BIOSORPTION DYNAMICS OF HEAVY METALS (Pb^{2+}, Cu^{2+} AND Zn^{2+}) BY PONGAMIA OIL CAKE FROM BINARY AND TERNARY SYSTEMS

A PROJECT REPORT

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BONAFIDE CERTIFICATE

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ABSTRACT

The competitive adsorption properties of the heavy metal ions Pb^{2+}, Cu^{2+}, Zn^{2+} in binary and ternary systems on Pongamia Oil Cake (POC) were studied under batch systems. Specific Surface area of Defatted POC of size <150 µm was determined using BET Analysis. The surface area was found to be $0.93 m^2/gm$. Langmuir competitive model was used to evaluate the nature of competition among the metal ions in binary and ternary systems. The effects of the presence of one metal ion on the biosorption of the other metal ion were investigated in terms of equilibrium isotherm. Experimental results indicated that the uptake capacity of one metal ion was reduced by the presence of other metal ions. Among these metal ions, Pb^{2+} shows greater affinity for adsorption on to the adsorbent with the removal efficiency of 99.3% than that of Cu^{2+}(98.6%) and Zn^{2+}(97%). Thus the equilibrium studies shows that the selectivity of metal ions on POC followed the order of $Pb^{2+} > Cu^{2+} > Zn^{2+}$.

Keywords: Biosorption, heavy metal, Langmuir competitive model, Pongamia Oil Cake, Electroplating effluent

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVATIONS

µm	micrometer
AAS	Atomic Absorption Spectroscopy
As	Arsenic
BET	Brunauer, Emmett, Teller
Cd	Cadmium
C_e	Concentration at equilibrium
Cr	Chromium
Cu	Copper
$CuSO_4{\cdot}5H_2O$	Copper Sulphate pentahydrate
DDTC	Diethyldithiocarbamate
FT-IR	Fourier Transform Infrared Analysis
gm	gram
HCl	Hydrochloric acid
Hg	Mercury
K_L	Langmuir constant
L	Litre
m	meter
mg	milligram
N	Normality
NaOH	Sodium Hydroxide
Ni	Nickel
Pb	Lead
$Pb(NO_3)_2$	Lead Nitarte
POC	Pongamia Oil Cake
ppm	Parts Per Million
q_e	Amount of metal adsorbed at equilibrium

LIST OF ABBREVATIONS

q_m	Maximum adsorption capacity
R^2	Regression coefficient
SEM-EDS	Scanning Electron Microscope - Energy Dispersive X-Ray Spectrometer
STIC	Sophisticated Test and Instrumentation Centre
Zn	Zinc
$ZnSO_4.7H_2O$	Zinc Sulphate heptahydrate

CHAPTER 1
INTRODUCTION

1.1 POLLUTION

Freshwater ecosystems are aquatic systems which contain drinkable water or water of almost no salt content. They provide the majority of our nation's drinking water resources, water resources for agriculture, industry, sanitation, as well as food including fish and shellfish. They also provide recreational opportunities and a means of transportation. In addition, freshwater ecosystems are home to numerous organisms. Human activities are causing species to disappear at an alarming rate due to pollution. Aquatic species are at a higher risk of extinction than mammals and birds. Pollution has been very damaging to aquatic ecosystems, and may consist of agricultural, urban, and industrial wastes containing contaminants such as sewage, fertilizer, and heavy metals that have proven to be very damaging to aquatic habitats and species. Metals are notable for their wide environmental dispersion from such activity, their tendency to accumulate in select tissues of the human body and their overall potential to be toxic even at relatively minor levels of exposure. Today heavy metals are abundant in our drinking water, air and soil due to our increased use of these compounds. They are present in virtually every area of modern consumerism from construction materials to cosmetics, medicines to processed foods, fuel sources to agents of destruction, appliances to personal care products. It is very difficult for anyone to avoid exposure to any of the many harmful heavy metals that are so prevalent in our environment

Table 1.1 Release of Heavy metals from different industries (Environmental Protection Agency, 1986)

EXAMPLES OF HAZARDOUS WASTE GENERATED BY INDUSTRIES	
WASTE GENERATOR	**WASTE TYPES**
Chemical Manufacturers	Acids and Bases, Spent Solvents, Reactive Waste Wastewater Containing heavy metals
Electroplating Inustries	Sludges containing Heavy Metals, Cyanide Waste
Paper industry	Waste Containing Heavy Metals, Ignitable Solvents
Leather and Tanning Industries	Toluene and Benzene, waste water containing heavy metals
Printing industries	Heavy Metals solutions, ink sludges, solvents

1.2 ELECTROPLATING

Electroplating industries contribute one of the chief sources for release of heavy metals in environment. Electroplating industry is India is spread throughout the country. They are mainly in small scale sectors with over 300,000 small scale units. Electroplating is the application of' a metal coating to a metallic or other conducting surface by an electro chemical process. The article to be plated is made the cathode of an electrolysis cell through which a direct electric current is passed. The article is immersed in an aqueous solution containing the required metal in an oxidised form, either as an aquated cation or as a complex ion. The anode is usually a bar of the metal being plated. During electrolysis metal is deposited onto the surface of an article and metal from the bar dissolves into the bath. Articles are generally electroplated to (i) alter their appearance,(ii) to provide a protective coating, (iii) to give the article special surface properties, (iv) to give the article engineering or mechanical properties. Metals used for plating are costly metals having superior qualities like nickel, cadmium, platinum, gold, silver, chromium. The pollutants from the electroplating industries are invariably hazardous, as the effluents contaminate air, water and soil. Some of the polluting agents have deleterious effect on human health, examples being copper, zinc, lead, nickel, etc.

1.2.1 ZINC PLATING

Zinc plating is the most common and economical type of plating. Zinc plating is a soft, protective by nature, decorative, ductile, and marginally solderable and also serves as an effective undercoat for paints. It is sacrificial coating, so that part does not corrode. Zinc plating is available in clear, yellow, black and olive green. Trivalent chromate passivations are available if requested

1.2.2 COPPER PLATING

Copper is a soft metal with excellent electrical and thermal conductivity and provides good solderability. Copper is plated for use in industrial and decorative applications. It is also used to mask off areas of steel components in the case hardening process. Best under coat for better adhesion and brightness on case hardened steel, nitrided components, alloy steels, cast iron.

1.2.3 LEAD PLATING

In lead plating by immersion, either tin or antimony is added to the molten lead, the principal materials subjected to lead plating forms chemical compounds with lead or solid solutions of appreciable concentration. Lead plating by metallization is primarily used to coat large prefabricated structural members. Electroplating with lead is carried out in fluosilicate, fluoborate, perchlorate, and sulfamate electrolytes.

1.3 TOXICOLOGICAL ASPECTS OF HEAVY METALS

The term heavy metal refers to any metallic chemical element that has a relatively high density and is toxic or poisonous at low concentrations. Due to their mobility in aquatic ecosystems and their toxicity to higher life forms, heavy metals in surface and groundwater supplies have been prioritised as major inorganic contaminants in the environment. Even if they are present in dilute, undetectable quantities, they can exhibit toxic characteristics.

1.3.1 ZINC

Due to the effects upon plants zinc is a serious threat to the productions of farmlands. Despite of this zinc-containing manures are still applied. Zinc can interrupt the activity in soils, as it negatively influences the activity of microrganisms and earthworms. The breakdown of organic matter may seriously slow down because of this.

1.3.2 COPPER

Copper is an essential substance to human life, but in high doses it can cause anemia, liver and kidney damage, and stomach and intestinal irritation. People with Wilson's disease are at greater risk for health effects from overexposure to copper.

1.3.3 LEAD

In humans exposure to lead can result in a wide range of biological effects depending on the level and duration of exposure. High levels of exposure may result in toxic biochemical effects in humans which in turn cause problems in the synthesis of haemoglobin, effects on the kidneys, gastrointestinal tract, joints and reproductive system, and acute or chronic damage to the nervous system.

1.4 NEED FOR THE REMOVAL OF HEAVY METALS

Continuous discharge of industrial, domestic and agricultural wastes in rivers and lakes causes deposit of pollutants in sediments. Such pollutants include heavy metals, which endanger public health after being incorporated in food chain. Excessive amounts of some heavy metals can be toxic through direct action of the metal or through their inorganic salts or via organic compounds from which the metal can become easily detached or introduced into the cell. Exposure to different metals may occur in common circumstances, particularly in industrial setting. Accidents in some environments can result in acute, high level exposure. Some of the heavy metals are toxic to aquatic organisms even at low concentration. Hence there is a need to remove the heavy metals from the aquatic ecosystems.

1.5 CONVENTIONAL METHODS FOR THE TREATMENT OF METALS

Over the last few decades, several methods have been devised for the treatment and removal of heavy metals. Numerous industries discharge a variety of toxic metals into the environment. The commonly used methods for removing metal ions are chemical precipitation, ion exchange, reverse osmosis and solvent extraction

1.5.1 CHEMICAL PRECIPITATION:

Precipitation of metals is achieved by the addition of coagulants such as alum, lime, iron salts and other organic polymers. The large amount of sludge containing toxic compounds produced during the process is the main disadvantage.

1.5.2 SOLVENT EXTRACTION

Liquid-liquid extraction (also known as solvent extraction) of metals from solutions on a large scale has experienced a phenomenal growth in recent years has gained widespread usage for waste reprocessing and effluent treatment. Solvent extraction involves an organic and an aqueous phase. The aqueous solution containing the metal or metals of interest is mixed with the appropriate organic solvent and the metal passes into the organic phase. In order to recover the extracted metal, the organic solvent is contacted with an aqueous solution whose composition is such that the metal is stripped from the organic phase and is re-extracted into the stripping solution.

1.5.3 MEMBRANE PROCESS

The membrane process applicable to wastewater treatment includes reverse osmosis and electrodialysis. These processes involve ionic concentration by the use of selective membrane with a specific driving force. For reverse osmosis, pressure difference is employed to initiate the transport of solvent across a semipermeable membrane and electro dialysis relies on ion migration through selective permeable membranes in response to a current applied to electrodes. The application of the membrane process described is limited due to pretreatment requirements. The methods are expensive and sophisticated, requiring a higher level of technical expertise to operate.

1.5.4 ION EXCHANGE

In this process, metal ions from dilute solutions are exchanged with ions held by electrostatic forces on the exchange resin. The disadvantages include limitation on the concentration in the effluent to be treated, high cost and partial removal of certain ions.

1.5.5 ADSORPTION

Adsorption is the most common form of sorption used in ‘traditional’ clean-up technologies but unless it is clear which process (absorption or adsorption) is operative, sorption is the preferred term, and can be used to describe any system where a sorbate (e.g. an atom, molecule, a molecular ion) interacts with a sorbent (i.e. a solid surface) resulting in an accumulation at the sorbate – sorbent interface (Borda and Sparks, 2008).

1.6 DISADVANTAGES OF CONVENTIONAL METHODS FOR TREATMENT OF WASTEWATER CONTAINING HEAVY METALS

Metals are a class of pollutants, often toxic and dangerous, widely present in industrial and household wastewaters. Electroplating and metal finishing operations, electronic circuit production, steel and aluminium processes to name but a few industries, produce large quantities of wastewater containing metals. Although metal precipitation using a cheap alkali such as lime has been the most favoured option, other separation technologies are now beginning to find favour. Consequently precipitation produces large quantities of solid sludge for disposal. The metal hydroxide sludge resulting from treatment of electroplating wastewater has been classified as a hazardous waste. The versatility, simplicity and other technology characteristics will contribute to the overall process costs, both capital and operational. At present many of these technologies such as ion exchange represent significant capital investments by industry.

1.7 BIOSORPTION

The search for new technologies involving the removal of toxic metals from wastewaters has directed attention to biosorption, based on binding capacities of various biological materials. Till dates, research in the area of biosorption suggests it to be an ideal alternative for decontamination of metal containing effluents. Biosorbent are attractive since naturally occurring biomass/adsorbents or spent biomass can be effectively used.

Biosorption can be defined as the ability of biological materials to accumulate heavy metals from wastewater through metabolically mediated or physico-chemical pathways of uptake (Fourest and Roux, 1992).

Biosorbents intended for bioremediation environmental applications are waste biomass of crops, algae, fungi, bacteria, etc., which are the naturally abundant. Biosorption by microorganisms have various disadvantages, and hence many low cost adsorbents (industrial/agricultural waste products/byproducts) are increasingly used as biosorbents.

1.7.1 BIOSORPTION OF HEAVY METALS

A large number of microorganisms belonging to various groups, viz. bacteria, fungi, yeasts, cyanobacteria and algae have been reported to bind a variety of heavy metals to different extents (Gadd, 2004). The role of various microorganisms by biosorption in the removal and recovery of heavy metal(s) has been well reviewed and documented. Most of the biosorption studies reported in literatures have been carried out with living microorganisms. However due to certain inherent disadvantages, use of living microorganisms for metal removal and recovery is not generally feasible in all situations. For example, industrial effluents contain high concentrations of toxic metals under widely varying pH conditions. These conditions are not always conducive to the growth and maintenance of an active microbial population. There are several advantages of biosorption of using non living biomass and they are as follows:

- Growth independent nonliving biomass is not subject to toxicity limitation by cells.
- The biomass from an existing fermentation industry, which essentially is a waste after fermentation, can be a cheap source of biomass.
- The process is not governed by physiological constraints of microbial cells.
- Because nonliving biomass behaves as an ion exchanger, the process is very rapid, requiring anywhere between few minutes to few hours. Metal loading is very high on the surface of the biomass leading to very efficient metal uptake.
- Metals can be desorbed readily and then recovered. If the value and the amount of metal recovered are insignificant and if the biomass is plentiful, the metal loaded biomass can be incinerated, eliminating further treatment.

1.7.2 BIOSORPTION IN BINARY AND TERNAY SYSTEMS

The degree of removal of metal ions from wastewaters by biosorption depends on several parameters, in particular, on the competitive interactions of co-ions when present in the solution. The interactions can either be “ two- way:, that is, the interacting elements can mutually affect each other’s concentration, by increasing or decreasing the level of either of the elements involved, or of “one- way”, by decreasing or increasing the level of only one of the interacting elements, the effect being non mutual.. Despite this, the majority of biosorption studies have focused on single metal solutions. However, in the last five years biosorption investigations have increasingly evaluated metal uptake from multi component metal solutions.

1.8 OIL CAKE

The solid residue that is left after certain oily seeds, such as cottonseed and linseed, has been pressed free of their oil. It is ground and used as cattle feed or fertilizer. In particular, the oil cake, which is used as an adsorbent, is generated during the squeezing of the certain agro products like olive, neem, soy, linseed, cottonseed, sunflower seeds etc., to get the oil and it may constitute a promising low-cost adsorbent among biomaterials, since this substance is produced in great quantities. Recently some of these oil cakes have been tested as biosorbents for heavy metals in order to maximize metal removal efficiency and minimize preparation costs (Rao and Khan, 2009).

1.9 PONGAMIA PINNATA

Pongamia pinnata, popularly known as karanj belongs to the natural order *Leguminosae* and family *Papilionaceae*, is a medium sized glabrous avenue tree with a spreading crowns upto 18 m. found almost throughout India and distributed further Eastwards, chiefly in the littoral regions of South-Eastern Asia and Northern Australia. In India the availability of the seed has been estimated to be 1,300,000 ton per year. The seeds contain 27-39% of fatty oil which is used for leather dressing, soap making, lubrication, and illumination. The non-fatty components of the oil include the principal furanoflavonoid, karanjin and a novel furano-diketone, pongamol. Pongamia cake, containing about 28-34% crude protein, is not commonly used as a feed for livestock and poultry due to the harmful effects of antinutritional/toxic factors present in the seed cake.

1.10 OBJECTIVES

The objectives of the present work are:

- To investigate the biosorption of divalent metal ions Pb^{2+}, Cu^{2+} and Zn^{2+} from single, binary and multi-component aqueous solutions using pongamia oil cake.
- To characterize the adsorbent using FT-IR, BET and SEM-EDS analysis.
- To present experimental equilibrium data for the ternary system containing Pb^{2+},Cu^{2+} and Zn^{2+}.
- To develop the suitable models represent dynamic behavior of biosorption equilibrium data of the three-metal systems.

CHAPTER 2

REVIEW OF LITERATURE

2.1 INTRODUCTION

Heavy metals are natural constituents of the earths crust. Human activities have drastically altered the biochemical, geochemical cycles and balance of some of the heavy metals. Heavy metals are stable and tend to persist and accumulate in the environment. They cannot be degraded or destroyed. Aquatic systems are particularly sensitive to pollution possibly due to the structure of their food chains. In many cases harmful substances enter the food chain and are concentrated in fish and other edible organisms (Fortsner, 1983).

As the heavy metals move from one ecological tropic level to another, metallic species start damaging the ecosystem. They also become difficult to track as they move up trophic levels. They accumulate in living tissues throughout the food chain. Due to biomagnifications, humans receive the maximum impact, since they are at the top of the food chain (Volesky, 2001).

Many metallic elements play an essential role in the functioning of living organisms. However, overabundance of the essential trace elements can cause toxicity symptoms or death (Volesky, 1990). There are many sources through which metal pollution of the environment occurs which include geological weathering, industrial processing of ores and metals, leaching of metals from garbage and solid waste dumps (Fortsner, 1983).

There is tremendous need to control heavy metal emissions into to the environment. The use of biological materials, including living and non-living micro-organisms, in the removal and possibly recovery of toxic substances from industrial wastes, has gained important credibility during recent years, because of the good performance and low cost of these materials. The natural affinity of biological compounds for metallic elements could contribute to the purification of metal loaded wastewater (Sahin *et al*., 2005).

2.2 TOXIC METALS IN EFFLUENT

At present, heavy metal wastes from the electroplating industries are the threat to the environment. In the wake of industrialization, consequent urbanization and ever increasing population, the basic amenities of life viz. air, water and land are being polluted. Industrial complexes have become the focus of environmental pollution (Shukla *et al*., 2007a).

The main pollutant from the electroplating industries complexes is the effluent which contains heavy metals such as Cu^{2+}, Zn^{2+}, Pb^{2+}, Cr^{6+}, Ni^{2+}, Hg^{2+}, Cd^{2+} etc. and various organic compounds such as phenols, formaldehyde etc. (Rajendran *et al*., 2003). Many industries discharge heavy metals such as Cu^{2+}, Zn^{2+}, Pb^{2+}, Cd^{2+} and Ni^{2+} in their wastewaters (Krishnani *et al*., 2008).

Table.2.1 The tolerance limit for heavy metals in the electroplating effluent (Central Pollution Control Board)

S.No	Electroplating Industries	Concentration (mg / L)
1	Lead (as Pb)	0.1
2	Copper (as Cu)	3.0
3	Zinc (as Zn)	5.0
4	Cadmium (as Cd)	2.0
5	Nickei (as Ni)	3.0
6	Iron (as Fe)	3.0
7	Hexavalent Chromium (as Cr)	0.1

2.3 NEED FOR THE REMOVAL OF HEAVY METALS

Heavy metals cannot be destroyed through biological degradation, as is the case with most organic pollutants. Incidence of heavy metal accumulation in fish, oysters, mussels, sediments and other components of aquatic ecosystems have been reported from all over the world (Naimo, 1995, Sayler *et al*., 1975).

The amount of heavy metals (As^{3+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, Cr^{6+}, Ni^{2+}, Hg^{2+} and Cd^{2+}) produced from metal industry, agricultural activity, and waste disposal has increased dramatically. Ni^{2+} is a non-biodegradable toxic heavy metal ion present in wastewater. The main source of Ni^{2+} pollution in the water derives from industrial production processes such as galvanization, smelting, mining, batteries manufacturing and metal finishing. Ni^{2+} can cause serious health and ecological problems when released into the environment (Nordberg *et al*., 2005, Muhammad *et al*., 2007).

Heavy metal pollution in the aquatic system has become a serious threat today and of great environmental concern as they are non-biodegradable and thus persistent. Metals are mobilized and carried into food web as a result of leaching from waste dumps, polluted soils and water (Paknikar *et al*., 2003).

The heavy metals even at relatively low concentrations are toxic to biological processes and thus prevent the effective degradation of organic wastes. Adenosine triphosphate, carbonic anhydrase, cytochrome oxidase are some of the key enzymes which help in the synthesis of heme, are inhibited by Pb^{2+}. The enzymes that generate cellular energy in the citric acid cycle are adversely affected by As^{3+}. The activity of the pyruvate dehydrogenase is inhibited since it forms a complex with As^{3+}, which prevents the generation of ATP molecules (De, 1992).

Metals such as Cu^{2+} and Zn^{2+} are known to be essential to plants, humans, and animals, but they can also have adverse effects if their availability in water exceeds certain threshold values. Among the important heavy metals, Pb^{2+} is reportedly the least mobile. Cu^{2+} has been shown to remain bound up as insoluble complexes, whereas Zn^{2+} and Cd^{2+} are considerably more mobile (Xue *et al*., 2009).

Although, some heavy metals, such as Cu^{2+} and Zn^{2+}, have known functions as micronutrients in plants, they become toxic at high levels (Pandey, 2008). High accumulation of metals affects both growth and metabolism of plants (Baccouch *et al*., 1998). The phytotoxic effect of heavy metals depends on metal concentration, plant species, pH and other factors in soil (Barman *et al*., 2000, Chandra *et al*., 2004).

Table.2.2 Types of heavy metals and their effect on human health (Hima *et al*., 2007)

Heavy metals	Major Sources	Effect on human Health
Arsenic	Pesticides, fungicides, metal smelters	Bronchitis, dermatitis
Cadmium	Welding, electroplating, pesticide fertilizer Cd, Ni batteries, nuclear fission plant	Kidney damage, bronchitis, Gastrointestinal disorder, bone marrow, cancer
Lead	Paint, pesticide, electroplating automobile emission, mining, burning of coal	Liver, kidney, gastrointestinal damage, mental retardation
Manganese	Welding, fuel addition, ferromanganese production	Inhalation or contact causes damage to central nervous system
Mercury	Pesticides, batteries, paper industry	Damage to nervous system, protoplasm poisoning
Zinc	Refineries, brass manufacture, electroplating, plumbing	Corrosive effect on skin, cause damage to nervous membrane

2.4 CONVENTIONAL METHODS FOR REMOVAL OF HEAVY METALS

Removal of heavy metals from large volumes of wastewaters requires a cost effective remediation technology like chemical precipitation, lime coagulation, ion exchange, reverse osmosis and solvent extraction (Kalin *et al*., 2005, Veglio and Beolchini 1997, Gavrilescu, 2004, Iyer *et al*., 2005, Rich and Cherry, 1987).

2.4.1 PRECIPITATION AND FLOCCULATION

Sodium diethyldithiocarbamate is used as a trapping agent and poly-ferric sulphate and polyacrylamide are used as flocculants to remove copper in the copper-electroplating wastewater. The influences on the trapping copper by different agents such as diethylammonium diethyldithiocarbamate and ammonium pyrrolidinedithiocarbamate were studied and the results show that the dosage of DDTC depends only on the content of complex copper, but not on the total amount of copper in the wastewater. When the molar ratio of DDTC to Cu^{2+} is between 0.8 and 1.2, Cu^{2+} removal efficiency could be higher than 99.6%. Poly-ferric sulphate have little effects on the Cu^{2+} removal, but it have significant effects on the flocculating volume, precipitation rate and nephelometric of the upper clean water (Yijiu Li *et al*., 2003).

The effect of effluent composition on the efficiency of the hydroxide precipitation of Cu^{2+} modelling lime as the precipitant has been predicted using the solubility domain approach. The presence of gypsum and calcite as secondary precipitates had little effect on the observed residual Cu^{2+} solubilities, with Cu^{2+} mobility being governed by the least-soluble kinetically precipitated phase (Baltpurvins *et al*., 1996).

The removal of Cd^{2+} and Pb^{2+} from electroplating effluents by carbonate precipitation method was studied at different pH. When the pH was brought to 7.5, residual concentration of Pb^{2+} and Cd^{2+} were 0.60 and 0.25 mg/L respectively. Carbonate precipitation of metals using calcium or sodium carbonate is very limited (Patterson *et al*., 1975).

2.4.2 CEMENTATION

Cementation is the displacement of a metal from solution by a metal higher in the electromotive series. It offers an attractive possibility for treating any wastewater containing reducible metallic ions. In practice, a considerable spread in the electromotive force between metals is necessary to ensure adequate cementation capability. Due to its low cost and ready availability, scrap iron is the metal used often. Cementation is especially suitable for small wastewater flow because a long contact time is required. Removal and recovery of Pb^{2+} ion by cementation on iron sphere packed bed has been reported (Angelidis *et al*., 1989).

2.4.3 MEMBRANE TECHNIQUE

In most cases, process wastewaters from the electroplating and metal-finishing industries must be treated to remove heavy metals before being discharged. Reverse osmosis is ideal for this wastewater treatment for many of these operations since it allows both recovery of the heavy metals and reuse of the product water in the process. The reverse osmosis process has been used in the treatment and recovery of wastewater containing Cu^{2+}, Zn^{2+}, Pb^{2+}, Cr^{6+}, Ni^{2+} (Schrantz, 1975, Sato *et al*., 1977, Cartwright, 1985).

Pb^{2+} is removed from storage battery industry wastewater by using emulsion liquid membrane (ELM) technique. The storage battery industry wastewater has an initial Pb^{2+} concentration of 4.2 ppm (average) and a pH value of 1.4. Emulsion liquid membrane consisted of kerosene and mineral oil as organic solvents, sorbitan monooleate as a surfactant, di-2-ethylhexyl phosphoric acid (D_2EHPA) as a carrier or extractant, and sulphuric acid (H_2SO_4) as a stripping agent. The system which adjusted to a pH value of 4.0, obtained the maximum Pb^{2+} removal in first 5 min of the treatment studies and exhibited a low turbidity and swelling at the end of the experiment (Levent Gurel *et al*.,2005).

Many industrial wastewater streams contain toxic metal cations, like Ni^{2+}, Zn^{2+}, etc. or their oxyanions in up to few hundred mg/dm^3, which must be removed before water recycling or discharging directly into surface waters. In a membrane technique, ultrafiltration, completed with complexation was investigated. During the experiments, impact of conditions of membrane, pH and polymer/metal ratio have been investigated. The study series were carried out both of Zn^{2+} and Ni^{2+}. 8. The volume ratio of the polymer bounding agent and metal ion because of environmental and economical aspects should be about unit (Gabor Borbely *et al*., 2009).

2.4.4 ION EXCHANGE

Ion exchange resins are available selectively for certain metal ions. The cations are exchanged for H^+ or Na^+. The cation exchange resins are mostly synthetic polymers containing an active ion group such as SO_3H. The natural materials such as zeolites can be used as ion exchange media (Van der Heen, 1977). The modified zeolites like zeocarb and chalcarb have greater affinity for metals like Ni^{2+} and Pb^{2+} (Groffman *et al*., 1992). Ion exchange, in the presence of large quantities of competing mono-and divalent ions such as Na^+ and Ca^{2+}, ion exchange is almost totally ineffective.

Table.2.3. Performance characteristics of toxic metals removal and recovery technologies. (Eccles 1999)

PERFORMANCE CHARACTERISTICS					
Technology	**pH change**	**Metal selectivity**	**Influence of suspended solids**	**Tolerance to organic molecules**	**Conc. for metal (mg/L)**
Electrochemical	Tolerant	Moderate	Can be engineered to be tolerant	Can be accommodated	>10
Ion Exchange	Limited tolerance	Selective	Intolerant	Can be poisoned	<100
Membrane	Limited tolerance	Moderate	Intolerant	Intolerant	>10
Precipitation a) Hydroxide b) Sulphide	Tolerant	Non-selective	Tolerant	Tolerant	>10
	Limited tolerance	Limited selectivity	Tolerant	Tolerant	>10
Solvent extraction	Some systems tolerant	Selective	Intolerant	Intolerant	>100

2.5 NEED FOR BIOSORPTION

Conventional methods with various disadvantages like incomplete metal removal, high reagent and energy requirements, generation of toxic sludge or other waste products that require careful disposal has made it uneconomical to removing heavy metals from aqueous effluents (Holan and Volesky, 1994).

The recovery of heavy metals using conventional techniques is neither economical nor eco-friendly (Sarkar and Gupta, 2003, Shukla *et al*., 2007b). So, there is a continuous search for an economic and ecofriendly approach of heavy metals removal.

Biosorption, a biological method of environmental control, has emerged as an alternative to conventional waste treatment facilities as it has advantages of low operating cost, effective in dilute solutions, generates minimum secondary waste, completes within a short time period and have no toxicity limits for heavy metals (Dadhich *et al*., 2004, Ahalya *et al*., 2007).

Biosorption technologies in which biomass are used to accumulate heavy metals are methods that could replace conventional processes for the remediation of polluted wastewaters (Gavrilescu, 2004). Biomasses that are by-products from other commercial processes with little commercial value represent good candidates for the development of inexpensive biosorption processes (Psareva *et al*., 2005, Chubar *et al*., 2004). The major advantage of biomass by-products over microbial systems is that there is no cost of growing a sufficient quantity of bacterial or algae biomass (Schneegurt *et al*., 2001).

2.6 ADSORPTION

Adsorption is one of the promising processes for the removal of heavy metals from water. The process is suitable even when the metal ions are present in concentration as low as 1mg/l (Chong & Volesky, 1995).

Activated carbon (powdered or granular) has been used as adsorbent for the removal of Pb^{2+}, Cd^{2+} and other heavy metals especially when associated with organic particulate matter in water (Sorg *et al*.1978, Huang & Smith, 1981).

Hydroxides of Alumina, Iron (Cowan *et al*. 1991, Gerth *et al.*, 1983) been used as adsorbents for the removal of heavy metals. However, the cost of adsorbent becomes relatively high when pure sorbents are used therefore there is an increasing trend for substituting the pure sorbents with natural by-product in order to make the process economically feasible.

2.7 BIOSORPTION

Biosorption can be defined as "a non-directed physico-chemical interaction that may occur between metal /radionuclide species and microbial cells" (Shumate and Stranberg, 1985).

The biosorption process involves a solid phase (sorbent or biosorbent, usually a biological material) and a liquid phase (solvent, normally water) containing a dissolved species to be sorbed (sorbate, a metal ion). Due to higher affinity of the sorbent for the sorbate species the latter is attracted and bound with different mechanisms. The process continues till equilibrium is established between the amount of solid-bound sorbate species and its portion remaining in the solution. While there is a preponderance of solute molecules in the solution, there are none in the sorbent particle to start with. This imbalance between the two environments creates a driving force for the solute species. The heavy metals adsorb on the surface of biomass thus, the biosorbent becomes enriched with metal ions in the sorbate (Hima *et al*., 2007).

Biosorption of heavy metals from aqueous solutions is a relatively new process that has proven very promising in the removal of contaminants from aqueous effluents. Biosorption is becoming a potential alternative to the existing technologies for the removal and/or recovery of toxic metals from wastewater. The major advantages of biosorption technology are its effectiveness in reducing the concentration of heavy metal ions to very low levels and the use of inexpensive biosorbent materials (Ayhan Demirbas, 2008).

2.7.1 MECHANISMS OF BIOSORPTION

The mechanism involved in biosorption can be classified into various criteria that are, based on cell metabolism, they are classified as metabolism dependent and non- metabolism dependent, while based on location of the sorbate species it is classified as extra cellular accumulation/precipitation, cell surface sorption /precipitation and intra cellular accumulation. The adsorbed ions are transported across the membrane in the same mechanism by which metabolically important ions such as potassium, magnesium, and sodium are conveyed. These mechanisms comprise (i) physical adsorption e.g., electrostatic interaction has been demon-strated to be responsible for Cu^{2+} biosorption by bacterium *Zooglea ramigera* and alga *Chorella vulgaris* (Aksu et al.,1992), (ii) ion exchange e.g., biosorption of Cu^{2+} by fungi *Ganoderma lucidium* and *Asperigillus niger* (Muraleedharan and Venkobachr, 1990), (iii) complexation e.g., biosorption of Cu^{2+} by *C. vulgaris* and *Z. ramigera* takes place through both adsorption and formation of co-ordinate bonds between metals and amino or carboxyl groups of cell walls (Aksu *et al*., 1992).

2.8 EFFECT OF pH AND TEMPERATURE IN BIOSORPTION

When the pH value was lower than 3, the uptake went up sharply with the increase of pH. The maximum metal uptake for Pb^{2+}, Cu^{2+} and Zn^{2+} was obtained at pH value 5, probably due to acidic dissociation of the phenolic hydroxyl groups, resulting in stronger complexing ability with metal ions (Ayhan Sengil and Mahmut Ozacar, 2009). With increasing pH, Pb^{2+}, Cu^{2+} and Cd^{2+} species starts to hydrolyze and entirely precipitate into $Pb(OH)_2$, CuO and $Cd(OH)_2$ at pH > 6.0 (Xue *et al*.,2011).

The biosorption of $Ni^{2+}$and Cu^{2+} ions from aqueous solution by dried *Streptomyces coelicolor* A3 (2) was studied as a function of concentration, pH and temperature. The optimum pH range for nickel and copper uptake was 8.0 and 5.0, respectively. Metal ion uptake experiments were carried out at different temperatures where the best ion uptake was found to be at 30°C (Ayten Ozturk, 2004).

The effect of temperature on the removal of Pb^{2+} and Cd^{2+} from the aqueous effluent was studied using *Caladium bicolor* biomass as biosorbent in a batch sorption process. The result showed that the most suitable sorption temperature was 40ºC with maximum sorption capacities of 49.02 mg/g and 52.63 mg/g for Pb^{2+} and Cd^{2+} respectively (Michael Horsfall, 2005).

The effect of pH and metal concentrations on biosorption of Zn^{2+}, $Cu^{2+}$and Co^{2+} onto *Oscillatoria angustissima* biomass from single, binary and ternary metal solutions have been studied using Response Surface Methodology and observed that lower pH range (4.0-5.0), which facilitates adequate availability of all the metal ions. The inhibition dominance observed was $Cu^{2+} > Zn^{2+}$, $Cu^{2+} > Co^{2+}$ and Zn^{2+} - Co^{2+}, due to this the biosorbent exhibited net affinity for Cu^{2+} sorption over Zn^{2+} or Co^{2+} (Gupta *et al*., 2007).

The biosorption capacities for both Zn^{2+} at pH 6.0 and for Cu^{2+} at pH 5.0 were higher at 40°C than at 30°C. The maximum capacities for Zn^{2+} biosorption were 95.24 and 172.4 mg/g at 30°C and 40°C, respectively, and those for Cu^{2+} biosorption were 32.36 and 39.84 mg/g at 30°C and 40°C, respectively. Although temperature effect was not significant on the maximum capacity for Cu^{2+} biosorption, the amount of Cu^{2+} adsorbed at lower initial Cu^{2+} concentrations was slightly increased at higher temperature (Hsuan-Liang Liu *et al*., 2004).

The effect of temperature on the adsorption of Pb^{2+} by using the non living biomass *Spirogyra neglecta* as biosorbent was studied by setting at three different temperatures (40, 50 and 60°C) in the shaking incubator. Pb^{2+} adsorption uptake was found to increase with the increase in temperature (Modher A. Hussain *et al*., 2010).

The pH of the aqueous solution is an important controlling parameter in the heavy metal adsorption processes. Metal binding is strongly pH dependent and the maximum uptake of metal ion by the rice husk was at pH 5.5–6 ± 0.1(Krishnani *et al*., 2008).

2.9 BIOSORBENTS

The uses of non living bio-materials as metal-binding agents or natural biopolymers are industrially attractive because of their capability in lowering metal ion concentration to parts per billion due to their high affinity for cationic metals (Bailey *et al.*,1999). Natural materials and certain wastes from agricultural operations have potential to be used as low cost adsorbents (Deans and Dixon, 1992).

The adsorption data fit in both Freundlich and Langmuir isotherms and is well described by pseudo second order kinetics for the removal of chromium from an aqueous solution by using neem leaf powder as an adsorbent (Venkateswarlu *et al*., 2007).

Adsorption of Cd^{2+}, Ni^{2+}, Zn^{2+} ions from aqueous solution onto bagasse fly ash (BFA) was also studied and the equilibrium metal removal decreases with an increase in the concentration of the other metal ion and the combined action of Cd^{2+}, Ni^{2+} and Zn^{2+} ions on BFA is generally found to be antagonistic (Srivastava *et al*.,2006).

The study reports by the Milling agrowaste of *Cicer arientinum* (chickpea) was also used as biosorbent for the removal of heavy metals (Pb^{2+}, Cd^{2+}, Ni^{2+}, Zn^{2+},Cu^{2+}) when present singly or in binary and ternary systems. The biosorbent removed heavy metal ions efficiently from aqueous solutions with the selectivity order of Pb^{2+}>Cd^{2+}>Zn^{2+} >Cu^{2+} > Ni^{2+} (Asma *et al.*, 2005).

The capacity of raw rice bran for Cr^{6+} and Ni^{2+} removal from aqueous solutions was investigated and adsorption models (Langmuir, Freundlich) for describing sorption equilibrium for wastewater treatment applications, were used to represent the experimental data and equilibrium data fitted well to the Freundlich isotherm model. Cr^{6+} and Ni^{2+} were sorbed due to strong interactions with active sites of the sorbent (Oliveira *et al*., 2005).

By-products of soybean and cottonseed hulls, rice straw and sugarcane bagasse were evaluated as metal ion adsorbents in aqueous solutions (Marshall and Champagne, 1995, Marshall *et al.,* 1993).

The adsorption of Cu^{2+} and Cr^{6+} by red fir sawdust to take place primarily on components such as lignin and tanin rather onto cellulose backbone of the sawdust (Bryant *et al*., 1992).

The potential of using tartaric acid modified rice husk (TARH) was used as a sorbent for the removal of Cu^{2+} and Pb^{2+} from semiconductor electroplating wastewater. Application of Langmuir isotherm indicated that there was no difference in the sorption capacity of TARH for Cu^{2+} and Pb^{2+} in synthetic solution and wastewater (Wong *et al*., 2003).

A large number of waste materials of organic origin like oil cakes, dead leaves of trees, bark, roots, seed shells, and saw dust from various plants in the form of powder have been utilized for the removal of heavy metals and their adsorption properties have been explored (Moonis khan *et al.*,2012).

2.10. OIL CAKE AS ADSORBENT

The recent studies have demonstrated that seed press cakes can be used as adsorbents for the removal of toxic heavy metals. Sunflower oil cake is used as adsordent for the removal of the methylene blue from the waste water (Karagoz *et al*., 2008).

The adsorption behavior of various heavy metals on mustard oil cake (MOC) was studied. The mustard oil cake shows maximum adsorption capacity for Cu^{2+} followed by Zn^{2+}, Cr^{6+}, Mn^{2+}, NI^{2+}, Cd^{2+} and Pb^{2+} The adsorption of Cu2+ was found to be dependent on initial concentration of solution, pH, adsorbent dose, temperature and contact time (Ajmal *et al*., 2005).

The effects of adsorbent dosage, Cr^{6+} concentration, pH and contact time on the adsorption of Cr^{6+} from aqueous solutions onto different agricultural wastes, viz., sugarcane bagasse, maize corn cob and Jatropha oil cake under various experimental conditions has been studied. Jatropha oil cake had better adsorption capacity than sugarcane bagasse and maize corn cob under identical experimental conditions. The applicability of the Langmuir and Freundlich adsorption isotherms was tested. The results showed that studied adsorbents can be an attractive low cost alternative for the treatment of wastewaters in batched or stirred mode reactors containing lower concentrations of chromium (Garg *et al*., 2007).

An activated carbon has been prepared from gingelly oil cake (GOC) by zinc chloride treatment and its Cr^{6+} removal capacity is compared with that of commercial activated carbon (CAC). Both Langmuir and Freundlich models fit well to explain the adsorption phenomenon for GOC and CAC (Nagashanmugam and Srinivasan, 2011).

Biosorption potential of mustard oil cake (MOC) for Ni^{2+} from aqueous medium was studied. Linear and non-linear isotherms comparison suggests applicability of Temkin model at 303 and 313 K and Freundlich model at 323 K. Kinetics studies revealed applicability of Pseudo-second-order model (Moonis Ali Khan *et al*., 2012).

2.11 BIOSORPTION OF METALS IN BINARY AND TERNARY MIXTURE

Much of the work on the adsorption of heavy-metal ions by various types of adsorbents has focused on the uptake of single metals. Because of the fact that industrial effluents generally contain several metals, it is necessary to study the simultaneous sorption of two or more metals and also to quantify the interference of one metal with the sorption of the other (Srivastava *et al.*, 2006).

Cu^{2+} and Pb^{2+} removal from aqueous solutions by rice husk ash was investigated using batch and fixed bed techniques, static and dynamic systems, respectively. The removal of $Pb^{2+}$from single component solution does not depend on system, whereas Cu^{2+} ions from single component solution were more adsorbed in fixed bed. This behavior was also observed for both metal ions in a binary equimolar mixture (Vieira *et al*., 2011).

Equilibria and mechanisms involved in the adsorption process of metal ions (Cr^{3+}, Zn^{2+}, Ni^{2+}, Cu^{2+} and Pb^{2+}) from aqueous solutions using coniferous barks as biosorbent substrate were investigated and Langmuir adsorption data was found to fit their model (Fabienne Martin-Dupont *et al.*, 2002).

The simultaneous biosorption capacity of Cu^{2+}, $Cd^{2+}$and Zn^{2+} on dried activated sludge were 0.32 mmol/g for metal system such as Cu^{2+}- Cd^{2+}, 0.29 mmol/g for Cu^{2+}-Zn^{2+} and 0.32 mmol/g for Cd^{2+}-Zn^{2+}. The results showed that the biomass had a net preference for Cu^{2+} followed by Cd^{2+} and Zn^{2+} (Hammaini *et al*. 2003).The potentiality of rice husks for removing Cd^{2+} and Pb^{2+} ions from laboratory effluent was evaluated (Ricardo *et al*., 2000).

The competitive adsorption characteristics of the combinations of binary mixtures of aqueous metal ion species Ca^{2+}(aq), Cd^{2+}(aq), Pb^{2+}(aq), and Hg^{2+}(aq) on a functionalized activated carbon were investigated and the adsorption follows the order of Hg^{2+}(aq) > Pb^{2+}(aq) > Cd^{2+}(aq) > Ca^{2+}(aq) (Xiao *et al.*, 2004).

The biosorption of Pb^{2+}, Cd^{2+} and Zn^{2+} ions onto *Eichhornia crassipes* biomass in binary and ternary systems was studied in batch.The equilibrium data for the removal of Pb^{2+}, Cd^{2+} and Zn^{2+} ions showed that the uptake of the metal ions from binary and ternary systems followed the order: Pb^{2+}>Cd^{2+}> Zn^{2+}. The multi-element effect on *Eichhornia crassipes* biomass was found to be antagonistic and the Pb^{2+}–Zn^{2+}, Pb^{2+}–Cd^{2+} and Pb^{2+}-Cd^{2+}- Zn^{2+} systems showed good fitting to the Langmuir Competitive Model. Finally, the removal of Pb^{2+} ions in the presence of comparable amounts of either Cd^{2+} or Zn^{2+} or both ions, showed greater potential than the removal of Cd^{2+} and Zn^{2+} in the presence of Pb^{2+} (Courtie Mahamadi and Tichaona Nharingo, 2010).

The competitive adsorption properties of the heavy metal ions Pb^{2+}, Cu^{2+} and Cd^{2+}ions in binary and ternary systems on black carbon (BC) isolated from the burning residue of wheat straw were studied in batch systems. Equilibrium and kinetic adsorption data showed that the selectivity of metal ions on BC followed the order of Pb^{2+} > Cu^{2+} > Cd^{2+}. Kinetic studies were performed, and the rate kinetics was fitted well with the pseudosecond-order model. The Freundlich adsorption isotherm was applicable to the adsorption process, and its constants were evaluated (Xue *et al.*, 2011).

The equilibrium sorption capacity of the formaldehyde-cross-linked brown seaweed *Ascophyllum nodosum* biomass was studied using two-metal systems comprising either (Cu^{2+} + Zn^{2+}), (Cu^{2+} + Cd^{2+}), or (Zn^{2+} + Cd^{2+}) (de Carvalho *et al.*, 1995). They found that there is a mutual interference in the sorption uptake of the two metals in each combination and so decrease in sorption compared to single metal system. The sorption capacities for single metals decrease in the order Cu^{2+} > Cd^{2+} > Zn^{2+}. The inhibition dominance observed in two metal sorption systems was Cu^{2+} > Zn^{2+}, Cu^{2+} > Cd^{2+}, Cd^{2+} –Zn^{2+}.

Six fungal and 10 natural adsorbents were analysed for their Cu^{2+}, Cd^{2+} and Pb^{2+} uptake capacity from single, binary and ternary metal ion system. The selectivity order for metal ion towards the studied biomass matrices was Pb^{2+} (40- 90%)>Cd^{2+} (2-53%)>Cu^{2+} (2-30%) (Amna shoaib *et al.*, 2011).

Micro-organisms and microbial products can be highly efficient to uptake soluble and particulate forms of metals, particularly from dilute solutions. The biosorption of Pb^{2+}, Cr^{3+} and Cu^{2+}metal species using *Rhodococcus opacus* strain was studied and the influence of Cr^{3+} and Cu^{2+} on Pb^{2+} biosorption capacity in binary and ternary systems was evaluated and biosorption capacity of the Pb^{2+} ions was found to be reduced by the presence of the other competing metal ions (Bueno *et al*., 2008).

The biosorption of Pb^{2+}, Cu^{2+} and Zn^{2+} ions on *Rhizopus arrhizus* has been studied for three single-component and two binary systems. The characteristic parameters for the Freundlich adsorption model have been determined and the competition coefficients for the competitive biosorption of Pb^{2+}-Cu^{2+} at pH 4.0 and 5.0, and Pb^{2+}-Zn^{2+} at pH 5.0 have been calculated. For the individual single-component isotherms, Pb^{2+} has the highest biosorption capacity followed by Cu^{2+}, then Zn^{2+}. The capacity of Pb^{2+} in the two binary systems is always significantly greater than those of the other metal ions, in agreement with the single-component data (Sag *et al.*, 2000).

CHAPTER 3
MATERIALS AND METHODS

3.1 PREPARATION OF BIOSORBENT

The biosorbent, pongamia oil cake, was obtained from the local dealers of oil cake processing industries. The raw pongamia oil cake was crushed into fine powder using mortar and pestle. The ground biosorbent was sieved and particles less than 150 micron were collected and stored for adsorption studies. Then the fat from the pongamia oil cake was removed by the soxhlet extraction process using n-hexane as solvent in 1:5 ratios for 16 hours at 40 °C.

3.2 PREPARATION OF METAL SOLUTIONS

A series of batch experiments were conducted to study the biosorption mechanism, biosorption isotherm and adsorption kinetics. Stock solutions of metal ions was prepared by dissolving $Pb(NO_3)_2$, $CuSO_4{\cdot}5H_2O$, $ZnSO_4.7H_2O$ (analytical reagent) in deionized water and further diluted to 10–100 mg/L concentrations for the experiments. The solution pH was adjusted (Ecotester pH 1, Oakton, USA) to 5 by adding 0.1N HCl or 0.1N NaOH into the solutions with known initial metal ion concentrations.

3.3 BATCH EXPERIMENT

Biosorption experiments were carried out in batch process using 250 ml conical flasks. In the determination of equilibrium biosorption isotherm, 0.5g POC and 100mL of the desired concentration of metal ion solutions were transferred into the 250mL flask, and shaken in a horizontal shaker (Orbitek, India) for 120 min (the time required for equilibrium to be reached between metal ion biosorbed and in solution). The experiments were performed at 35 ±2°C and 150 rpm.

3.4 ATOMIC ABSORPTION SPECTROSCOPY (AAS)

The samples were diluted to 10 ppm by adding respective proportion of distilled water and the metals were quantified at particular wavelength of 283.3 nm (Lead), 324.8 nm (Copper) and 213.9 nm (Zinc) by using Atomic Absorption Spectrophotometer (Shimadzu AA-6300, Japan).

3.5 FOURIER TRANSFORM INFRARED ANALYSIS (FT-IR)

The sample was prepared by taking 5 mg of the adsorbent and it was encapsulated in KBr metal solutions to prepare the translucency sample disks. The spectra of the adsorbent are measured within the range of 400-4000 cm^{-1} wave number. The spectrum was plotted using the same scale on the transmittance axis for the adsorbent before and after adsorption. The FT-IR spectra of the adsorbents display a number adsorption peaks, including the complex nature of the studied adsorbent.

3.6 SURFACE AREA ANALYSIS BY BET ANALYSIS

The pongamia oil cake, defated by soxhlet extraction process was sieved to get particle size of 150 microns and collected about 5 gms. The surface area of the defated pongamia oil cake was measured by the BET analysis at Shraddha Analytical Services laboratory, Mumbai.

3.7 SCANNING ELECTRON MICROSCOPE - ENERGY DISPERSIVE X-RAY SPECTROMETER (SEM-EDS)

5 grams of pongamia oil cakes at different stage such as raw, defatted and after biosorption in ternary mixture were collected. The morphological characteristics and the elemental composition of pongamia oil cakes were evaluated by using a scanning electron microscope (JEOL Model JSM - 6390LV, Japan) with the attachment of the energy dispersive spectrometer (JEOL Model JED – 2300, Japan) at Sophisticated Analytical Instrument Facility (SAIF) at STIC, Kochi.

CHAPTER 4
RESULTS AND DISCUSSIONS

4.1 CHARACTERIZATION OF ADSORBENT

4.1.1 BET Analysis

Specific Surface area of Defatted POC of size <150 µm was determined using BET Analysis. The surface area was found to be 0.93 m^2/gm.

4.2 EFFECT OF pH ON ADSORPTION OF Pb^{2+}, Cu^{2+} AND Zn^{2+} BY POC

pH is an important parameter which affects the adsorption of metals ions(Pb^{2+},Cu^{2+},Zn^{2+}) on to an adsorbent. It influences the nature of metal ion as well as the surface characteristics of an adsorbent. The effect of pH on the adsorption of these metal ions onto POC was studied by varying the pH 3 to 7 while maintaining the other parameters like adsorbent dosage contact time and initial metal ion concentration at constant. The optimum pH was maximum adsorption is given in the table 4.1. At higher pH these bivalent metal ions will be hydrolysed and gets precipitated.(Xue *et al.*,2011)

Table 4.1. Optimum pH for adsorption of Pb^{2+}, Cu^{2+} and Zn^{2+} by POC

Metal ions	pH
Pb^{2+}	5
Zn^{2+}	5
Cu^{2+}	4-5

4.3 EFFECT OF ADSORBENT DOSE ON ADSORPTION OF Pb^{2+}, Cu^{2+} AND Zn^{2+} BY POC

The effect of adsorbent dose was studied by varying the adsorbent dose from 1 to 5 g/L, while the other process parameters were kept constant. It was observed that as the adsorbent dosage increases, the removal efficiency increases due to the increase in adsorption sites. Fig.4.1 shows the increase in removal efficiency with increase in dosage (Namasivayam *et al.*,1998).

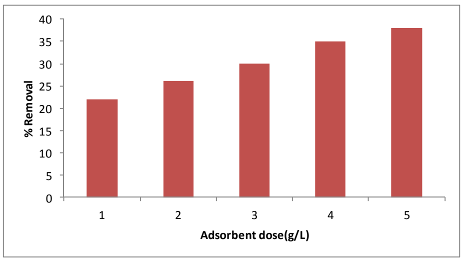


Figure 4.1. Effect of Adsorbent dosage on adsorption of metal ions.

4.4 EFFECT OF INITIAL METAL ION CONCENTRATION

The effect of initial metal ion concentration on the adsorption of Pb^{2+}, Cu^{2+}, Zn^{2+} were studied by varying the concentration of metal ions from 50mg/L to 100mg/L for Pb^{2+}, 10 mg/L to 50 mg/L for Cu^{2+} and 10 to 40 mg/L for Zn^{2+} (Ayhan sengil *et al.*,2009) where the other parameters pH, adsorbent dosage, Volume, temperature and time at constant. The removal efficiency is found to be 99.3% (Pb^{2+}), 98.6% (Cu^{2+}) and 97.4% (Zn^{2+}). The amount of Pb adsorbed is greater than Cu^{2+} and Zn^{2+}. This difference in adsorption may be due to ionic radius and electronegativity. It was reported that, greater the electronegativity and ionic size, greater will be the affinity for sorption (Sag *et al.*, 2002) the electronegativities and ionic radius of these metal ions were given in the table 4.2.

TABLE 4.2. Some Physicochemical parameters of metal ions in solution(Ayhan Sengil *et al.*,2009)

Metal ion	Electonegativity (pauling)	Effective ionic radius(pm)	Ionic potential	Enthalpy of hydration (KJ/mol)	Hydrolysis constants, pK_h	Hydrated radius(nm)
Pb^{2+}	2.33	119	2	-1556	7.8	0.401
Cu^{2+}	1.90	73	2.6	-2174	7.5	0.419
Zn^{2+}	1.65	74	9.36	-2047	7.2	0.43

Fig4.2 shows The effect of initial metal ion concentration

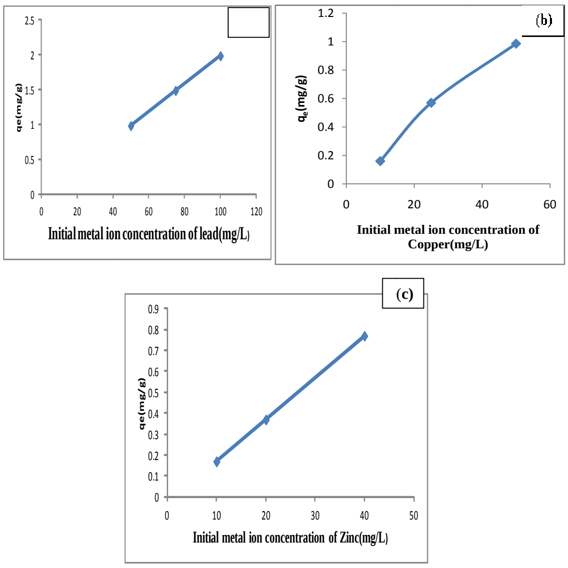


Figure 4.2. Effect of Initial Metal ion concentration on Adsorption of Pb^{2+} (a), Cu^{2+} (b) and Zn^{2+} (c)

4.5 THE COMPETITIVE BIOSORPTION OF METAL IONS FROM BINARY AND TERNARY METAL SOLUTIONS

In binary systems, the effect of presence of one metal ion over the adsorption of other metal ions was investigated. The difference in adsorption of Pb^{2+} ions in the presence Cu^{2+} and Zn^{2+} at their increasing concentrations were given in fig 4.3, 4.4, 4.5.

From the fig 4.3, it is found that as the concentration of interfering metal ion (Cu^{2+}) increases from 10 – 50 mg/L, the adsorption of Pb^{2+} ions decreases when compared to its adsorption in single metal solution at different concentration (50-100 mg/L). (Ayhan Sengil *et al.*, 2009). At the same time, the adsorption of of Pb^{2+} is also found to be greatly reduced when the concentration of Zn^{2+} is 40 mg/L when the initial metal ion concentration is 50 mg/L.

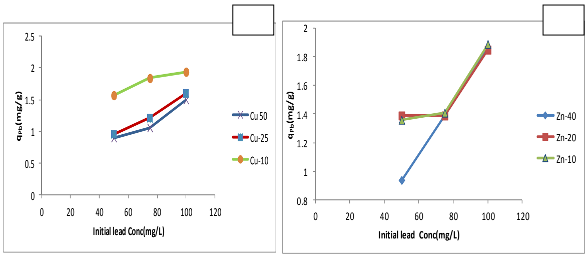


Figure 4.3. Comparison of Adsorption Isotherm of Pb^{2+} on POC with the presence of increasing concentrations of Cu^{2+} (a) and Zn^{2+} (b)

The uptake of Cu^{2+} in the presence of Pb^{2+} and Zn^{2+} were given in fig 4.4.The adsorption of Cu^{2+} is greatly affected with increasing concentration of Pb^{2+}(50,75,100mg/L). The metal uptake is high when it is present as single solution with initial metal ion concentration of 50mg/L (98.6%). As the Pb^{2+} concentration increases, the adsorption quantity decreases. The presence of Zn^{2+} also decreases the uptake of Cu^{2+}. When the initial concentration of Cu^{2+} is 25mg/L with Zn^{2+} at 20 mg/L, the Cu^{2+} uptake is greatly reduced and with Cu^{2+} at 50 mg/L and Zn^{2+} at 40 mg/L, adsorption quantity decreases significantly.

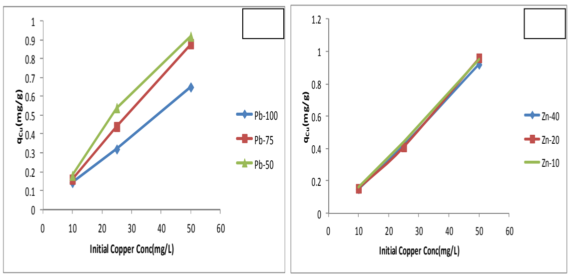


Figure 4.4. Comparison of Adsorption Isotherm of Cu^{2+} on POC with the presence of increasing concentrations of Pb^{2+} (a) and Zn^{2+} (b)

The uptake of Zn^{2+} is affected by the presence of both Pb^{2+} and Cu^{2+}. The uptake of Zn^{2+} decreases with increasing concentration of Pb^{2+}(50,75,100 mg/L) and Cu^{2+} (10,25,50 mg/L).(Fig 4.5)

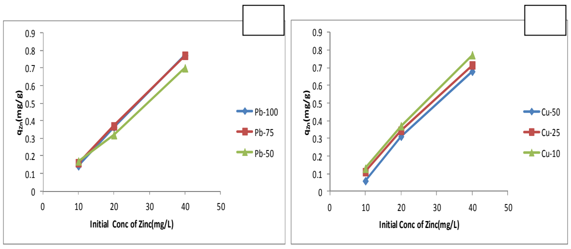


Figure 4.5. Comparison of Adsorption Isotherm of Zn^{2+} on POC with the presence of increasing concentrations of Pb^{2+} (a) and Cu^{2+} (b)

In ternary systems, the interaction of metal ions were investigated at its maximum and minimum concentrations. It is found that, when the primary metal ion is present at its maximum concentration, the interference of other metal ions is significantly less but as the metal ion concentration decreases, the other metal ions will compete for the adsorption site, which result in decrease of metal uptake.

4.6 THE LANGMUIR COMPETITIVE MODEL (LCM)

To analyse the nature of competition among Pb^{2+}, Cu^{2+} and Zn^{2+}ions, the Langmuir Competitive Model (Weber and Digiano, 1996), was applied to the binary and ternary sorption equilibrium data. When compared to the monocompetent Langmuir Model, in this model, the rate of desorption still depends on only the adsorbing component. The rate of adsorption, however must account for available sites only [ie.,$(1-\sum_{i=1}^{n}\emptyset^{\circ}_{m.i})^{-1}$. After setting adsorption and desorption rates equal, it can be shown that the extent of adsorption, $q_{e,i}$ of the *i*th solute from an n-solute mixture is given by

$$q_{e,i} = q_{m,i}K_{L,i}C_{e,i}(1+\sum_{j=1}^{n}K_{L,j}C_{e,j})^{-1} \qquad (1)$$

Where $q_{m,1}$ and $K_{L,I}$ are physical parameters and $C_{e,I}$ are equilibrium concentrations in the mixture of the solutes. In a system where the concentrations of the solutes are sufficiently large that surface coverage is substantially complete, the unit term in equation (1) may be neglected, and after some algebraic manipulation, the expression can be linearised as shown in equations (2) and (3) for the binary and ternary metal systems respectively:

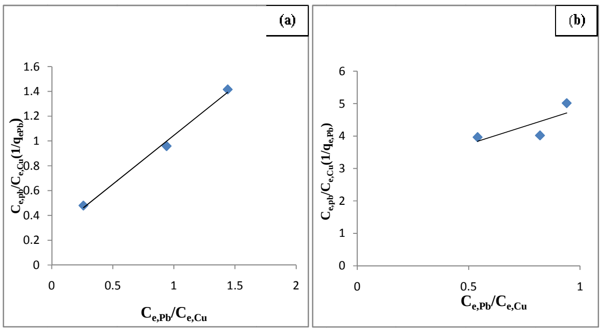
$$\frac{C_{e,1}}{C_{e,2}\,q_{e,1}} = \frac{C_{e,1}}{q_{m,1}\,C_{e,2}} + \frac{K_{L2}}{K_{L1}q_{m,1}} \qquad (2)$$

$$\frac{C_{e,1}}{q_{e,1}(K_{L2}C_{e,2}+K_{L1}C_{e,1})} = \frac{C_{e,1}}{q_{m,1}(K_{L2}C_{e,2}+K_{L1}C_{e,1})} + \frac{1}{q_{m,1}K_{L1}} \qquad (3)$$

Plots of $C_{e,1}/C_{e,2}q_{e,1}$ as a function of $C_{e,1}/C_{e,2}$ and $C_{e,1}/q_{e,1}(K_{L2}C_{e2}+K_{L3}C_{e3})$ as a function of $C_{e,1}/(K_{L2}C_{e2}+K_{L3}C_{e3})$ would give intercepts of $K_{L2}/K_{L1}q_{e,1}$ and $1/q_{m,1}K_{L1}$ and a slopes of $1/q_{m,1}$ for the binary and ternary systems, respectively. The graphs were plotted using equations (2) and (3) and the sorption parameters obtained were given in the table.

The sorption dynamics of the mixture was probed using q_e'/q_e ratios, were the prime denotes the presence of other metal ions. In general, three possible types of behavior are exhibited. $q_e'/q_e > 1$, synergism ie., the effect of the mixture is greater than that of the individual adsorbates in the mixture, $q_e'/q_e < 1$, antagonism ie., effect of the mixture is less than that of each of the individual adsorbates in the mixture and $q_e'/q_e = 1$, non interaction ie., the mixture has no effect on the adsorption of each of the adsorbates in the mixture.

In binary systems, the graphs were plotted for different combinations of Pb^{2+} -Cu^{2+}, Pb^{2+} -Zn^{2+}, Cu^{2+} -Zn^{2+} with initial metal ion concentrations varying from 50 to 100 mg/L for Pb^{2+}, 10-50 mg/L for Cu^{2+}, 10-40 mg/L for Zn^{2+}. The data fitted the Langmuir Competitive Model with R^2 values >0.9, which shows that the interaction can be well explained by this model. From the values obtained, it is clear that all the metal ions equally interfere with the adsorption of other metal ions



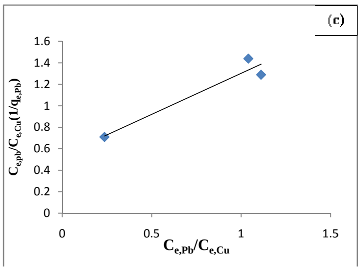
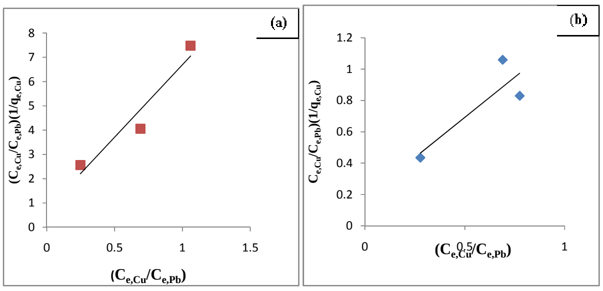


Figure 4.6. Pb^{2+} sorption with initial concentration of 50 mg/L(a), 75 mg/L(b) and 100 mg/L(c) in the presence of different concentration of Cu^{2+}(10,25,50 mg/L)



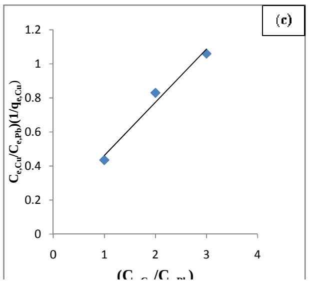
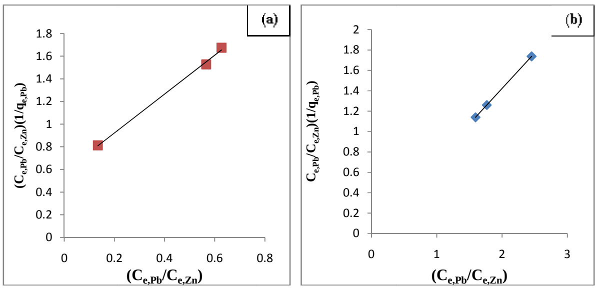


Figure 4.7. Cu^{2+} sorption with initial concentration of 10 mg/L(a), 25 mg/L(b) and 50 mg/L(c) in the presence of different concentration of Pb^{2+} (50,75,100 mg/L)



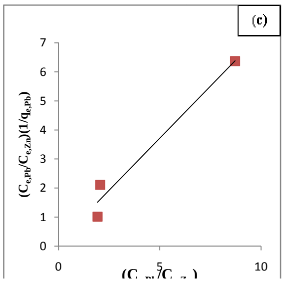
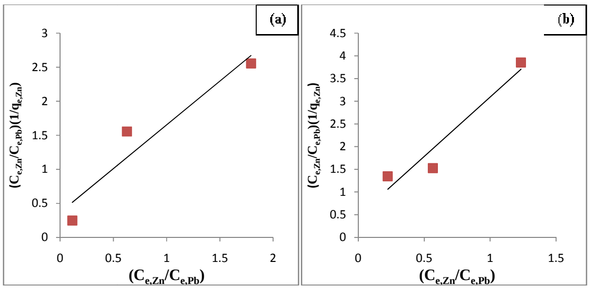


Figure 4.8. Pb^{2+} sorption with initial concentration of 50 mg/L(a), 75 mg/L(b) and 100 mg/L(c) in the presence of different concentration of Zn^{2+} (10,20,40 mg/L)



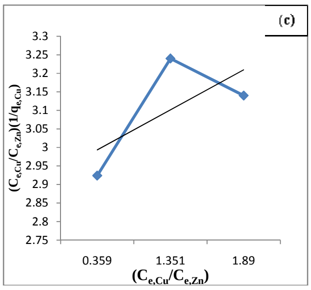
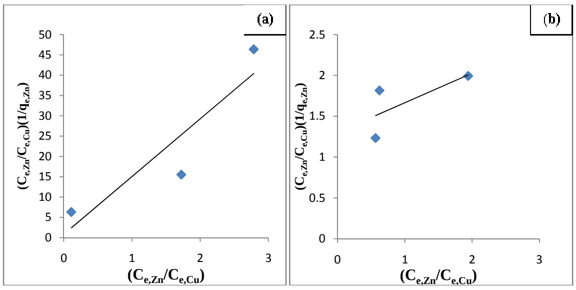


Figure 4.10. Cu^{2+} sorption with initial concentration of 10 mg/L(a), 25 mg/L(b) and 50 mg/L(c) in the presence of different concentration of Zn^{2+} (10,20,40 mg/L)



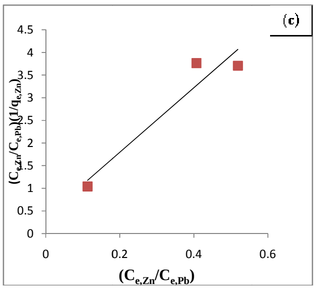
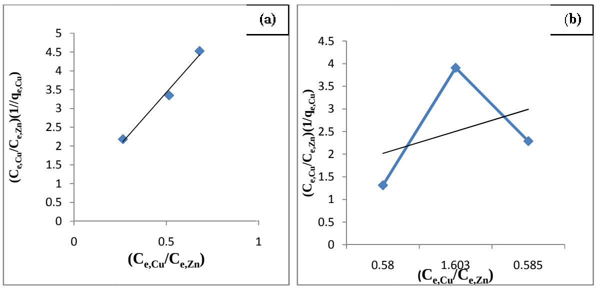


Figure 4.9. Zn^{2+} sorption with initial concentration of 10 mg/L(a), 20 mg/L(b) and 40 mg/L(c) in the presence of different concentration of Pb^{2+} (50,75,100 mg/L)



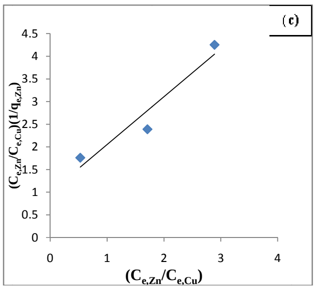


Figure 4.11. Zn^{2+} sorption with initial concentration of 10 mg/L(a), 20 mg/L(b) and 40 mg/L(c) in the presence of different concentration of Cu^{2+} (10,25,50 mg/L)

In ternary system also, the R^2 values were >0.98, indicating that the ternary equilibrium data can be adequately represented by Langmuir Competitive Model. The q_m values shows that the affinity followed the order of $Pb^{2+} > Cu^{2+} > Zn^{2+}$. From this, it is assumed that the adsorption preference of an adsorbent may be due to physiochemical properties of adsorbate like ionic size, ionic charge, concentration and the characteristics of binding sites such as structure, functional groups, surface properties, etc.,

The metal ions thus compete for the adsorption sites on the suface of POC, with Pb^{2+} showing maximum affinity due to its higher electronegativity comparing to Cu^{2+} and Zn^{2+}.

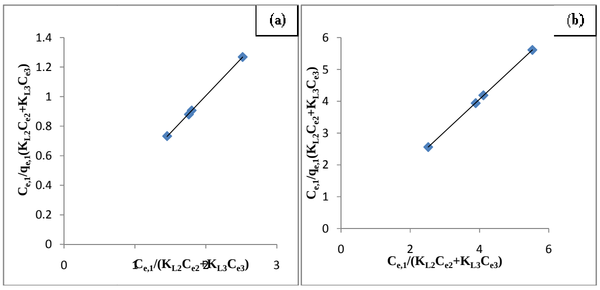


Figure.4.12. Pb^{2+} sorption with initial concentration of 100 mg/L(a), 50 mg/L(b) in the presence of different concentration of Zn^{2+} and Cu^{2+}

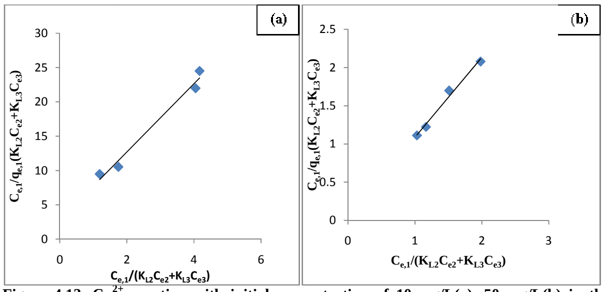


Figure 4.13. Cu^{2+} sorption with initial concentration of 10 mg/L(a), 50 mg/L(b) in the presence of different concentration of Zn^{2+} and Pb^{2+}.

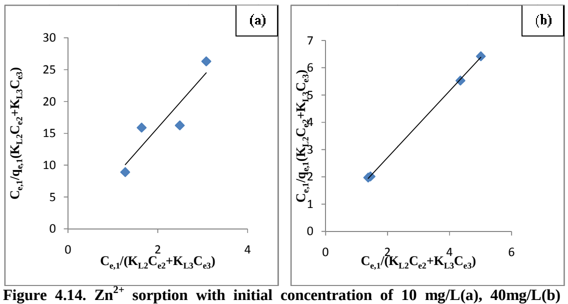


Figure 4.14. Zn^{2+} sorption with initial concentration of 10 mg/L(a), 40mg/L(b) in the presence of different concentration of Cu^{2+} and Pb^{2+}

The q_e'/q_e ratios were given in the table 4.2. From the values in the table, it is found that, all the ratios were <1, which indicated that the adsorption of metal ions decreased in the presence of other metal ions in the binary as well as ternary systems. Hence the effect is antagonistic.

Table 4.3. Adsorption parameters for Single Binary and Ternary System

System	Metal ion(+interferent)	q_e (mg/g)	q_m (mg/g)	q_e'/q_e	K_{L2}/K_{L1}	R^2
A)Pb as primary metal ion						
single	Pb	2.4	3.04	1		0.997
Binary						
Pb-Cu	Pb-Cu(100)	1.68	1.268	0.7	0.32	0.9945
	Pb-Cu(75)	1.37	0.456	0.57	1.21	0.5803
	Pb-Cu(50)	1.142	1.30	0.47	0.70	0.9294
Pb-Zn	Pb-Zn(100)	1.7	1.395	0.7	0.184	0.9681
	Pb-Zn(75)	1.39	1.43	0.57	0.04	1
	Pb-Zn(50)	0.93	0.5827	0.38	0.33	0.99
Ternary						
Pb-Cu-Zn	Pb-Cu-Zn(100)	1.982	1.98	0.825		0.998
	Pb-Cu-Zn(50)	0.984	0.905	0.41		1
B) Cu as Primary metal ion						
Single	Cu	0.974	1.80	1		0.9902
System	**Metal ion(+interferent)**	**q_e (mg/g)**	**q_m (mg/g)**	**q_e'/q_e**	**K_{L2}/K_{L1}**	**R^2**
Binary						
	Cu-Pb(25)	0.49	0.97	0.50	0.1756	0.7419
	Cu-Pb(10)	0.157	0.167	0.16	0.1206	0.9271
Cu-Zn	Cu-Zn(40)	0.95	9.25	0.97	26.66	0.4471
	Cu-Zn(20)	0.43	2.05	0.44	3.14	0.1383
	Cu-Zn(10)	0.154	0.177	0.158	0.115	0.9853
Ternary						
Cu-Pb-Zn	Cu-Pb-Zn(50)	0.926	0.955	0.95		0.985
	Cu-Pb-Zn(10)	0.1615	0.201	0.165		0.981
C)Zn as primary metal ion						
Single	Zn	0.86	1.46	1		0.99
Binary						
Zn-Pb	Zn-Pb(40)	0.748	0.14	0.86	0.05	0.9183
	Zn-Pb(20)	0.35	0.381	0.40	0.1817	0.9263
	Zn-Pb(10)	0.156	0.777	0.18	0.285	0.9139
Zn-Cu	Zn-Cu(40)	0.722	0.9470	0.83	0.943	0.9243
	Zn-Cu(20)	0.342	2.764	0.39	3.60	0.5019
	Zn-Cu(10)	0.1	0.07	0.11	0.057	0.8331
Ternary						
Zn-Pb-Cu	Zn-Pb-Cu(40)	0.774	0.719	0.9		0.997
	Zn-Pb-Cu(10)	0.129	0.125	0.15		0.833

The q_e'/q_e value is very less for the sorption of Pb^{2+} ions in the presence of Cu^{2+} and Zn^{2+} at the concentration of 50mg/L and 40 mg/L respectively, which indicated the interference of these metal ions over the adsorption of Pb^{2+}. In ternary system, the suppression effect of Cu^{2+} and Zn^{2+} is greater (q_e'/q_e =0.38) when the initial concentration of Pb^{2+} is 50 mg/L than that of the effect when the initial concentration is 100 mg/L.

The uptake of Cu^{2+} is greatly reduced by both Pb^{2+} and Zn^{2+}. The effect of interfering metal ions is noticed higher when the initial metal ion concentration of Cu^{2+} is less (10 mg/L), q_e'/q_e ratios are 0.15 and 0.16 for Pb^{2+} and Cu^{2+} respectively. In ternary system with concentration of Cu^{2+} at 50 mg/L, the suppression effect of Pb^{2+} and Zn^{2+} is very less(q_e'/q_e =0.95), but with minimum concentration of Cu^{2+}, the interference is significantly increased(q_e'/q_e =0.165)

In binary system, the effect of Cu^{2+} on adsorption of Zn^{2+} is high (q_e'/q_e =0.11) when compared to effect caused by Pb^{2+} (q_e'/q_e =0.18). In the same way, the interaction is higher in ternary systems when the initial concentration of Zn^{2+} is 10 mg/L.

CHAPTER 5

CONCLUSION

From the studies, the biosorption equilibrium data were correlated with the Competitive Langmuir model and it is found to provide the best fit. The biosorption of binary and ternary mixture of heavy metals (Pb^{2+}, Cu^{2+} and Zn^{2+}) was found to be competitive. The effect is said to be antagonistic,where the biosorption capacity is reduced when compared to single systems. Biosorption of Pb^{2+} ions was preferential to that of Cu^{2+} and Zn^{2+}, with the selectivity order of Pb^{2+}> Cu^{2+} > Zn^{2+}. This trend may due to the electronegativity and ionic radius of metal ions

CHAPTER 6

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