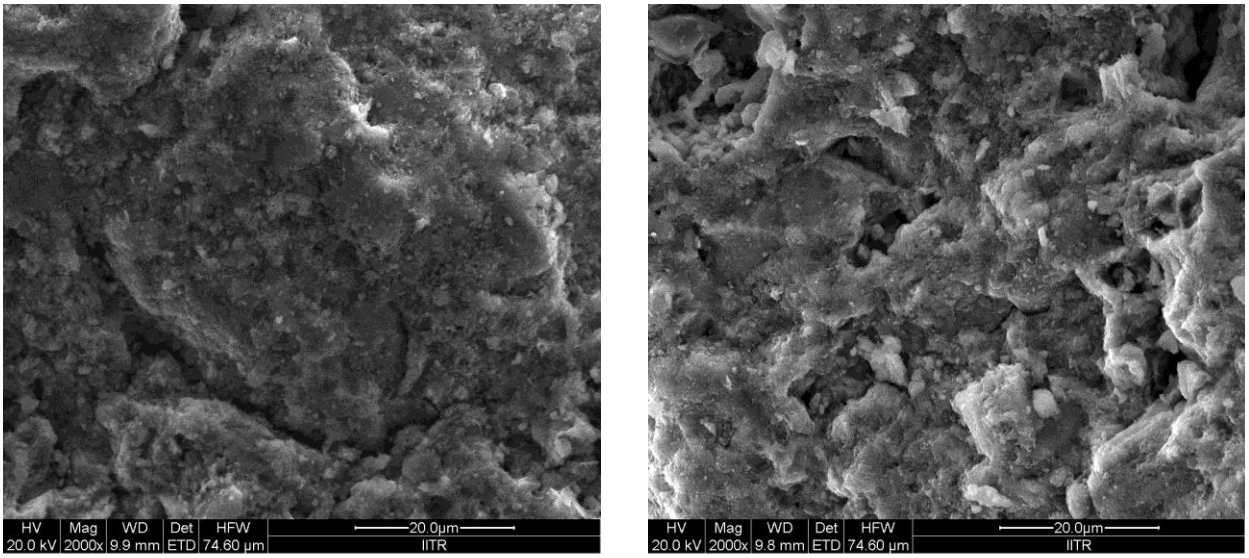


Fig 5.15 FTIR characterization of RL

5.2.1.4 FE-SEM of Laterite soil

The field emission scanning electron microscopy is generally used to characterize the differences observed on the surface of the adsorbents before and after the adsorption has taken place. The FE-SEM pictures have been shown in Fig 5.16. From these pictures a marked difference is observed between the before and after pictures. Both the pictures are depicted in a magnification of 2000x. In the after adsorption picture there is presence of small light colored particles on the surface of the adsorbent, this may indicate the presence of chromium and lead. Also the surface of the adsorbent appears to be distorted and deformed when compared to the picture before exposure to the metal particles; this distortion may be due to the dual presence of chromium and lead, since both the metals are highly toxic when used in high quantities as done in the present study.


a)Before Adsorption

b)After adsorption

Fig 5.16 FE-SEM characterization of laterite soil

5.2.2 Batch Adsorption Studies

The adsorption studies were carried out in an orbital shaker at an rpm of 150 and a temperature of 305K and the various parameters like contact time, adsorbent dose and pH have been optimized.

5.2.2.1 Effect of Time

During the time optimization studies it was found that the removal percentage of both Cr and Pb increased with the increase in time but after about four hours the increase observed was almost constant as a result the equilibrium time of adsorption was fixed at 4hr. When compared to the literature the contact time for optimum metal removal by laterite soil varies from 10 min to 24 hr. the contact time of four hours has also been reported by Maji et al, 2007 for removal of arsenic from water. The graph showing the optimization study of time has been depicted in Fig 5.17

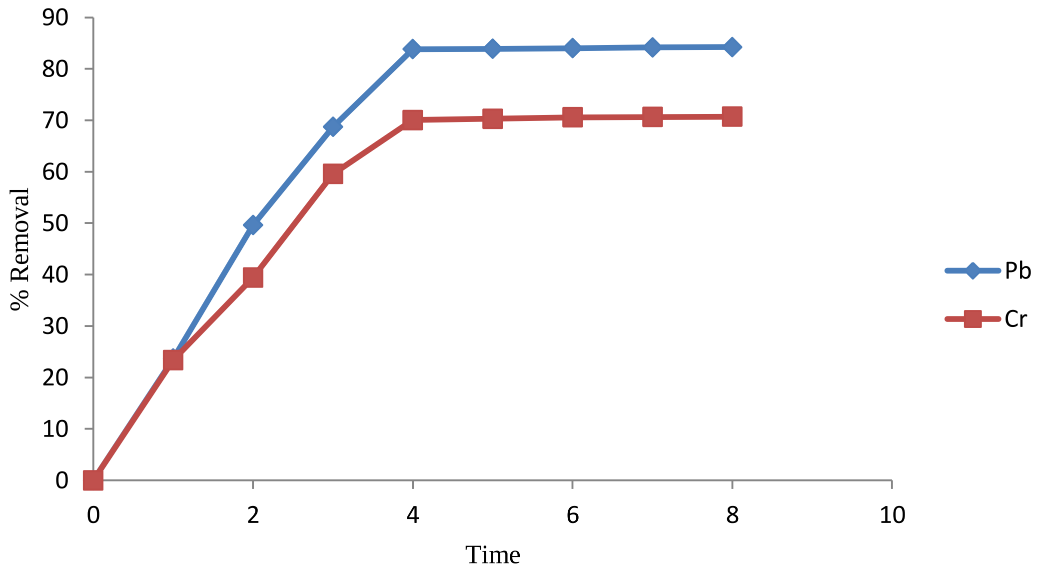


Fig 5.17 Time optimization study

5.2.2.2 Effect of adsorbent dose

In this study the contact time was kept constant at 4 hr and the adsorbent dose was varied from 5g/l to 40g/l. The adsorbent dose selected for the present study was 10 g/l as it showed good removal for both lead and chromium. Even though the Cr removal showed an increase of about 2 to 3% for the dose quantities of 30 and 40 g/l they were not selected because the subsequent lead removal was similar to the removal observed for the 10g/l dose. Since the aim of the present study is the simultaneous removal of Cr and Pb hence 10g/l adsorbent dose was chosen as it showed similar removals in less quantity of adsorbent. The dose optimization study is depicted in Fig. 5.18

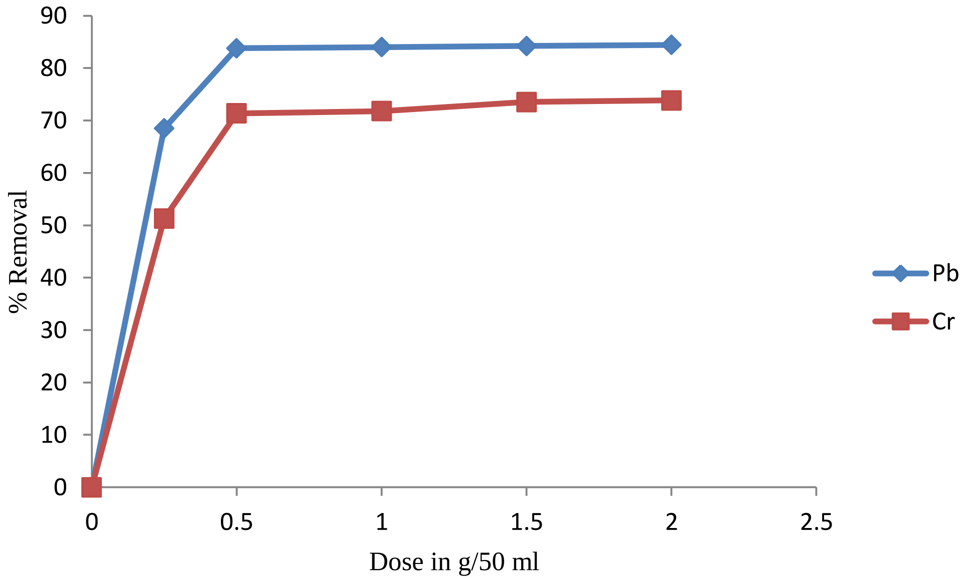


Fig 5.18 Dose optimization study

5.2.2.3 Effect of pH

In this study the dose and time were kept constant at 10g/l and 4 hr respectively and the pH was varied as 3, 6, 9 and 12. Both lead and chromium performed good in acidic and neutral conditions as compared to the basic conditions. The removal percentage for both the metal ions was least in the case of pH 12. This trend has been noted by various researchers such as Lukman et al., 2013; Reed et al., 1996. Cr performs well in acidic conditions due to it being able to convert to Cr^{3+} from Cr^{6+}.Since both Cr and Pb performed well at pH 6; it was the pH that was maintained for further studies. The effect of pH on the metal uptake has been depicted in Fig. 5.19

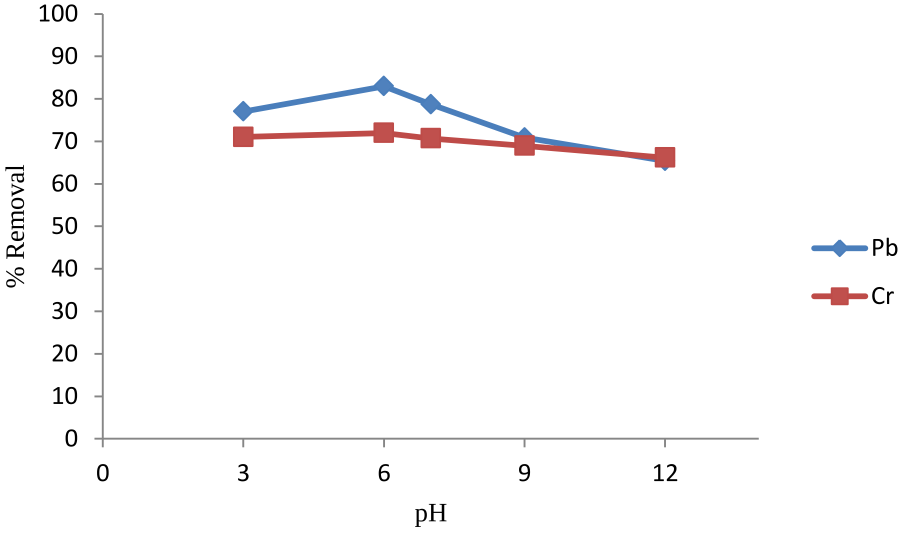


Fig 5.19 Effect of pH on metal uptake

5.2.2.4 Effect of initial concentration

In this study the contact time was kept at 4 hr, the dose at 10 g/l and the pH was maintained at 6. The trend observed when the initial concentration was taken in the range of 5, 10, 15 and 20 was that the percentage removal improved minutely with increase in the concentration of the metal solution. Generally most of the studied performed using laterite soil as an adsorbent has involved the removal of arsenic from water. There have been very few studies on the removal of other ions. There has been absolutely no study on the removal of lead and chromium. There is a study on the removal of Zn by laterite by Aminah and Izzat, 2011 in which the authors have reported a minute increase in the removal percentage with increase in concentration. The graph depicting the removal percentage for different concentrations has been depicted in Fig 5.20.

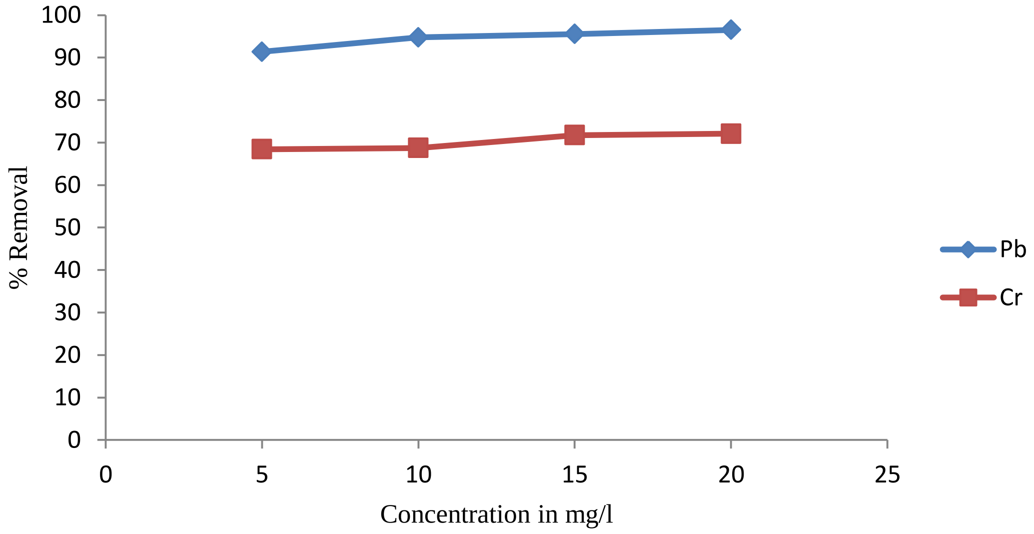


Fig 5.20 Effect of different in initial concentrations

5.2.2.5 Kinetics of the adsorptive study using laterite soil

The knowledge of the kinetics of any adsorption process is crucial to design an industrial scale separation process. The experimental data have been analysed by two kinetic models, namely, pseudo-first orderand second order. The linear forms of these models are presented as:

Pseudo First order

$$\log(q_e - q_t) = \log(q_e) - \frac{K_1 t}{2.303}$$

Pseudo Second Order

$$\frac{t}{q_t} = \frac{1}{K_{s2} q_e^2} + \frac{t}{q_e}$$

In the present study the pseudo second order model fit better to the experimental data as a result only the second order model has been shown in the present study. The pseudo-second-order kinetic model fit at a fixed initial concentration of 5 mg/l with the respect to time for both Cr and Pb, is depicted in the Fig. 5.21 and 5.22. The values of model-predicted or theoretical q_e fitted well with the experimental equilibrium adsorption capacity.

For example, predicted values of q_e by the pseudo-second-order model for Cr were 0.1169, 0.1971, 0.2978 and 0.3502 mg/g compared to experimental data as 0.1182, 0.2114, 0.2868, 0.3491 and 0.4404 respectively, and for Pb the predicted values were 0.1360, 0.2394, 0.3207, 0.3863 and 0.4194 mg/g and the corresponding calculated values were 0.1183, 0.248, 0.3435 and 0.4192 mg/g respectively at a temperature of 305 K. the various parameters for the pseudo-second order kinetics is depicted in Table 5.2.

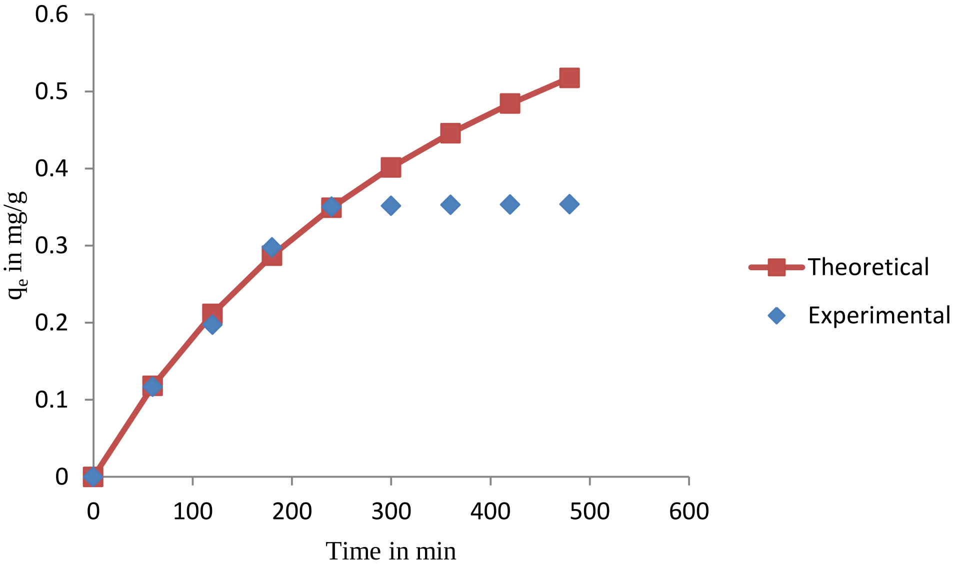


Fig 5.21 Pseudo-second order model for Cr

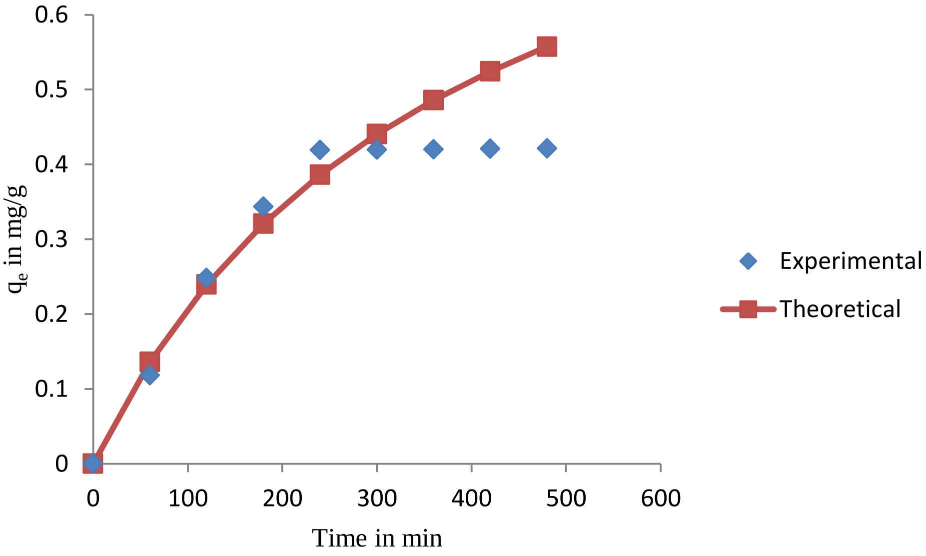


Fig 5.22 Pseudo-second order model for Pb

Table 5.2 Parameters for the Pseudo-second order model

For t=8h, C_o=5mg/l, m=10g/l, T= 305K		
Parameters	**Chromium**	**Lead**
K_s (g/mg min)	0.038	0.052
q_e (mg/g)	0.059	0.050
R^2 (Non-linear)	0.9240	0.9577
SSE	0.028	0.036
RMSE	0.021	0.023

5.2.2.6 Equilibrium study

To get a better understanding of the design parameters of an adsorption system, it is essential to discover the most suitable correlation for the adsorption equilibrium data. Equilibrium studies were performed to estimate the conditions for maximum lead and chromium uptake by the latertite soil. The isotherm data was found out by using the Cr and Pb concentrations as 5, 10, 15 and 20 mg/l with a fixed adsorbent dose of 10g/l at three different temperatures of 298, 305 and 315 K.

The equilibrium data at the three temperatures is depicted in Fig. 5.23 and 5.24. This data can be fitted by using the different isotherm models such as Langmuir isotherm and Freundlich isotherm. In the present study both the Langmuir and the Freundlich isotherms were examined, but since the Freundlich isotherm gave a better goodness of fit hence it has been presented in this study, the various parameters for Pb and Cr are presented in Table 5.3. The assumption supposed by the Freundlich isotherm is that it assumes a surface to be heterogeneous with an inconsistent distribution of heat of adsorption over the surface. The non-linear Freundlich isotherm equation can be written as:

$$q_e = K_F C_e^{\frac{1}{n}}$$

The adsorption loading can be calculated as:

$$q = \frac{C_o - C_e}{m}$$

Where q_e= amount of adsorbate in mg/g
n= adsorption intensity
K= adsorption Capacity
C_o=initial concentration in mg/l
C_e= concentration after time t in mg/l

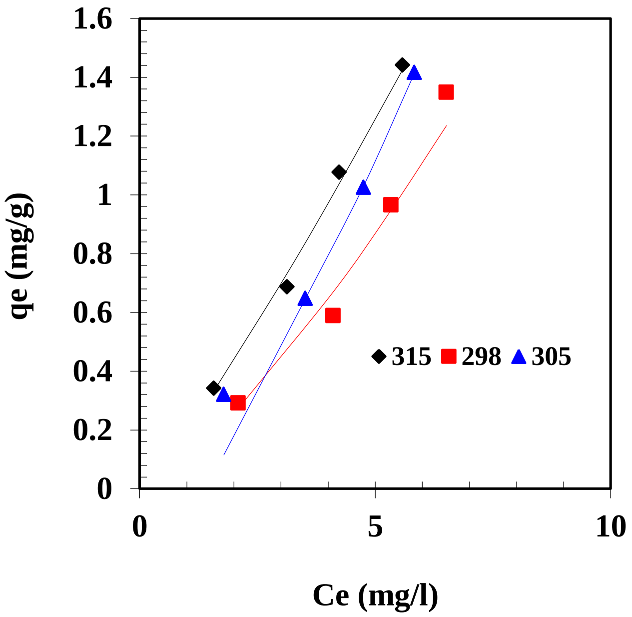


Fig 5.23 Freundlich isotherm for Cr

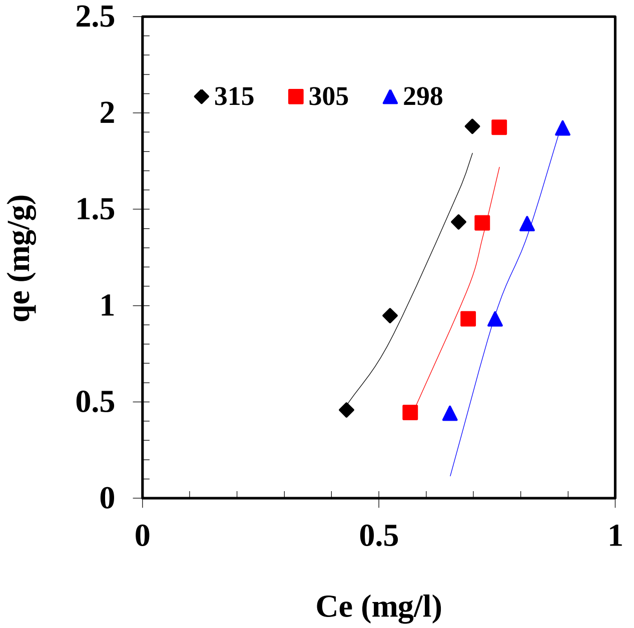


Fig 5.24 Freundlich Isotherm for Pb

Table 5.3 adsorption isotherm constants for adsorption of Cr and Pb on RL

Temperature (K)	**Constants for Cr**			**Constants for Pb**		
	K_F (mg/l)	n	R_F^2	K_F (mg/l)	n	R_F^2
298	0.1024	1.3289	0.9897	4.1294	3.186	0.9906
305	0.0923	1.547	0.9922	6.901	4.946	0.9800
315	0.1971	1.1505	0.9976	4.785	2.733	0.9874

5.2.2.7 Adsorbent Regeneration Study

In this study the used adsorbent was treated with 50 ml of 1M NaOH solution and was shaken for 4 hr at 150 rpm and 305 K temperature. The adsorbent was regenerated three times and three experimental run were performed to test its metal uptake ability. The regenerated adsorbent showed good results in the first run the percentage removal was almost similar to when the fresh adsorbent was used. But in the subsequent run the percentage removal decreased drastically for chromium but it still showed good removal for lead. The percentage removal of metals by the reused adsorbent is shown in Fig 5.25.

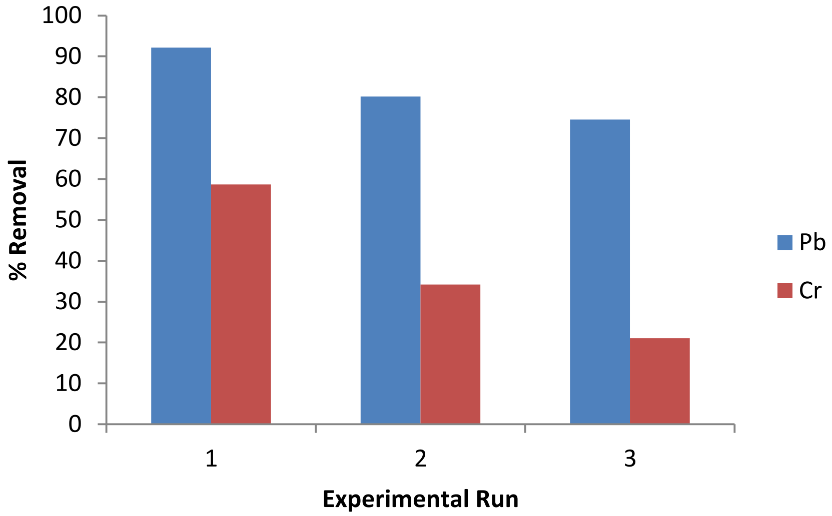


Fig 5.25 Adsorption capacity of the regenerated laterite soil

Even though laterite soil shows good regeneration potential, it is not advisable to reuse laterite soil as it adds to the cost of the process thus taking away its novelty of being a low cost process. It is better to use fresh laterite soil for the adsorption.

CHAPTER 6

CONCLUSION AND RECOMMENDATIONS

6.1 Conclusion

Based on the experimental study conducted the various conclusions that can be drawn are:

- Both techniques were able to bring down high levels of metal concentration to near and in some cases below the prescribed limit of heavy metals in surface waters.
- The grass species Vetiver Zizanioides proved to be a good choice for Pb and Cr removal using the mechanism of rhizofiltration.
- Vetiver grass was able to remove about 77 to 78% of Cr and about 80 to 98% Pb from the synthetic wastewater samples at constant pH of 7.3.
- The plant showed better uptake ability at the pH range of 6 to 9 when compared to the high basic and acidic conditions (pH 3 and 12).
- It showed good resistance to extreme pH conditions during its acclimatization period, it was only when high concentration of metals (20ppm) were added along with the extreme conditions that it started to disintegrate but even then it was able to remove about 50 to 53% of lead and 80 to 84 % of chromium.
- Chromium followed a fast uptake mechanism and most the removal happened within the first 24 hr whereas lead followed a slower mechanism and most of the lead removal happened gradually spanning the entire study period of 15 days.
- Most of the absorbed chromium was stored in the stem (363.05g/kg) and leaves (332.3g/kg) of the plant whereas most of lead was stored in the roots (610.157g/kg) and stem (283.9 g/kg) of the plant.
- Natural laterite showed good results when compared to the surface modified soil, thus establishing the fact that no modification was needed for it to uptake Pb and Cr.
- Laterite soil showed best removal at an adsorbent dose of 10 g/l, contact time of 4 hr, temperature of 305K, rpm of 150 and at a pH of 6 for both lead and chromium.
- Laterite soil was able to remove about 96% of Pb and about 72% of Cr
- The data generated by the experiment fit well to the Freundlich isotherm and followed the pseudo-second order model.

6.2 Recommendations

Vetiver Zizanioides and Laterite soil performed very well in the removal of Cr and Pb from synthetic water, the recommendations based on the present study are:

- The present study for both plant sapling and laterite soil has been done in batch mode, this study can be carried out further in continuous mode, in order to better simulate industrial conditions.

- Both the plant and laterite soil can be used in an experimental setup to simulate a constructed wetland system and experiments can be performed both in batch as well as continuous modes.

- Since both Vetiver grass and Laterite soil performed well for the binary component removal, studies including simultaneous removal of more than two components can be conducted.

- Since the Vetiver grass translocated the metals to the shoots the recovery potential of these metals by using the technique of Phytomining can be investigated.

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