

WASTE WATER TREATMENT USING LOW COST NATURAL ADSORBENTS

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By

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Waste Water Treatment Using Low Cost Natural Adsorbents

Ph.D. Thesis under the Faculty of Engineering

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Certificate

This is to certify that the thesis entitled “**Waste Water Treatment Using Low Cost Natural Adsorbents**” is an authentic original work done by USHAKUMARY.E.R under my supervision and guidance in School of Engineering Cochin University of Science and Technology. No part of this thesis has been presented for any other degree from any other institution.

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Declaration

I hereby declare that the work presented in the thesis entitled “**Waste Water Treatment Using Low Cost Natural Adsorbents**” is based on the original work done by me under the supervision of Prof. G. MADHU, Division of Safety and Fire Engineering School of Engineering Cochin University of Science and Technology. No part of this thesis has been presented for any other degree from any other institution.

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Dedicated to

My Parents and Teachers

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Abstract

Heavy metals are major toxic pollutants with severe health effects on humans. They are released into the environment from a variety of industrial activities. Cadmium, lead, zinc, chromium and copper are the most toxic metals of widespread use in industries such as tanning, electroplating, electronic equipment manufacturing and chemical processing plants. Heavy metals contribute to a variety of adverse health environmental effects due to their acute and chronic exposure through air, water and food chain. Conventional treatment methods of metal removal are often limited by their cost and ineffectiveness at low concentrations. Adsorption, the use of inactivated biomass as adsorbents offers an attractive potential alternative to their conventional methods. Mango peel and *Alisma plantago aquatica* are naturally occurring and abundant biomass can offer an economical solution for metal removal.

The Cd(II), Pb(II), Zn(II), Cr(III) and Cu(II) adsorption by milled adsorbents of mango peel and *Alisma plantago aquatica* were evaluated in batches. The batch studies revealed that the adsorption was influenced by the initial metal concentration, the biomass dose and solution pH. Percentage of metal removal decreased with increasing metal concentration. Three adsorption isotherm models namely Langmuir, Freundlich and Dubinin-Radushkevich were used to analyse the equilibrium data. Equilibrium is best described by Langmuir isotherm model ($R^2 \approx 1$). Isotherm studies have been used to determine the thermodynamic parameters of the process. Kinetic parameters of adsorption such as pseudo first order, second order and intraparticle diffusion rate constant were determined and fitted with second order kinetic model. The maximum amount of heavy metals (q_{\max}) adsorbed at equilibrium was 17.3, 31.05, 25.25, 16.4 and 24.8 mg/g mango peel for Cd(II), Pb(II), Zn(II), Cu(II) and Cr(III) respectively and for *Alisma plantago*

aquatica, (q_{\max}) adsorbed at equilibrium was 19.3, 27.25, 26.67, 21.41 and 26.88 mg/g for Cd(II), Pb(II), Zn(II), Cu(II) and Cr(III) respectively. A desorption study for the solid support regeneration was also conducted. Temperature change in the range of 20-50°C was found to affect the adsorption capacity. Enthalpy data revealed that the adsorption is endothermic in nature. The surface morphology and surface functionality of the adsorbents were studied using scanning electron microscope and Fourier transform infrared spectroscopy (FTIR) respectively. FTIR analysis of mango peel and *Alisma plantago-aquatica* revealed the presence of hydroxyl, carboxyl and carbonyl groups which participate in the adsorption of metal ions. Batch desorption studies indicated that 0.1N hydrochloric acid solution gave the highest desorption of the loaded metal. The performance of continuous flow packed bed adsorption system with the *Alisma plantago aquatica* was evaluated by plotting the breakthrough curves. It was observed that the breakthrough is a strong function of the flow rates and the height of the packed bed. The zinc removal yield decreased with increasing flow rates. Adam Bohart and Wolborska models were applied to the experimental data obtained from dynamic studies on packed bed and were observed to fit the data well with good correlations. The model parameters, including the mass transfer coefficient and kinetic parameters were estimated. The results suggest that mango peel and *Alisma plantago-aquatica* have high possibility to be used as effective and economical adsorbent for heavy metal removal.

Keywords : Adsorption, heavy metals, equilibrium, thermodynamics, kinetics, packed bed column

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INTRODUCTION

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1.1 Introduction

Water pollution due to development in technology, continues to be of great concern. With increasing generation of heavy metals from technological activities, many aquatic environments face metal concentrations that exceed water quality criteria designed to protect the environment, animals and humans.

Heavy metals are chemical elements with a specific gravity that is at least 5 times the specific gravity of water and is toxic or poisonous even at low concentrations. Some well known toxic metallic elements are arsenic, (sp.gravity 5.7); iron.(7.9); chromium.(7.19); cadmium,(8.65); lead,(11.34); and mercury,(13.54).

Heavy metals are highly dispersed in a wide variety of economically important minerals. They are released to the environment during mineral extraction process. Therefore, mining activities are considered as the primary anthropogenic source of heavy metals.

Heavy metal ions are discharged into water system from various industrial activities such as electroplating industries, electronic equipment manufacturing, and chemical processing plants. Due to rapid development of industrial activities, the levels of heavy metals in water systems have substantially increased. Heavy metals can easily enter the food chain because of their high solubility in water.

Cadmium, copper, chromium, lead and zinc are extremely toxic heavy metals of widespread use in many industries. The heavy metals pollution represents an important problem, with human health concerns and serious ecological consequences. It is therefore essential to remove heavy metals from industrial waste waters and drinking water.

Plant materials are mainly comprised of cellulose materials that can adsorb heavy metal cations in aqueous solution. Numerous waste biomass sources are available in nature in which adsorption properties have been reported e.g rice husk, saw dust, tea and coffee waste, orange peel peanut shells, activated carbon, dry tree leaves and barks (Asma et al., 2005; Ferda and Selen, 2012; Kishore et al., 2008;; Nuria et al., 2010). Adsorption of heavy metal ions occur as a result of physicochemical interaction, mainly ion exchange or complex formation between metal ions and the functional groups present on the cell surface.

1.2 Health Effects Due To Heavy Metals

The international community is beginning to recognize the adverse health effects of heavy metals (Jiaping, 2012). Heavy metal toxicity can result in damaged or reduced mental and central nervous function, lower energy levels, and damage to blood composition, lungs, kidneys, liver, and other vital organs. Long-term exposure may result in slowly progressing physical, muscular, and neurological degenerative processes that mimic Alzheimer's disease, Parkinson's disease, muscular dystrophy, and multiple sclerosis. Allergies are not uncommon,

and repeated long-term contact with some metals (or their compounds) may cause cancer. For some heavy metals, toxic levels can be just above the background concentrations naturally found in nature. Therefore, it is important to learn about heavy metals and take protective measures against excessive exposure (*Prakasham et al., 1999*).

Heavy metals are associated with myriad adverse health effects, including allergic reactions (e.g., beryllium, chromium), neurotoxicity (e.g., lead), nephrotoxicity (e.g., mercuric chloride, cadmium chloride), and cancer (e.g., arsenic, hexavalent chromium). Humans are often exposed to heavy metals in various ways—mainly through the inhalation of metals in the workplace or polluted neighborhoods, or through the ingestion of food (particularly seafood) that contains high levels of heavy metals or paint chips that contain lead (Jarup,2003).

1.3 Environmental Pressures

Stricter regulations with regard to the metal discharges are being enforced particularly in industrialized countries. Toxicology of heavy metals confirms their dangerous impacts. Due to their high toxicity, industrial wastewaters containing heavy metals are strictly regulated and must be treated before being discharged in to the environment. The currently practiced technologies for removal of heavy metals from industrial effluents appear to be inadequate and expensive. They often cause secondary problems with metal bearing sludges. It is therefore essential to develop alternative technologies to treat metal bearing effluents.

1.4 Conventional Methods

Several technologies have been used to treat metal containing aqueous solution, for the last few decades (Wang et al., 2004). Major draw backs of the conventional processes can be summarized as follows:-

- 1) Membrane process(Reverse osmosis technique)
 - The concentration of metal ions in the feed stream has to be reasonably low for successful operation of membrane processes.
 - As metal concentration increases, the rejection of the membrane is lowered; membrane scaling is often noted and also high energy will be required to treat them
 - Cost of membrane is high and productivity decreases with time.
- 2) Precipitation and clarification techniques.
 - It requires excessive amount of chemicals. Consequently, the cost of precipitation can be prohibitively high.
 - Metal complexed with other reagents cannot be treated. The complex has to be broken prior to the precipitation.
 - Not effective in case of wastewater containing very low concentration of metal.
- 3) Activated carbon process
 - Activated carbons are costly.
 - The activation process must be repeated after every regeneration process following the elution of the saturated carbon.
 - After every regeneration step, the activated carbon loses some of its weight and its uptake capacity reduces by approximately 10-20%.
 - A carbon loss also adds some extra cost to the process, adding to the costs of the regeneration and activation steps.

- 4). Ion exchange process
- Precipitates such as calcium sulphate or ferric oxide can foul ion-exchange resins.
 - Ion exchange resins are often very expensive than adsorbents.
 - Resin ions in every cycle have to be replaced.

The metal removal capacity of resins is usually affected by the presence of calcium and magnesium ions in the solution.

1.5 Adsorption

Adsorption has emerged as promising technique for metal removal. The processes can occur at an interface between any two phases, such as, liquid-liquid, gas-liquid, or liquid-solid interfaces (Barakat, 2011). Moreover, adsorption is coming to be regarded as a practicable separation method for purification or bulk separation in newly developed material production processes of, for example, high- tech materials and biochemical and biomedical products.

Surface characteristics and pore structures of adsorbents are the main properties in determining adsorption equilibrium and rate properties which are needed for plant design. New adsorbents are continuously being developed, introducing new applications for adsorption technology. Adsorption equilibrium is the fundamental factor in designing adsorption operations.

When adsorption takes place with suspended adsorbent particles in a vessel, adsorbate is transported from the bulk fluid phase to the adsorption sites in the adsorbent particle. In this type of situation, changes in the amount adsorbed or concentration in the fluid phase can be predicted by solving the set of differential equations describing the mass balances in the particle, at the

outer surface and between the particle and the fluid phase. Determination of diffusion parameters should be done with a simple kinetic system. These discussions are also applicable to the analysis and design of adsorption operation in a vessel or differential reactor. Another powerful technique for determining the rate parameters involved in an adsorption packed column gives the basic relations used for calculation of breakthrough curves.

Advantages of adsorption:

- Metals at low concentration can be selectively removed.
- Effluent discharge concentration meets the govt. regulation.
- System operates over the broad pH ranges (2-9).
- System is effective over a temperature ranges of 4-90°C.
- System offers low capital investment and low operation cost.
- Convert metal pollutant to metal product.
- System offers simple design, easy operation

Adsorption is a good weapon in the fight against toxic metals threatening our environment.

1.6 Types of Adsorption

There are two types of adsorption phenomena, physical adsorption and chemical adsorption (Jiaping, 2012) .

1.6.1 Physical adsorption (Vander Waals adsorption)

Physical adsorption is the result of intermolecular forces of attraction between molecules of the solid adsorbent and the substance adsorbed. It is a readily reversible phenomenon. In industrial adsorption operations this reversibility is used for the recovery of adsorbent for reuse, for recovery of adsorbed substance or for the fractionation of the mixtures.

1.6.2 Chemisorption

Chemisorption is the result of chemical interaction between the solid adsorbent and the adsorbed substance. The adhesive force and the heat liberated are much greater those that found in physical adsorption. The process is frequently irreversible. Some substances which under condition of low temperature undergo only physical adsorption substantially. But they exhibit chemisorption at high temperatures and sometimes both the phenomena may occur at the same time. Chemisorption is of particular importance in catalysis.

1.7 Factors Affecting Adsorption

1.7.1 pH

The pH value of the metal solution plays an important role in the whole adsorption process and particularly on the adsorption capacity. The pH of the solution would affect both aqueous chemistry and surface binding sites of the adsorbents. The effect of pH in turn depends on the charge on the adsorbent surface. If the adsorbent surface is negatively charged, at lower pH, the large number of H⁺ ions present neutralizes the negatively charged adsorbent surface, thereby reducing hindrance to the diffusion, and a better adsorption is obtained. If the surface charge of the adsorbent is positively charged, the H⁺ ions may compete effectively with the cations of the solution causing a decrease in the amount of metal ion adsorbed (Jiaping, 2012).

1.7.2 Contact time

The amount adsorbed on to the adsorbent is in a state of dynamic equilibrium with the amount desorbed from the adsorbent. The time required to attain this state of equilibrium is termed as the equilibrium time. The amount adsorbed at the equilibrium time reflects the maximum adsorption capacity of the adsorbent under the operating conditions.

1.7.3 Concentration

Whatever be the mechanism of adsorption from the solution, it is certain that the extent depends mainly on the available surface of the adsorbent. The process of adsorption is almost invariably reversible and a definite equilibrium is reached in a short time dependant on the concentration of the solution and quantity of the adsorbent.

1.7.4 Temperature and Pressure

Increase of temperature and decrease of pressure increase the extent of adsorption. This fact that heat is absorbed in the process of adsorption is implied in the Le Chatliers principles. As in the case of the heat of the solution the different heats of adsorption, viz, the differential and integral heat must be distinguished. If accurate values were to be obtained the results would probably throw much light on the adsorption phenomena. Many attempts have been made to determine heats of adsorption experimentally.

1.7.5 Surface area (particle size)

The adsorbents with smaller particle size have a higher ability in the adsorption process with large external surface. Therefore more metal ions could be removed than the large particles. The adsorption increases as the particle size decreases, because the surface area increases when the particle size decreases. Such an effect is probably due to the inability of the large ions to penetrate all the initial pore structure of the adsorbent.

1.8 Types of Adsorbents

Most of the adsorption researches have been concentrated on the use of bacteria and fungi for the removal of heavy metals. Both viable and inactive cells have been studied. This generally involves culturing of these micro-

organisms using chemicals. A potential economical alternative would be to use, naturally abundant materials such as waste biomass. These natural materials can be easily processed and used for metal removal, and hence can offer an economical solution to the problem of heavy metal pollution.

1.9 Objectives

The main objective of the present study was the evaluation of adsorption capacity of two different adsorbents namely mango peel and *Alisma Plantago Aquatica* in the removal of five heavy metals cadmium, copper, chromium, lead and zinc ions in batch and continuous systems. In order to achieve this objective, the following investigations were carried out.:-

- Determination of effects of different experimental parameters like initial concentration, biomass dose, pH of the solution on metal uptake in batch system.
- Determination of kinetic parameters using model equations available in literature on adsorption.
- Evaluation of isotherm modeling studies for establishing adsorption equilibria.
- Determination of thermodynamic parameters to establish the effect of temperature on adsorption.
- Establishing recovery and reuse of the adsorbents using different regenerants.
- Evaluation of performance of continuous flow packed bed column systems containing adsorbent.
- Analysis of the packed bed column using suitable mathematical models.

1.10 Scope of Study

Heavy metal contaminants are present in wastewater from many industries such as metal manufacturing, electroplating, dye and paint, chemicals and fertilizer. Heavy metal removal has become a serious environmental concern due to the toxic and cumulative nature of heavy metals in various life forms. Adsorption method has proven to be an excellent way to treat effluent and also cost effective technique. A new low cost locally available biomaterial was tested for its ability to remove Cd(II), Pb(II), Zn(II), Cr(III) and Cu(II) from aqueous solution. Different adsorbent materials had been used to remove heavy metals from waste water; in this study new adsorbent was used directly for adsorption experiment with out any treatment. Mango peel waste was evaluated as a new sorbent for adsorption of Cd(II) and Pb(II) ions from aqueous solution by Iqbal et al., (2008). In this present study mango peel is used for removal five metal ions Cd(II), Pb(II), Zn(II), Cr(III) and Cu(II) from aqueous solution. The *Alisma plantago aquatica* is new adsorbent for the heavy metal removal from wastewater.

1.11 Thesis Framework

The thesis is divided into three sections based on the three major modules of the present work. Each section forms a separate chapter (Chapters 3, 4 & 5). The second chapter provides an up-to-date review of literature in the areas related to the research in the thesis Chapter 6 presents the concluding remarks of the present study.

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LITERATURE REVIEW

2.1	Introduction
2.2	Heavy Metals in the Environment
2.3	Waste Water Treatment Options for Heavy Metal Removal
2.4	Sources and Impacts of Heavy Metals
2.5	Adsorption
2.6	Types of Adsorbents
2.7	Adsorption Mechanisms
2.8	Factors Affecting Adsorption
2.9	Equilibrium Models
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2.11	Adsorption Thermodynamics
2.12	Adsorption in Packed Column
2.13	Conclusions

2.1 Introduction

Environmental pollution due to development in modern industrial practice is one of the most significant problems of this century. Of this the contamination of water resources by hazardous pollutants has attracted much serious attention in the last few decades. This is particularly due to their toxic, acute and chronic health effects.

2.2 Heavy Metals in the Environment

Most of the heavy metals are classified as hazardous pollutants due to their toxicity. It has been established beyond any doubt that dissolved heavy metals escaping into the environment pose serious health hazard. They accumulate in living tissues throughout the food chain, which has humans at its top (Volesky,1999). Removal of heavy metal ions from wastewater is essential due to their extreme toxicity towards aquatic life and humans. The

increasing environmental pressures have led to stricter regulations with regard to metal discharges particularly in industrialized countries. Hence, there is a need for controlling the heavy metal emission into the environment.

2.3 Waste Water Treatment Options for Heavy Metal Removal

There are several different options currently available for the removal of heavy metals from industrial wastewaters. The most common treatment is chemical precipitation with lime or caustic soda where recovery of metals or water is not a consideration. This technique has certain major disadvantages such as residual solubility of the metals, large requirement of chemicals and generation of a large volume of sludge which requires careful disposal in further steps (Spearot and Peck,1984;Peters et al.,1985; Brierley et al.,1986). Other available treatments such as ion-exchange, reverse osmosis and electro dialysis require high capital investment and running cost (Aderhold et al.,1996). Adsorption is by far the most versatile and widely used technique for the removal of metal ions. Activated carbon has been the standard for industrial wastewater treatment for almost three decades (Fornwalt and Hutchins, 1966). Despite its widespread use, activated carbon still remains an expensive material. In recent years, the research interest in to the low-cost alternatives to activated carbon has grown.

2.4 Sources and Impacts of Heavy Metals

Heavy metals have been used by humans for thousands of years. Heavy-metal cations can be introduced into agricultural soils by application of fertilizers, limiting materials, sewage sludge, composts, and other industrial and urban waste materials. Therefore, heavy-metal adsorption reactions, in a competitive system, are important to determine heavy-metal availability to plants and their mobility throughout the soil. This study was conducted to

evaluate the selectivity sequence and estimate the competitive adsorption of several heavy metals in seven different soils with different chemical and mineralogical characteristics. The most common sequences were $Cr > Pb > Cu > Cd > Zn > Ni$ and $Pb > Cr > Cu > Cd > Ni > Zn$. Chromium, lead and copper were the heavy-metal cations most strongly adsorbed by all soils, whereas cadmium, nickel, and zinc were the least adsorbed, in the competitive situation (Paulo et al., 2001).

Cadmium occurs naturally in ores together with zinc, lead and copper. Cadmium compounds are used as stabilizers in PVC products, colour pigment, several alloys and, now most commonly, in re-chargeable nickel–cadmium batteries. Metallic cadmium has mostly been used as an anticorrosion agent. Cadmium is also present as a pollutant in phosphate fertilizers. Chromium is used in metal alloys and pigments for paints, cement, paper, rubber and other materials. The main human activities that increase chromium concentration in the environment are chemical, leather and textile manufacturing, steel and electro plating industries. Lead occurs in mines and smelters as well as welding of lead painted metal, and in battery plants. Low or moderate exposure may take place in the glass industry.

Cadmium exposure may cause kidney damage. Chromium ingestion beyond permissible quantities causes various chronic disorders in human beings (Prakasham et al., 1999). Strong exposure to chromium causes cancer in digestive tract and lungs (Donald et al., 1970) and may cause nausea, vomiting, severe diarrhea and hemorrhage (Browning, 1969). Copper may be found as contaminant in food , especially shellfish, liver, mushrooms, nuts and chocolate(Yu et al., 2000). Copper has been found to cause stomach and intestinal distress, kidney damage and anemia. Lead poisoning is headache, irritability, abdominal pain and various symptoms related to the nervous

system. Lead encephalopathy is characterized by sleeplessness and restlessness. Children may be affected by behavioral disturbances, learning and concentration difficulties. Recent research has shown that long-term low-level lead exposure in children may also lead to diminished intellectual capacity. Prolonged exposure to heavy metals such as cadmium, copper, lead, nickel, and zinc can cause deleterious health effects in humans (Lars Jarup, 2003)

Any metal or metalloid species may be considered a “contaminant” if it occurs where it is unwanted, or in a form or concentration that causes a detrimental human or environmental effect. Metals/metalloids include lead , cadmium , mercury , arsenic , chromium, copper , selenium, nickel , silver , and zinc . Other less common metallic contaminants include aluminium , cesium , cobalt , manganese , molybdenum, strontium , and uranium (Reena et al., 2011).

2.5 Adsorption

Adsorption can be a potential alternative to traditional treatment processes of metal ions removal (Ayhan, 2008; Mckat et al., 2000; Mohsen,2007). The phenomenon of adsorption has been described in a wide range of non-living biomass like potato peel waste (Mohammed and Devi, 2009), untreated Cocos Nucifara (Prasad and Satya, 2010), orange peel (Ferda and Selen, 2012), crab shell (Vijayaraghavan et al., 2005), untreated coffee grounds(Azouaou et al., 2010), as well as of living biomass like, microbial cell (Gopal et al., 2002), moss (Lee and Low,1989),yeast (Can and Jianlong, 2008), fungi (Sudha and Emilia, 2002), algae (Dumitru and Laura, 2012; Gupta and Rastogi, 2008; Mohammad Mehdi et al., 2011) orange peel (Ferda and Selen, 2012).

Adsorption has been proved to be an excellent way to treat industrial waste effluents, offering significant advantages like the low-cost, availability, profitability, easy of operation and efficiency (Demirbas, 2008).

The use of microbial biosorbents for removal of toxic heavy metals from waste waters offers a relatively low cost method with potential for metal recovery. Adsorption has distinct advantages over the conventional methods: the process does not produce sludges requiring further disposal, it could be highly selective, more efficient, easy to operate, can handle large volumes of waste waters containing low metal concentrations. The metal sequestering ability of microorganisms such as yeast, bacteria, fungi and algae have been investigated and reported. Adsorption technology based on the utilization of dead biomass offers certain major advantages such as lack of toxicity constraints, non requirement of nutrient supply, and recovery of bound metal species by desorption (Gadd, 1990).

2.6 Types of Adsorbents

In the last few decades, alternative sorbents for the treatment of heavy metal contamination have been investigated (Abdelwahab, 2007; Amany, 2007; Bayat, 2002; Cetin and Pehlivan, 2007; Mustafa, 2008; Nuria et al., 2010; Srinivasan and Viraraghavan, 2010; Wan and Hanfiah, 2007). There is a large volume of literature relating to the performance of different biosorbents for the removal of variety of heavy metals (Larous et al., 2005; Uysal and Ar, 2007; Qi. and Aldrich, 2008; Atalay et al., 2010). The agricultural residues seem to be preferred (Pollard et al., 1992; Nasernejad et al., 2005; Johnson et al., 2002; Horsfall et al., 2006) and green coconut shells are a most appropriate example for the adsorption removal of and organics (Crisafully et al., 2007). Plant materials are mainly comprised of cellulose materials that can adsorb

heavy metal cations in aqueous solution. Numerous waste biomass sources are available in nature in which some experimental adsorption properties have been reported e.g. rice husk (Kishore et al., 2008), saw dust (AjayKumar et al., 2008; Mehmet et al., 2007; Bin et al., 2000), tea and coffee waste (Amir et al., 2005; Amarasinghe and Williams, 2007), orange peel (Ferda and Selen 2012) peanut shells (Qin et al., 2007), activated carbon (Kadirvelu et al., 2001; Gulnaziya et al., 2008) dry tree leaves and barks (Benhima et al., 2008; King et al., 2006; Venkateswarlu et al., 2007). In literatures, studies were conducted using banana peel for As(III) (Suantak et al., 2012) and watermelon rind for Ni(II) and Co(II) (Lakshmi pathy and sarada, 2013).

Azouaou et al. (2010) studied the effect of various parameters on adsorption capacity using untreated coffee grounds as adsorbent. They found that the adsorption process is a function of the adsorbent concentration, pH, metal ion concentration and temperature.

Mishra and Pate (2009) examined the role of low cost adsorbents on lead and zinc ions removal from waste water.

Venkateswarlu et al. (2006) carried out investigations on *Azadirachta indica* (neem) leaf powder as an adsorbent on chromium removal from aqueous solution. The results indicated that the adsorption capacity is strongly depends on equilibrium pH.

Waleska et al. (2008) used the untreated coffee husks as adsorbents for the removal of heavy metal ions such as Cd(II), Cu(II) and Zn(II) from aqueous solution. The results indicated that the highest adsorption capacity occurred at distinct pH values for each metal ion.

2.6.1 Previous study using mango tree related adsorbent

Ashraf et al., 2011 carried out batch adsorption studies using mango biomass for Pb(II), Zn(II), Ni(II) and Cu(II) ions.

Murugan et al., (2010) investigated the potential of mango leaves powder for removal of Grey BL dye from aqueous solution. The comparison of adsorption capacities of guava and mango leaves powder for adsorption of Methylene Blue dye was studied by Patel and Vashi (2009).

Mango peel waste was evaluated as a new sorbent for adsorption of Cd(II) and Pb(II) ions from aqueous solution by Iqbal et al., (2008). FTIR analysis revealed that carboxyl and hydroxyl groups were the principle functional sites taking part in the adsorption process.

2.7 Adsorption Mechanisms

The complexity of the adsorbent structure implies that there are many ways for the metal to be captured by the cell. Adsorption mechanisms are therefore various and in some cases they are still not very well understood. Metal adsorption and biosorption onto agricultural wastes is a rather complex process affected by several factors. Mechanisms involved in the biosorption process include chemisorption, complexation, adsorption-complexation on surface and pores, ion exchange, microprecipitation, heavy metal hydroxide condensation onto the biosurface, and surface adsorption (Demirbas, 2008; Semerjian, 2010) They may be classified by the following different criteria.

2.7.1 Transport of the metal across the cell membrane

This phenomenon is associated with cell metabolism, it implies that this kind of adsorption may take place only with viable cells. Unfortunately, it is the toxicity of some elements, which does not allow investigation of

adsorption in the presence of high metal concentrations. In fact, little information is available about this kind of mechanism. Heavy metal transport across microbial cell membrane may be mediated by the same mechanism used to convey metabolically essential ions, such as potassium, magnesium and sodium. The metal transport system may become confused by the presence of heavy metal ions of the same charge and ionic radius (Brierley, 1990).

This kind of mechanism often takes place following cell surface binding, which is linked to metabolic activity. There are many examples in the literature where adsorption by living microorganism has been shown to comprise of two basic steps. Firstly, metabolism independent binding to cell walls and secondly, metabolism dependent intracellular uptake, whereby metal ions are transported across the cell membrane into the cell (Gourdon et al., 1990).

Holan and Volesky (1994) proposed that an additional metabolism, such as entrapment of metals in the form of insoluble micro deposits, could greatly contribute to lead and nickel adsorption by the biomass of marine algae.

2.7.2 Physical adsorption

Physical adsorption mechanism involves Van der waals' forces of attraction between the metal and the cell surface, which is not dependent on the cell metabolism. Tsezos and Volesky (1982) verified that thorium and uranium biosorption by fungal biomass of *Rhizopus arrhizus* is based on physical adsorption in the cell- wall chitin structure. Kuyucak and Volesky (1989) hypothesized that uranium, cadmium, zinc, copper and cobalt biosorption by dead biomass of algae, fungi and yeast takes place through electrostatic interaction between ions in solution and cells walls. Physical adsorption is furthermore responsible for copper, nickel, cadmium, zinc and lead biosorption by *Rhizopus arrhizus* (Fourest and Roux, 1992).

2.7.3 Ion exchange

Ion exchange is an important concept in heavy metal adsorption. Ozer et al. (2003) found that the biosorption capacities of Pb^{2+} , Ni^{2+} and Cr^{3+} onto *S.cerevisiae* increased in the order of $\text{Pb}^{2+} > \text{Ni}^{2+} > \text{Cr}^{3+}$ which increased with the atomic number increasing. Benguella and Benaissa (2002) investigated the biosorption characters of Cu^{2+} , Zn^{2+} and Cd^{2+} onto chitin, the results indicated that the biosorption capacity was correlated with ionic potential and ionic radius.

Ion exchange involves interaction between functional groups on the cell surface and the metal ions. Cell wall of microorganism contains polysaccharides as basic building blocks. The ion exchange properties of natural polysaccharides have been studied in detail and it is a well established fact that bivalent metal ions exchange with counter ions of the polysaccharides (TseZos and Volesky 1982). Alginates of marine algae usually occur as natural salts of K^+ , Na^+ , Ca^+ and Mg^{2+} . These metallic ions can exchange with the counter ions such as Co^{2+} , Cu^{2+} , Cd^{2+} and Zn^{2+} resulting in the biosorptive uptake of the metals (Kuyucak and Volesky 1989). Ion exchange was proposed to be the mechanism of copper biosorption by fungi *Ganoderma lucidum* (Muraleedharan and Venkobacher, 1990) and *Aspergillus niger*.

Yasemin and Zeki (2007) also hypothesized that adsorption of Ni(II), Cd(II) and Pb(II) from aqueous solution by shells of hazelnut and almond take place through ion exchange. The major components of the polymeric material in shell are lignin, tannins or other phenolic compounds. Based on the structure of the phenolic compounds a possible mechanism of ion exchange could be considered as a divalent heavy metal ion (M^{2+}) that attaches itself to two adjacent hydroxyl groups and two oxy groups which could donate two

pairs of electrons to metal ions forming four coordination number compounds and releasing two hydrogen ions into solution.

2.7.4 Complexation

The metal removal from solution may also take place through complex formation on the cell surface after interaction between the metal and active groups. Metal ions can bind to unidentate (single).ligands or to chelates (Cabral, 1992; Tsezos and Volesky, 1982) proposed that adsorption by *Rhizopus arrhizus* has a mechanism not only based on physical adsorption , but also on metal complexation with nitrogen of the chitin cell wall network. Cabral (1992) also hypothesized that metal complexation was found to be the only mechanism responsible for calcium, magnesium, cadmium, zinc, copper and mercury accumulation by *Pseudomonas syringae* .

2.7.5 Precipitation

Precipitation of the metals may take place both in solution and on the cell surface. Furthermore, it may be either dependence on the cellular metabolism if, in the presence of toxic metals, the microorganisms produce compounds, which favour the precipitation process. In case where precipitation is not dependent on the cellular metabolism, it may be a consequence of the chemical interaction between the metal and the cell surface. This phenomenon is the terminal step of uranium biosorption by *Rhizopus arrhizus* (Tsezos and Volesky, 1982) the formation of the complex uranium–chitin, mentioned above, is followed by the complex hydrolysis and the precipitation of the hydrolysis product uranyl hydroxide in the cell wall. Holan and Volesky (1994) proposed that an additional mechanism, such as entrapment of metals in the form of insoluble micro deposits, could greatly contribute to cadmium adsorption by the biomass marine algae.

2.8 Factors Affecting Adsorption

2.8.1 Contact time

The removal efficiency increased with an increase in contact time before equilibrium is reached. The amount adsorbed at the equilibrium time reflects the maximum adsorption capacity of the adsorbent under the operating conditions (Azouaou et al., 2010; Maria Martinez et al., 2006; Mohammad Mehdi et al., 2011).

2.8.2 pH

The pH of the solution was clearly an important parameter that controlled the adsorption process (Azouaou et al., 2010; Babu and Gupta 2008; Gupta and Rastogi, 2007; Hao Chen et al., 2010; Waranusantigul et al., 2003). The effect of pH in turn depends on the charge on the adsorbent surface.

2.8.3 Concentration

Different initial metal concentrations and a fixed concentration of biomass were used to calculate adsorption capacity. The initial and final concentrations of the solutions were measured by Atomic absorption spectrophotometer. These data were used to calculate the adsorption capacity of the adsorbent (Azouaou et al., 2010; Mausumi et al., 2006; Mohammad Mehdi et al., 2011).

2.8.4 Adsorbent dose

The adsorbent dosage is an important parameter because this determines the capacity of an adsorbent. The removal of metal ions increases with an increase in the adsorbent dosage. The effect of adsorbent dosage on adsorption was studied by varying the amount of adsorbents and keeping the other parameters constant (Azouaou et al., 2010; EI-Said et al., 2010; Saifuddin and Kumaran, 2005).

2.9 Equilibrium Models

During adsorption a rapid equilibrium is established between adsorbed metal ions and adsorbent. The equilibrium metal uptake q is calculated using the following equation:

$$q = \frac{(C_i - C_f)V}{M} \quad (2.1)$$

Where, V is the volume of the solution, C_i and C_f are initial and equilibrium concentrations and M is the dry mass of adsorbent (Can and Jianlong, 2007).

The most widely used isotherm equation for modeling the equilibrium is the Langmuir equation which is valid for monolayer sorption on to a surface with a finite number of identical sites and is given by equation

$$q = \frac{q_{\max} b C_f}{(1 + b C_f)} \quad (2.2)$$

Where q_{\max} is the maximum amount of the metal ion per unit weight of the adsorbent to form a complete monolayer on the surface bound at high C_f and b is a constant related to the affinity of the binding sites q_{\max} represents a practical limiting adsorption capacity when surface is fully covered with metal ions and assists in the comparison of adsorption performance particularly in cases where the sorbent did not reach its full saturation in experiments. q_{\max} and b can be determined from the linear plot of C_f/q versus C_f (Babu and Gupta, 2008).

The linearized form of this model equation is given as

$$\frac{C_f}{q} = \frac{C_f}{q_{\max}} + \frac{1}{b q_{\max}} \quad (2.3)$$

The empirical Freundlich model also considers mono molecular layer coverage of solute by the adsorbent. However, it assumes the adsorbent has a heterogeneous surface so that binding sites are not identical. This model takes the following form for a single component adsorption (Azouaou et al., 2010).

$$q = KC_f^{1/n} \quad (2.4)$$

Where K and n are the Freundlich constants characteristic of the system. K and n are indicators of adsorption capacity and adsorption intensity respectively. Through the Freundlich isotherm is more widely used, it provides no information on the monolayer adsorption capacity, in contrast to the Langmuir model (Aksu et al., 2003; Yu et al., 2000; Ferda et al., 2012)

$$\log q = \log K + \frac{1}{n} \log C_f \quad (2.5)$$

Langmuir and Freundlich isotherms are insufficient to explain the physical and chemical characteristics of adsorption. The Langmuir isotherm constants do not explain the chemical or physical properties of the adsorption process. However, the mean adsorption energy (E) calculated from the D-R isotherm provides important information about these properties.

Dubinin – Radushkevich (D-R) isotherm is commonly used to describe the adsorption isotherms of single solute systems (Azouaou et al., 2010; Elangovan et al., 2008).

The D-R isotherm is expressed as

$$q = q_{\max} \exp \left(-B \left[RT \ln \left(1 + \frac{1}{C_f} \right) \right]^2 \right) \quad (2.6)$$

$$\ln q = \ln q_{\max} - B e^2 \quad (2.7)$$

Where B is a constant related to the adsorption energy, R is the gas constant ($8.314 \times 10^{-3} \text{kJ/molK}$) and T is the absolute temperature

$$e = RT \ln \left(1 + \frac{1}{C_f} \right) \quad (2.8)$$

$$E = \frac{1}{(2B)^{0.5}} \quad (2.9)$$

This parameter gives information about the physical and chemical adsorption. With the magnitude of E between 8 and 16 kJmol^{-1} the adsorption process follows chemical ion exchange, while for the values of $E < 8 \text{ kJmol}^{-1}$, the adsorption process is of a physical nature.

Kumar et al. 2011 studied the adsorption behavior of nickel(II) from aqueous solution onto agricultural waste such as cashew nut shell . They found that the adsorption process is a function of the parameters such as solution pH, CNS dose, contact time, initial nickel(II) concentration and temperature. The Langmuir, Freundlich, Temkin and Dubinin–Radushkevich models were applied to describe the equilibrium isotherms using nonlinear regression analysis.

2.10 Kinetic Models

The prediction of adsorption rate gives important information for designing batch adsorption systems (Prasanna, 2007). The kinetics of adsorption was studied by using three kinetic models, first order, second order and intra particle diffusion models. These models take into account the adsorbed quantities that will enable us in determining the reactor volume (Azouaou, 2010; Gupta and Rastogi, 2007).

The kinetics in most cases follows the first order rate equation.

$$\frac{dq}{dt} = k_1(q_e - q) \quad (2.10)$$

Where q_e and q are the adsorption capacity at equilibrium and at time t respectively, and k_1 is the rate constant of the pseudo first order adsorption process. The integrated linear form of Eqn.(2.10) can be expressed as follows:

$$\log(q_e - q) = \log(q_e) - \frac{k_1}{2.303}t \quad (2.11)$$

Plot of $\log(q_e - q)$ vs. t gives a straight line for first order adsorption kinetics and the rate constant k_1 is computed from the plot.

The sorption data was also studied by second order kinetics

$$\frac{dq}{dt} = k_2(q_e - q)^2 \quad (2.12)$$

Where k_2 is the second order rate constant.

After integration,

$$\frac{1}{q_e - q} = \frac{1}{q_e} + k_2t \quad (2.13)$$

This can be written in the linear form on further simplification

$$\frac{t}{q} = \frac{1}{k_2q_e^2} + \frac{t}{q_e} \quad (2.14)$$

The applicability of this equation can be studied by a plot of t/q vs. t . Intra particle diffusion was characterized using the relationship between specific sorption (q) and the square root of time ($t^{1/2}$). The relation is expressed as follows (Mehmet et al., 2007; Meriem and Fatima, 2012).

$$q = k_d t^{1/2} \quad (2.15)$$

When the metal ion solution is mixed with the adsorbent, transport of the metal ions from the solution through the interface between the solution and the adsorbent occurs into pores in the particles. There are four main stages in the process of adsorption by porous adsorbents (i) solute transfer from the bulk solution to the boundary film that surrounds the adsorbent's surface, (ii) solute transport from the boundary film to the adsorbent's surface, (iii) solute transfer from the adsorbent's surface to active intraparticle sites, and (iv) interactions between the solute molecules and the available adsorption sites on the internal surfaces of the adsorbent. One or more of these four steps controls the rate at which solute is adsorbed. The first and second steps were very slow and were found to be the rate-determining step shows that the heavy metal ions diffused quickly among the particles at the beginning of the adsorption process, then intraparticle diffusion slowed down and stabilized.

2.11 Adsorption Thermodynamics

The concept of thermodynamics assumed that in an isolated system, where energy cannot be gained or lost, the entropy change is the driving force. In environmental engineering practice, both energy and entropy factors must be considered in order to determine what processes will occur spontaneously. The Gibbs free energy change, ΔG is the fundamental criterion of spontaneity. Reaction occurs spontaneously at a given temperature if ΔG is a negative quantity. The free energy of the sorption reaction considering the sorption equilibrium constant is given by the following equation (Hao Chen et al., 2010; Mohan and Singh, 2002)

$$\Delta G = -RT \ln b \quad (2.16)$$

Where ΔG is the changes in Gibbs free energy, R (8.314 J/mol K) is the universal gas constant, T (K) the absolute temperature and b (L/mol) the thermodynamic equilibrium constant.

Considering the relationship between free energy and the equilibrium constant, change in equilibrium constant can be obtained in the differential form as follows (Yuh et al., 2005)

$$\frac{d \ln b}{dT} = \frac{\Delta H}{RT^2} \quad (2.17)$$

After integration,

$$\ln b = -\frac{\Delta H}{RT} + Y \quad (2.18)$$

Where Y is a constant, the above equation can be rearranged to obtain

$$-RT \ln b = \Delta H - TRY \quad (2.19)$$

$$\text{Let } \Delta S = RY \quad (2.20)$$

Substituting equations (2.16) and (2.20) into (2.19), the Gibbs free energy change,

ΔG , can be represented as follows.

$$\Delta G = \Delta H - T \Delta S \quad (2.21)$$

A plot of Gibbs free energy (ΔG) versus temperature T was found to be linear. The values of enthalpy change ΔH and entropy change ΔS were determined from the slope and intercept of the plots.

2.12 Adsorption in Packed Column

Numerous studies on metal adsorption in batch systems have been

reported in the literature. However in the practical operation of full scale adsorption processes, continuous flow fixed bed column are often preferred. The performance of packed bed column is analysed using the fraction of effluent concentration (C/C_0) versus time curves. For adsorption, the plot is usually referred to as the breakthrough curve and for desorption it is the elution curve. Both curves are a function of the column flow parameters, sorption equilibrium and mass transport factors and much of the information needed to evaluate the column performance is contained in these plots of effluent concentration as a function of time or throughput volume. The general slope of this breakthrough curve depends mainly on the capacity of the column with the respect to the feed concentration bed depth. It is generally observed that decreasing the feed concentration increases the volume of the feed that can be processed and shifts the breakthrough curve to the right. As the concentration of the solute increases in the feed, the breakthrough curve becomes steeper (Valdman et al.,2001; Pakshirajan and Swaminathan, 2006; Sag.and Aktay, 2001; Sivakumar and Palanisamy, 2009).

Francisco et al. (2010) studied the fixed bed column using green coconut shells as adsorbent for the removal of toxic metal ions.

Upendra Kumar and Manas Bandyopadhyay (2006) carried out investigations on fixed bed of sodium carbonate treated rice husk and used for the removal of Cd(II). Different column design parameters like depth of exchange zone, adsorption rate, adsorption capacity, etc. was calculated. Effect of flow rate and initial concentration was studied.

2.12.1 Evaluation of breakthrough curve and mathematical models

The performance of packed beds is described through the concept of breakthrough curve. The time for breakthrough appearance and the shape o

breakthrough curve are very important characteristics for determining the operation and the dynamic response of an adsorption column. The results are given in terms of the maximum (equilibrium) capacity of the column, C_{\max} (mg), the amount of metal loading onto the adsorbent q_{eq} (mg/g) and the adsorption yield (adsorbed metal percent), %Y. The maximum equilibrium capacity of the column for the given feed concentration is equal to the area under the plot of the adsorbed metal concentration, C_{ads} versus time (hours) or the area behind the breakthrough curve. The amount of metal that remains in the effluent, C_{eq} (mg/l), is the area under the breakthrough curve.

$$C_{\max} = Q \int_0^a C_{\text{ads}} dt \quad (2.22)$$

$$C_{\text{eq}} = \frac{C_o t - \int_0^a C_{\text{ads}} dt}{t} \quad (2.23)$$

$$C_{\text{eq}} = \frac{W - q_{\text{eq}} X}{Qt} \quad (2.24)$$

Where Q, W and X are the flow rate (ml/min), metal loading into the column (mg) and the adsorbent weight (g).

The adsorption yield is the ratio of the maximum capacity of the column to the amount of metal loading into the column W (Sag et al., 2001; Aksu et al., 2003; Guibal et al., 1995).

$$Y = \frac{C_{\max}}{W} \times 100 \quad (2.25)$$

2.12.2 Adams-Bohart and Wolborska Models

The fundamental equations describing the relationship between C/C_o and t in a flowing system were established by Adams and Bohart for the adsorption of

chlorine on charcoal. Although the original work by Adams Bohart was done for the gas charcoal adsorption system its overall approach can be applied successfully in quantitative description of other systems. This adsorption model assumes that the adsorption rate is proportional to both the residual capacity of the activated carbon and the concentration of the adsorbing species. The Adams – Bohart model is used for the description of the initial part of the breakthrough curve and is given by the following equation, with parameters k and N_o (Sag et al., 2001; Aksu et al., 2003; Guibal et al., 1995)

$$\ln \frac{C}{C_o} = kC_o t - kN_o \frac{Z}{U_o} \quad (2.26)$$

Where C is the solute concentration (mg/l); Z the bed depth (cm); k the kinetic constant (l/mg hr); U_o the linear flow rate (cm/hr), defined as the ratio of the flow rate Q (ml/hr) to the cross sectional area A (cm²) and N_o the saturation concentration (mg/l).

Wolborska model is also used for the description of adsorption dynamics using mass transfer equations for diffusion mechanisms in the range of the low concentration breakthrough curve. The following relationship describes the concentration distribution in the bed for the low concentration region.

$$\ln \frac{C}{C_o} = \frac{\beta C_o}{N_o} t - \frac{\beta Z}{U_o} \quad (2.27)$$

Where β is the coefficient of the external mass transfer (1/hr). The expression of the Wolborska solution is equivalent to the Adams – Bohart relation if the coefficient k is equal to β/N_o . So the plot of $\ln(C/C_o)$ versus t would give information on both models (Sag et al., 2001; Aksu et al., 2003; Guibal et al., 1995)

Aksu and Gonen have applied Adam Boharts and Wolborska models among others to their experimental data on biosorption of phenol by immobilized activated sludge in a continuous packed bed. Both the models were found suitable for describing the whole or a definite part of the dynamic behavior of the column.

All the models, Adam Boharts and Wolborska models were applied for the dynamic removal of Cr(VI) ions by Chitin in packed column reactor (Sag and Aktay, 2001) and the breakthrough was best predicted by Adam Boharts model.

2.13 Conclusions

This chapter has presented a detailed survey of literature including the methodology followed in this thesis. The following chapters present the details of the research work carried out on the work related to heavy metal removal.

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SELECTION OF ADSORBENTS FOR THE STUDY

3.1 Introduction
3.2 Materials Used
3.3 Adsorption Experiments
3.4 Result And Discussion
3.5 Conclusions

3.1 Introduction

Numerous methods exist to remove detrimental metal ions from aqueous solutions. Several approaches have been reported in this direction utilizing inexpensive and effective adsorbent for removal of heavy metal ions from aqueous solutions (Abdelwahab 2007; Azouaou et al., 2010; Bayat, 2002; Cetin and Pehlivan, 2007; Mustafa 2008; Venkateswarlu et al., 2006). The advantages of the low cost adsorbents over the conventional adsorbents are as follows.

- 1) The efficiencies of various non-conventional adsorbents towards adsorbate removal vary generally between 50% and 90% depending on the characteristics and particle size of the adsorbent, and the characteristics and concentration of the adsorbate, etc. Hence low cost adsorbents can be employed efficiently in removal of heavy metals.
- 2) Non conventional adsorbents are much cheaper relative to conventional adsorbents, and when readily available locally lead to much reduced transportation costs.
- 3) Plant materials are rich in substances called as pectin and lignin which are good adsorbents of heavy metals

- 4) Non conventional adsorbents require simple alkali or acid treatment for the removal of lignin before application in order to increase their efficiency.
- 5) Non- conventional adsorbents require less maintenance and supervision.

The material developed for this purpose range from industrial wastes to agricultural waste products, biomass and various solid substances. In this paper, the use of six different inexpensive and readily available adsorbents was reported to determine their efficiency on removing heavy metal ions from aqueous solution.

3.2 Materials Used

The adsorbent used for the experiments are orange peel, lemon peel, banana peel, mango peel, neem leaves and the leaves of *Alisma plantago aquatica*.

The peels of orange, lemon, banana and mango were collected from local juice shops. They were then washed thoroughly with double distilled water to remove dust and other impurities. Then it was sun dried and cut into small pieces and ground to 250 mesh size. After screening they were again washed with double distilled water several times to remove color. Finally they were dried in an oven at $100\pm 5^{\circ}\text{C}$ for 6hours.

Neem leaves and the leaves of *Alisma plantago aquatica* were obtained from near by areas and were washed to remove dust and soluble impurities and were dried till the leaves became crisp, which were then crushed into a fine powder in a domestic grinder. The powder was sieved and washed number of times with double distilled water till the washings was free of color and turbidity. After drying it was preserved in glass bottles for use as an adsorbent.

3.3 Adsorption Experiments

All reagents used in this study were of analytical grade obtained either from Merck Germany. Stock solution of cadmium, lead, zinc, chromium and copper were prepared by metal nitrate salts in double distilled water and required concentration were obtained by diluting the stock solutions. These test methods cover the determination of metal ions in water samples which were prepared in accordance with ASTM methods Cd(D3557), Pb(D3559), Zn(D1691) Cr(D1687) and Cu(D1688).

Adsorption experiments were carried out by adding 0.2gm dried adsorbent per 100ml metal solutions. Samples are shaken in a temperature controlled incubator shaker at 30°C with 200rpm speed. After 2hour the samples were taken and filtered and analysed using Atomic Adsorption Spectrophotometer.

3.4 Result and Discussion

The selected adsorbents (orange, lemon, banana and mango peels and leaves of neem and *Alisma plantago aquatica*) were used at the concentration of 2gm/l in a batch adsorption technique. Table 3.1 shows the comparison of adsorbent capacity of various low cost adsorbents. When compared with other low cost adsorbents, the results of the present study indicate that adsorbent prepared from mango peel and *Alisma plantago aquatica* have better adsorption capacity in almost all cases.

Table 3.1: Summary of % Recovery and adsorbent capacity of various adsorbents, Initial concentration = 50 mg/l ; Adsorbent dose = 2gm/l

Adsorbent	Heavy metals	Final conc.(mg/l)	% Recovery	q (mg/g)
Orange peel	Cd(II)	15.9	68.21	17.05
	Pb(II)	4.20	91.60	22.90
	Zn(II)	29.00	42.00	10.50
	Cr(III)	6.80	86.40	21.60
	Cu(II)	19.68	60.64	15.16
Lemon peel	Cd(II)	27.10	45.80	11.45
	Pb(II)	3.84	92.32	23.08
	Zn(II)	47.40	5.20	1.30
	Cr(III)	25.14	49.72	12.43
	Cu(II)	7.37	85.26	21.32
Banana peel	Cd(II)	21.20	57.60	14.40
	Pb(II)	3.64	92.72	23.18
	Zn(II)	49.56	0.88	0.22
	Cr(III)	12.40	75.20	18.80
	Cu(II)	20.80	58.40	14.60
Mango peel	Cd(II)	19.25	61.50	15.38
	Pb(II)	15.44	69.12	17.28
	Zn(II)	18.18	63.64	15.91
	Cr(III)	15.24	69.52	17.38
	Cu(II)	16.55	66.90	16.73
Neem leaves	Cd(II)	20.7	58.60	14.65
	Pb(II)	3.98	92.04	23.01
	Zn(II)	31.12	37.76	9.44
	Cr(III)	24.30	51.40	12.85
	Cu(II)	17.50	65.00	16.25
<i>Alisma plantago aquatica</i> leaves	Cd(II)	13.6	72.80	18.20
	Pb(II)	3.72	92.56	23.14
	Zn(II)	11.10	77.80	19.45
	Cr(III)	11.32	77.16	19.29
	Cu(II)	12.53	74.94	18.74

3.5 Conclusions

Two suitable low cost naturally available material have been identified as the effective adsorbent to remove Cd^{2+} , Pb^{2+} , Zn^{2+} , Cr^{3+} and Cu^{2+} from aqueous solution. The fourth and fifth chapters deal with the detailed studies using mango peel and *Alisma plantago aquatica*.

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ADSORPTION STUDIES USING MANGO PEEL

- 4.1 Introduction**
- 4.2 Materials and Methods**
- 4.3 Results and Discussion**
- 4.4 Characterization of the Adsorbent**
- 4.5 Conclusions**

4.1 Introduction

Most of the adsorption studies have been focused on low cost adsorbents. Some of the advantages of using plant wastes for waste water treatment include involvement of simple techniques requirement of very little processing, good adsorption capacity, selective adsorption of heavy metal ions, low cost, free availability etc. In this work batch studies are carried out using mango peel.

4.2 Materials and Methods**4.2.1 Adsorbent**

The experiments were carried out using the adsorbent mango peel. The adsorbent samples were collected from the near by locality and washed several times with distilled water to remove dust and other impurities. Then drying, it was ground using domestic mixer and sieved to 250 mesh size. The sample is washed with distilled water to remove colour and dried in an oven at 80°C for 24 hours. The dried sample was stored in airtight bottles for further use without any chemical or physical treatment.



Figure 4.1 Fine grains of dry mango peel

4.2.2 Reagents

All reagents used in this study were of analytical grade obtained from Merck Germany. Stock solutions of cadmium, lead, zinc, chromium and copper were prepared by metal nitrate salts in double distilled water and the required concentrations were obtained by diluting the stock solutions. Test methods cover the determination of metal ions in water samples prepared in accordance with ASTM methods Cd(D3557), Pb(D3559), Zn(D1691) Cr(D1687) and Cu(D1688).

4.2.3 Instrument

The initial metal concentration and the concentration of the metal remaining on the solution were determined using Atomic absorption spectrophotometer as shown in figure 4.2 (Thermofisher iCE:3000). FTIR spectra were obtained on a PERKIN ELMER model Spectrum Two. A SEM was used to study the outer surface micro porosity and pore size of the dried adsorbent sample (HITACHI SU 6600).



Figure 4.2 Photograph of Atomic absorption spectrophotometer

4.2.4 Batch studies

A fixed amount of dry adsorbent 0.1g and 100ml of metal solution were placed in a volumetric flask and shaken at 200rpm using a temperature controlled incubator shaker at $25\pm 2^{\circ}\text{C}$. The Metal ion concentrations used were in the range of 10-100mg/l. The pH of the solution was maintained at 5.5 ± 0.5 and the contact time of 120min was used for batch tests. To study the effect of pH, the pH of the metal solution was adjusted to different values ranging from 2 to 7. The desired pH was adjusted by 0.1N HCl and 0.1 N NaOH solutions. Then, the samples were filtered to remove any fine particles and analyzed for the metal ions using atomic absorption spectrophotometer.

4.2.5 Equilibrium studies

Adsorption equilibrium studies were conducted to determine the nature

of the adsorption isotherms and the adsorption capacity of the adsorbent for the removal of metal ions. For the isotherm studies, the initial metal concentrations were varied from 10 to 100 mg/l using 1g/l (dry weight) adsorbent.

The adsorption flasks were agitated in an incubator shaker at 200rpm and samples were collected at specified time intervals and were analyzed for the residual metal concentration followed by separation of the biomass by filtration.

4.2.6 Kinetic studies

Kinetic studies were carried out in a volumetric flask and samples were collected at different intervals of 5min to 120 min. The samples were analysed for residual metal concentration.

4.2.7 Thermodynamic studies

The experiments were conducted at different temperatures in the range of 20 - 50°C in an incubator shaker for 2hours. The samples were filtered and analysed for residual concentration at the end of the experiments

4.2.8 Desorption studies

To check the potential for recovery and reuse of the adsorbent, batch regeneration and reuse studies were carried out using different regenerants. The studies were carried out using HCl, H₂SO₄, HNO₃, H₂C₂O₄, NaOH and Na₂CO₃ of known concentration of 0.1N with the metal loaded mango peel. To the biomass separated after adsorption, 100ml of the regenerant solution was added and the mixture was agitated in the shaker for 60 minutes at 200rpm. The samples were collected and analysed for the released metal concentration.

4.3 Results and Discussion

Thorough studies were carried out in order to determine the effects of the operational parameters on metal ion adsorption. The operational parameters studied included the time required for equilibrium, the biomass dose and the pH of the solution. The uptake of metal ions by the biomass of mango peel was initially evaluated in batch condition.

4.3.1 Effect of contact time

The purpose of the experiment was to determine the contact time required to reach the equilibrium between the solid phase (biomass) and liquid phase (effluent). Figure 4.3 shows that the percentage uptake increases with time and after some time, it reaches a constant value where no more metal ion can be removed from the solution (Azouaou et al., 2010; Maria Martinez et al., 2006; Mohammad Mehdi et al., 2011). At this point, the amount of metal ions being adsorbed by the adsorbent was in a state of dynamic equilibrium with the amount of metal ions desorbed from the adsorbent. The time required to attain this state of equilibrium is termed the equilibrium time. The amount of metal ion adsorbed at the equilibrium time reflects the maximum adsorption capacity of the adsorbent under these particular conditions. The result showed that the adsorption of metal ion increases with time up to 1 hour and then it becomes almost constant at the end of the experiment. It can be concluded that the rate of metal binding with biomass is more predominant during initial stages, which gradually decreases and remains almost constant after 120 min. The active adsorption sites of the adsorbent get involved in metal complexation as soon as the adsorbent is introduced into the system.

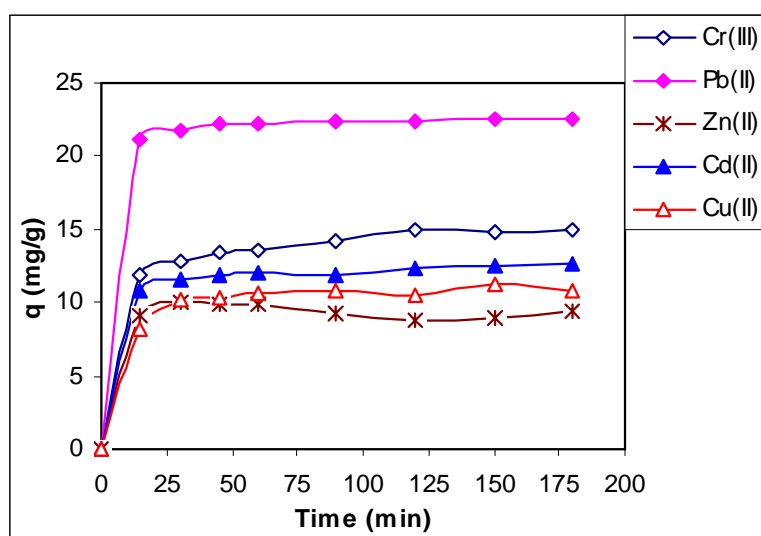


Figure 4.3 Metal uptake capacities at varying time intervals

(Initial concentration=50ppm, Adsorbent dose=0.3gm/100ml metal solution, temperature = $25\pm 2^{\circ}\text{C}$, pH=5, Orbital shaking speed=200rpm, Time 180min.)

4.3.2 Effect of Adsorbent dose

The effect of biomass dosage on metal adsorption is shown in Figure 4.4. The adsorption of metal ions increased with the adsorbent dosage and at adsorbent dosage above 0.4gm/100ml reached equilibrium. The percentage of metal removal increased with the increasing amount of biomass.(Azouaou et al., 2010; EI-Said et al., 2010; Saifuddin and Kumaran 2005). This may be attributed to the availability of more and more binding sites for complexation of metal ions. Further increment in adsorbent dose did not cause significant improvement in adsorption. This seems to be due to the binding of almost all ions to the adsorbent and equilibrium is reached between the ions bound to the adsorbent and those remaining unadsorbed in the solution.

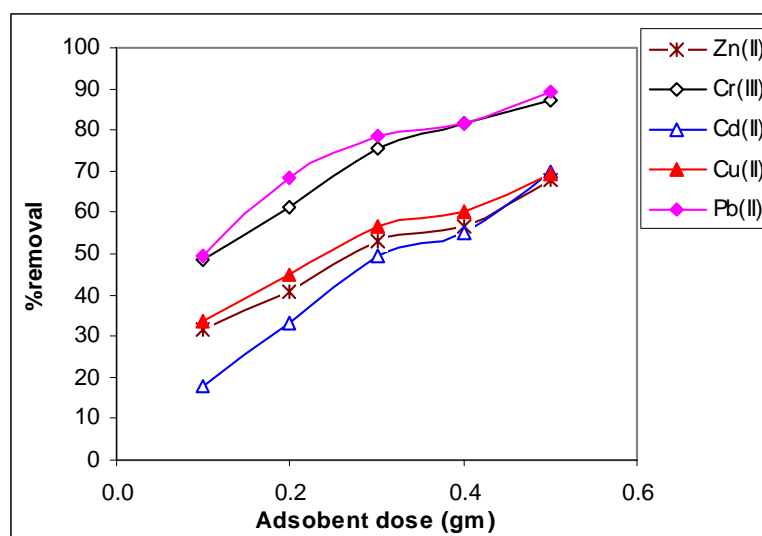


Figure 4.4 Effect of adsorbent dose on metal adsorption

(Initial concentration=50ppm, Adsorbent dose=0.1 to 0.5 gm/100ml metal solution, temperature = $25\pm 2^\circ\text{C}$, pH=5, Orbital shaking speed=200rpm, Time=120min.)

4.3.3 Effect of varying concentration of metal ions

The rate of adsorption is a function of initial concentration of metal ions. Figure 4.5 indicates that higher adsorption was found to take place at lower concentrations. This may be due to the interaction of all metal ions present in the solution with binding sites. At higher concentrations, more metal ions are left unadsorbed in solution due to saturation of adsorption sites (Azouaou et al., 2010; Mausumi et al., 2006; Mohammad Mehdi et al., 2011). The number of ions adsorbed from a solution of higher concentrations is more than that removed from less concentrated solutions.

According to SenthilKumar *et al.* (2010), at lower metal ions concentration, the percentage uptake was higher due to larger surface area of adsorbent being available for adsorption. When the concentration of metal ions became higher, the percentage removal decreased since the available sites for adsorption became less due to saturation of adsorption sites. At a higher concentration of metal

ions, the ratio of initial number of moles of metal ions to the adsorption sites available was higher, resulting in lower adsorption percentage.

However, different from the percentage uptake, with the increasing initial metal ions concentration from 10 mg/L to 100 mg/L, the amount of metal ions adsorbed at equilibrium increased. This occurred due to increase in driving force of the concentration gradient to overcome all mass transfer resistance of metal ions between aqueous and solid phases and accelerate the probable collision between metal ions and sorbents, thus resulting in higher uptake of metal ions (Chen *et al.*, 2005).

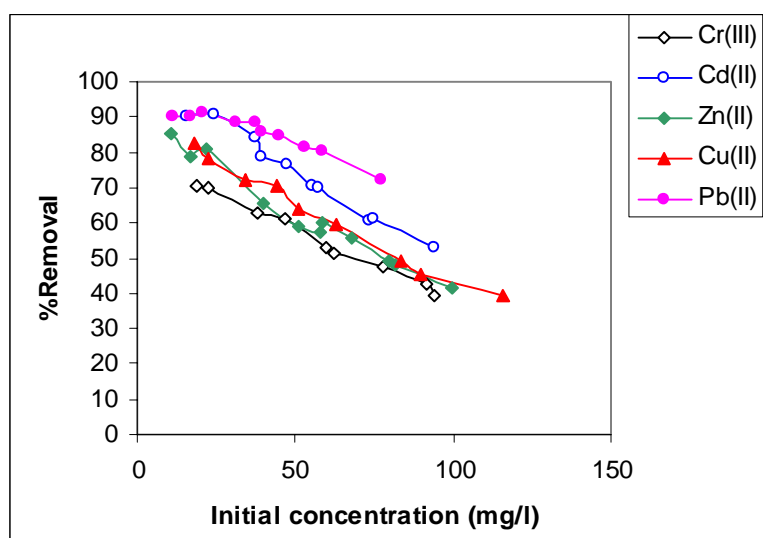


Figure 4.5 Effect of varying concentration of metal ions
(Initial concentration=10 to 100ppm, Adsorbent dose=0.3gm/100ml metal solution, temperature = $25\pm 2^\circ\text{C}$, pH=5, Orbital shaking speed=200rpm, Time=120min.)

4.3.4 Effect of pH

pH influences the surface charge of the adsorbent, the degree of ionization and the species of adsorbate. So the pH of the aqueous solution is an important controlling parameter in the heavy metal adsorption process

(Azouaou et al., 2010; Babu and Gupta 2008; Gupta and Rastogi 2007). The effect of pH on the adsorption of Cd(II), Pb(II), Zn(II), Cr(III) and Cu(II) by mango peel is shown in Figure 4.6. The effect of solution pH on the adsorption of metal ions onto mango peel was evaluated in the pH range of 2 to 8. The highest removal efficiency for Cd(II) and Cr(III) adsorption with mango peel was obtained at pH6, Pb(II) and Cu(II) at pH4 and Zn(II) at pH7. At pH 2, which had the highest acidity, metal ions uptake by mango peel was the lowest. pH range of 3 to 7, the percentage removal increased rapidly and the removal became consistent, ranging between 80% and 95%. At lower pH values, the adsorption efficiency was found to decrease.

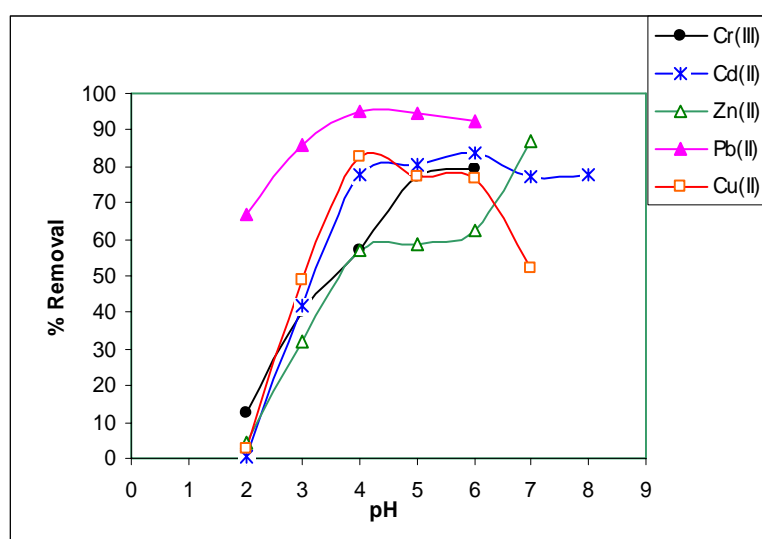


Figure 4.6 Effect of varying pH on metal ions adsorption
 (pH = 2 to 8, Initial concentration=50ppm, Adsorbent dose=0.3gm/100ml metal solution, temperature =25±2°C, Orbital shaking speed=200rpm, Time=120min.)

The low adsorption of metal ions at pH 2 was due to high concentration and high mobility of H⁺ ions, which competed with metal ions for the adsorption sites, hindering the adsorption of Cd²⁺ Pb²⁺ Zn²⁺ Cr³⁺ and Cu²⁺ ions by adsorbent. Protonated adsorption sites were incapable of binding metal

ions due to electrostatic repulsion between positively charged metal ions and positive charged sites. Hence, only low percentage of Cd^{2+} Pb^{2+} Zn^{2+} Cr^{3+} and Cu^{2+} ions were adsorbed. As the pH increased, there were fewer H^+ ions present in the solution and consequently more negatively charged sites were made available and this facilitated greater metal ions uptake by electrostatic attraction.

4.3.5 Adsorption isotherms

Adsorption isotherms show the distribution of solute between the liquid and solid phases and can be described by several mathematical relationships such as the standard Langmuir and Freundlich and Dubinin-Radushkevich models were as shown in the Figures 4.7–4.21. The linearized Langmuir and Freundlich adsorption isotherms obtained are shown in the Table 4.1 with the values of linear regression coefficients. In view of the values of the linear regression coefficients, Langmuir model fits very well to the sorption data in the studied concentration range studied.

The higher the b , the higher is the affinity of the adsorbent for metal ions. q_{max} can also be interpreted as the total number of binding sites that are available for adsorption and q as the number of binding sites that are in fact occupied by the metal ions at the concentration C_f (Volesky 1995). According to the above data, the affinity order of mango peel is $\text{Pb} > \text{Cr} > \text{Zn} > \text{Cd} > \text{Cu}$.

Langmuir isotherm, which represents that monolayer of metal ions are formed on adsorbent. The constant K and $1/n$ were determined by linear regression from the plot of $\log q$ against $\log C_f$. K is a measure of the degree or strength of adsorption. Small value of K indicates the more adsorption (Horsfall et al., 2006) while $1/n$ is used as an indication of whether adsorption remains constant (at $1/n=1$) or decreases with increasing metal ions

concentrations. The magnitude of the experimental q_{\max} for mango peel is found to be 31, 24.8, 24.5, 16.7 and 16mg/g for all the five which are Pb,Cr,Zn,Cd and Cu ions that are comparable with theoretically calculated q_{\max} .

An adsorption isotherm is characterized by certain constants, the values of which express the surface properties and affinity of the sorbent. The Freundlich constants k and $1/n$ are adsorption capacity and adsorption intensity which were determined for Cd(II),Pb(II),Zn(II) Cr(III) and Cu(II) at different temperatures and are summarized in the Table 4.1.The Langmuir constants of q_{\max} and b were determined from C_f/q versus C_f plot. The applicability of Langmuir isotherms implies that monolayer adsorption exist under the experimental conditions. The Langmuir isotherm constants do not explain the chemical or physical properties of the adsorption process. However, the mean adsorption energy (E) calculated from the D-R isotherm provides important information about these properties (Azouaou et al., 2010; Can and Jianlong 2007; Hao Chen et al., 2010). The adsorption energies are less than 2 kJmol^{-1} suggesting that the sorption process was dominated by physical forces at all studied temperatures.

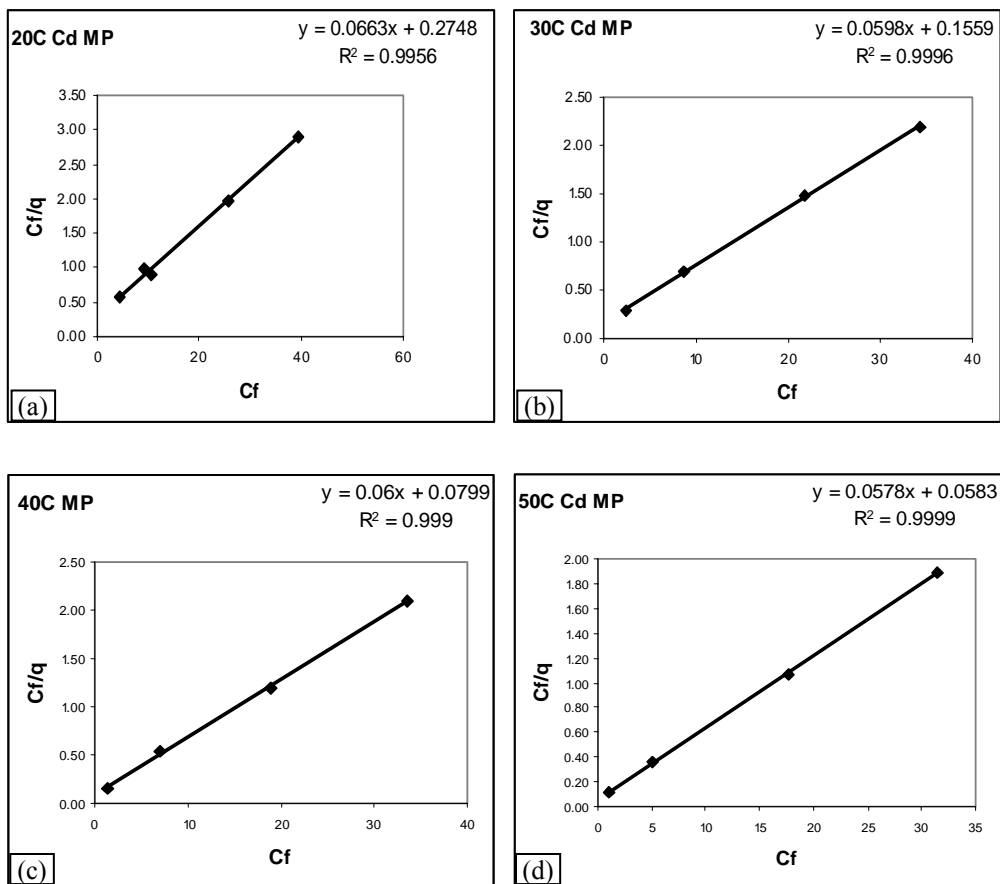


Figure 4.7 (a), (b) ,(c),(d) Langmuir plot for cadmium adsorption at 20,30, 40 and 50°C

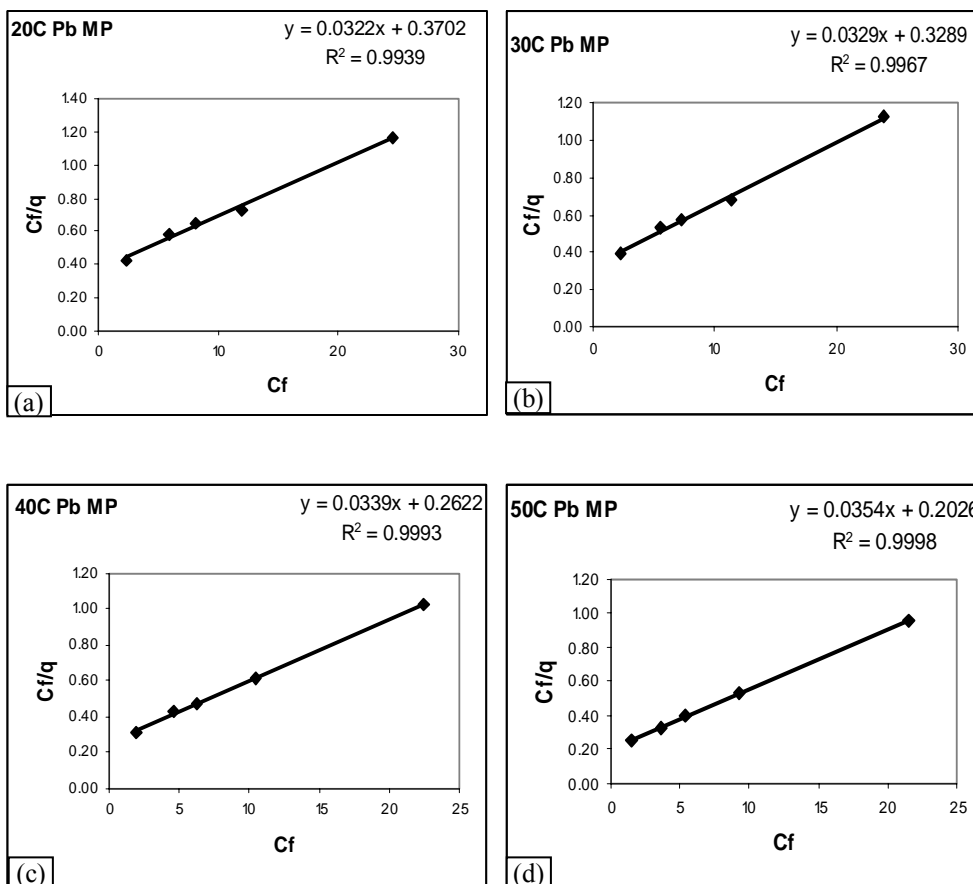


Figure 4.8 (a), (b), (c), (d) Langmuir plot for lead adsorption at 20, 30, 40 and 50°C

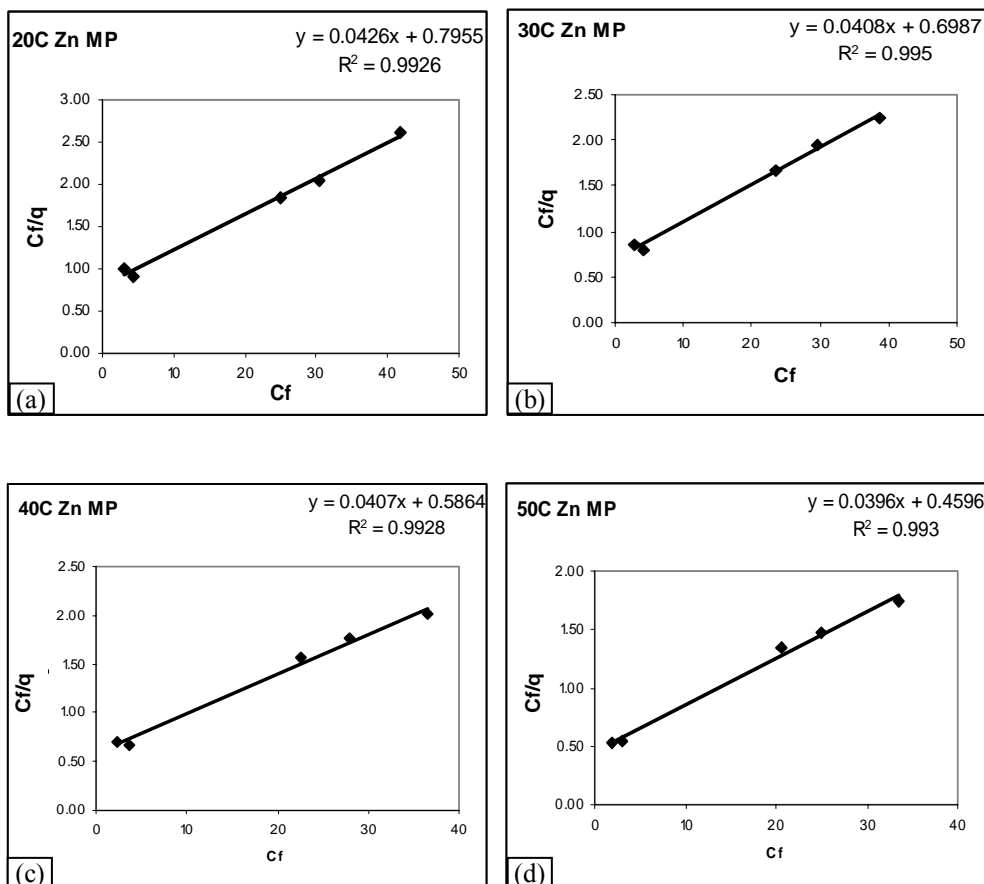


Figure 4.9 (a), (b), (c), (d) Langmuir plot for zinc adsorption at 20,30, 40 and 50°C

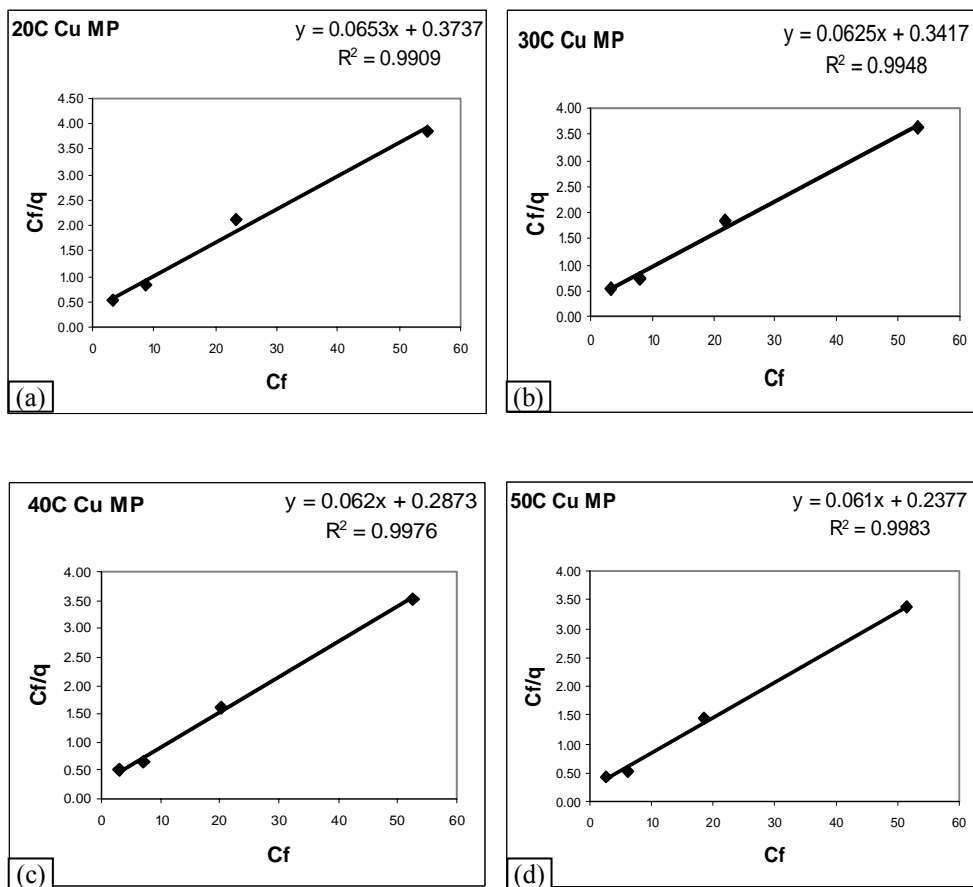


Figure 4.10 (a), (b), (c), (d) Langmuir plot for copper adsorption at 20,30, 40 and 50°C

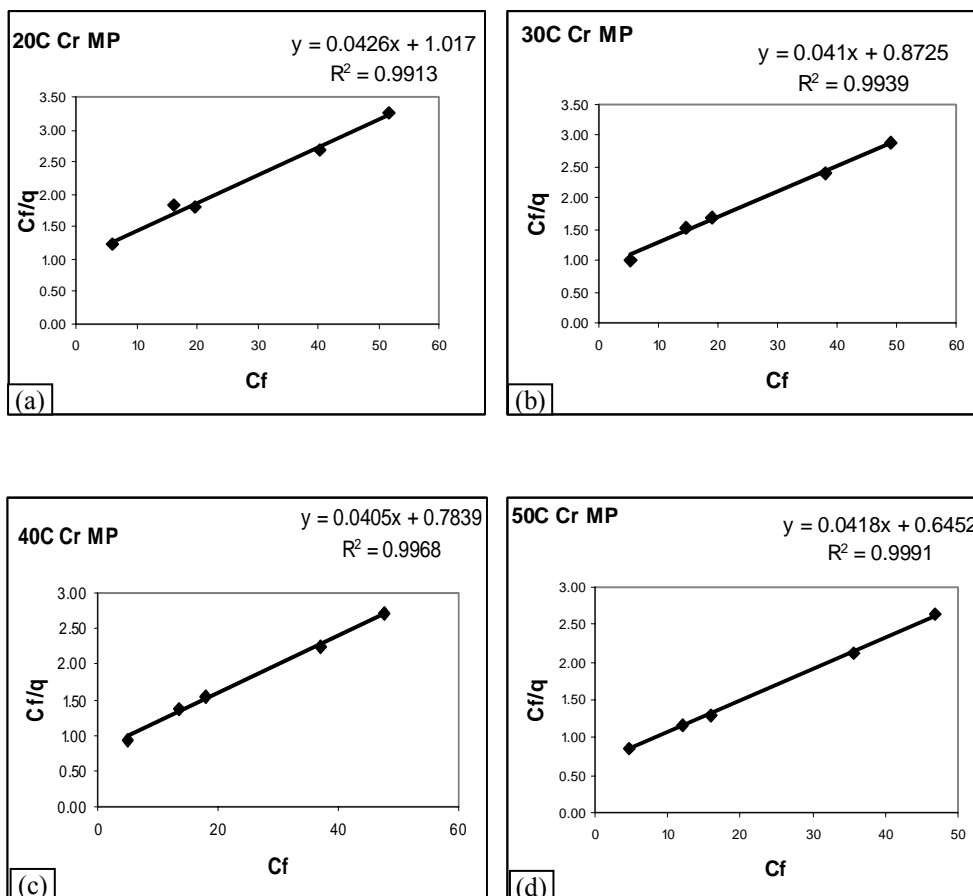


Figure 4.11 (a), (b), (c), (d) Langmuir plot for chromium adsorption at 20,30, 40 and 50°C

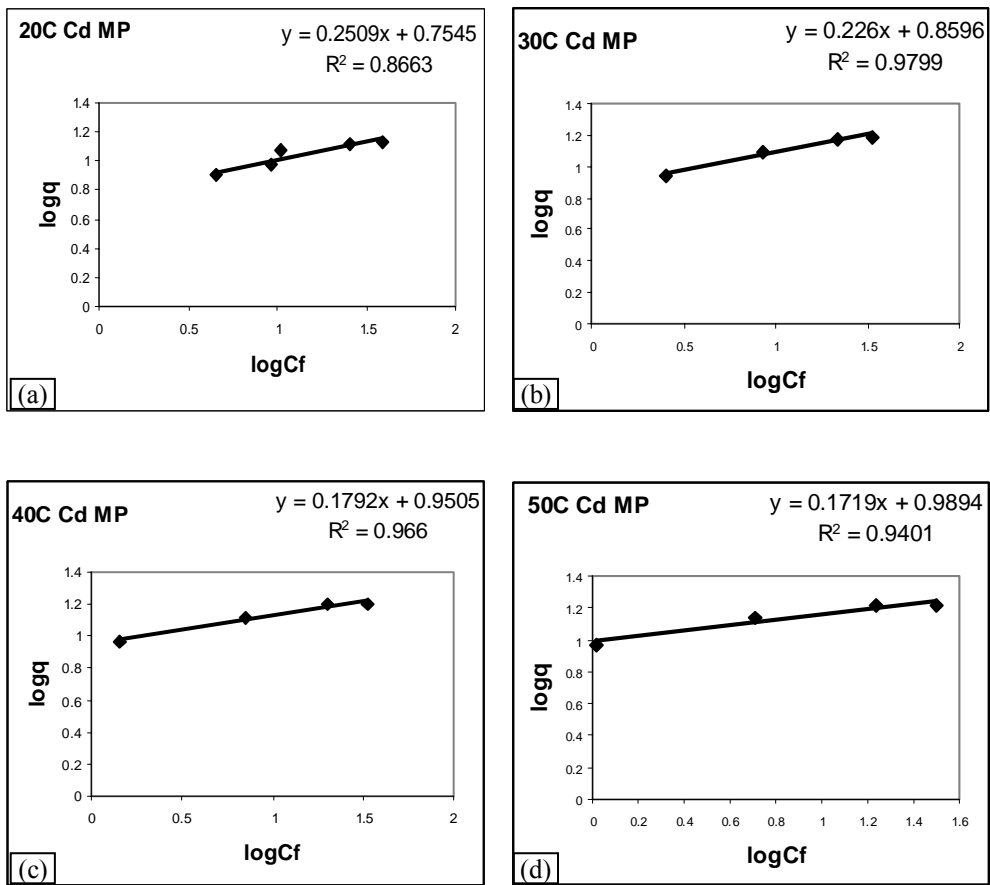


Figure 4.12 (a), (b), (c), (d) Freundlich plot for cadmium adsorption at 20,30, 40 and 50°C

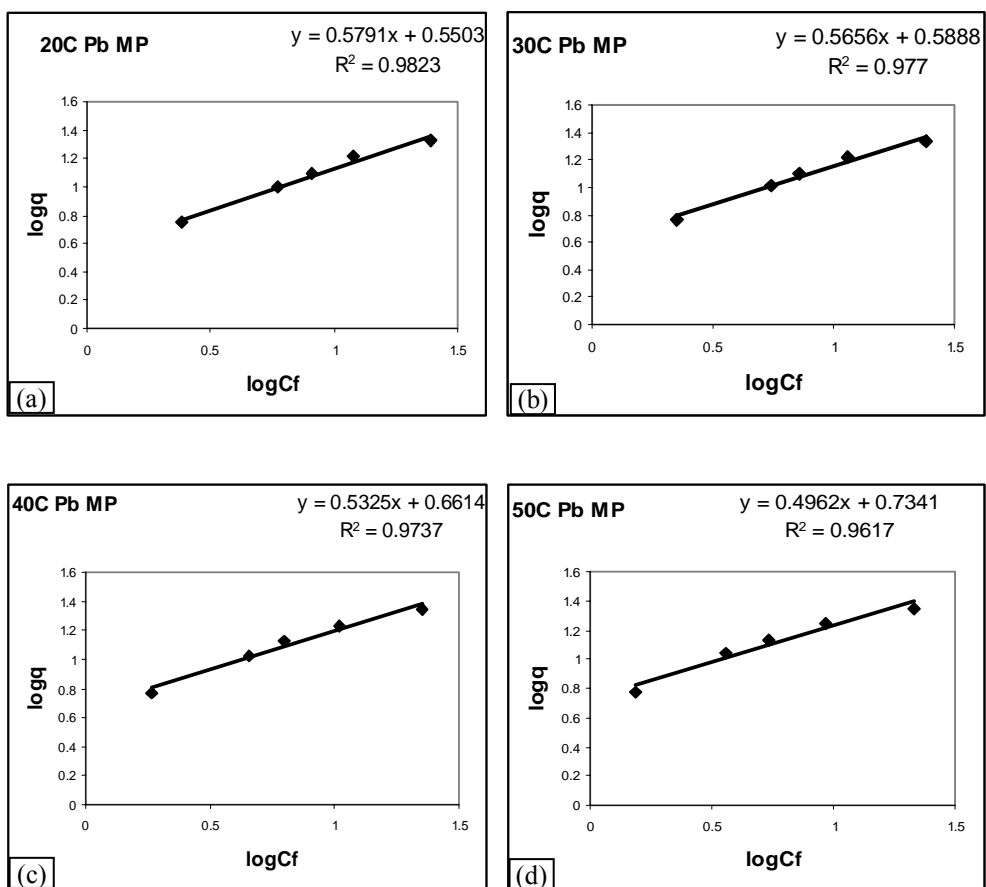


Figure 4.13 (a), (b), (c), (d) Freundlich plot for lead adsorption at 20,30, 40 and 50°C

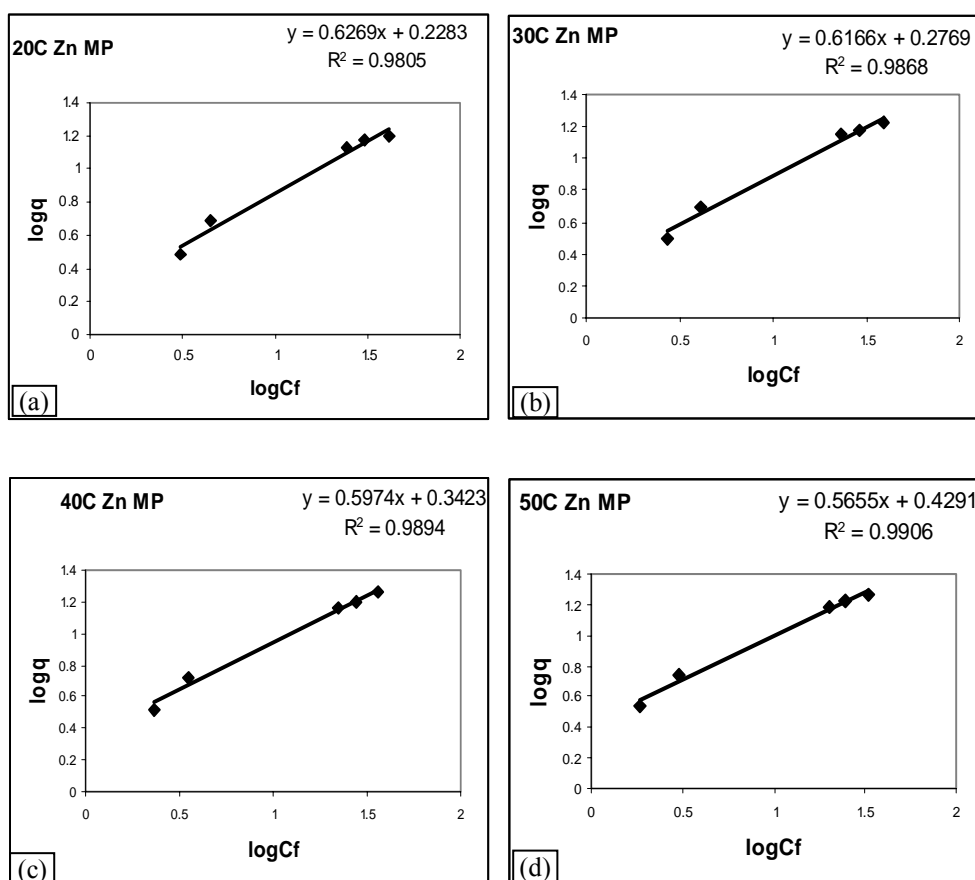


Figure 4.14 (a), (b), (c), (d) Freundlich plot for zinc adsorption at 20,30, 40 and 50°C

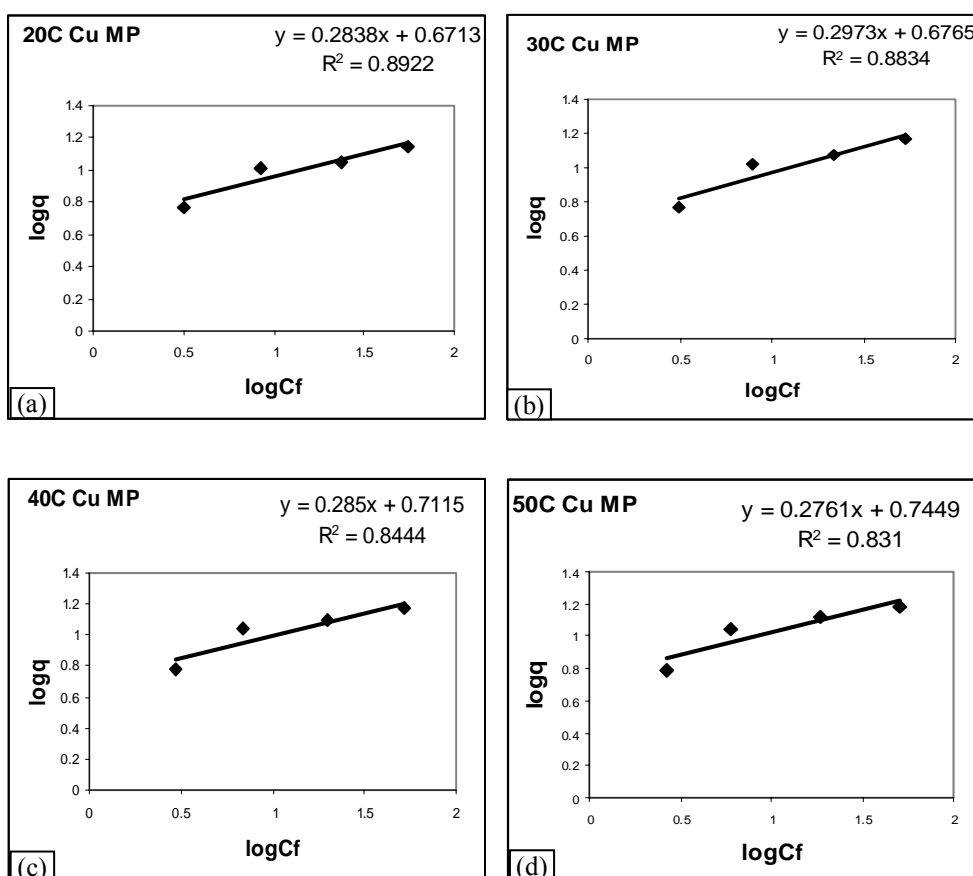


Figure 4.15 (a), (b), (c), (d) Freundlich plot for copper adsorption at 20,30, 40 and 50°C

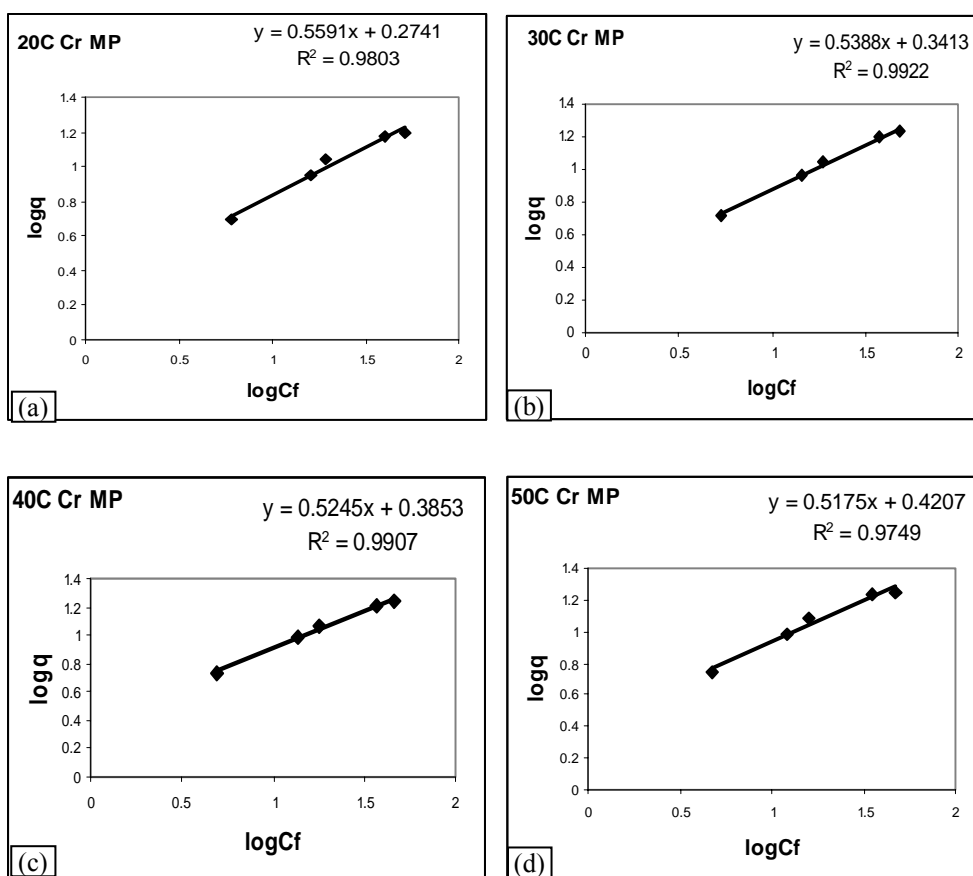


Figure 4.16 (a), (b), (c), (d) Freundlich plot for chromium adsorption at 20,30, 40 and 50°C

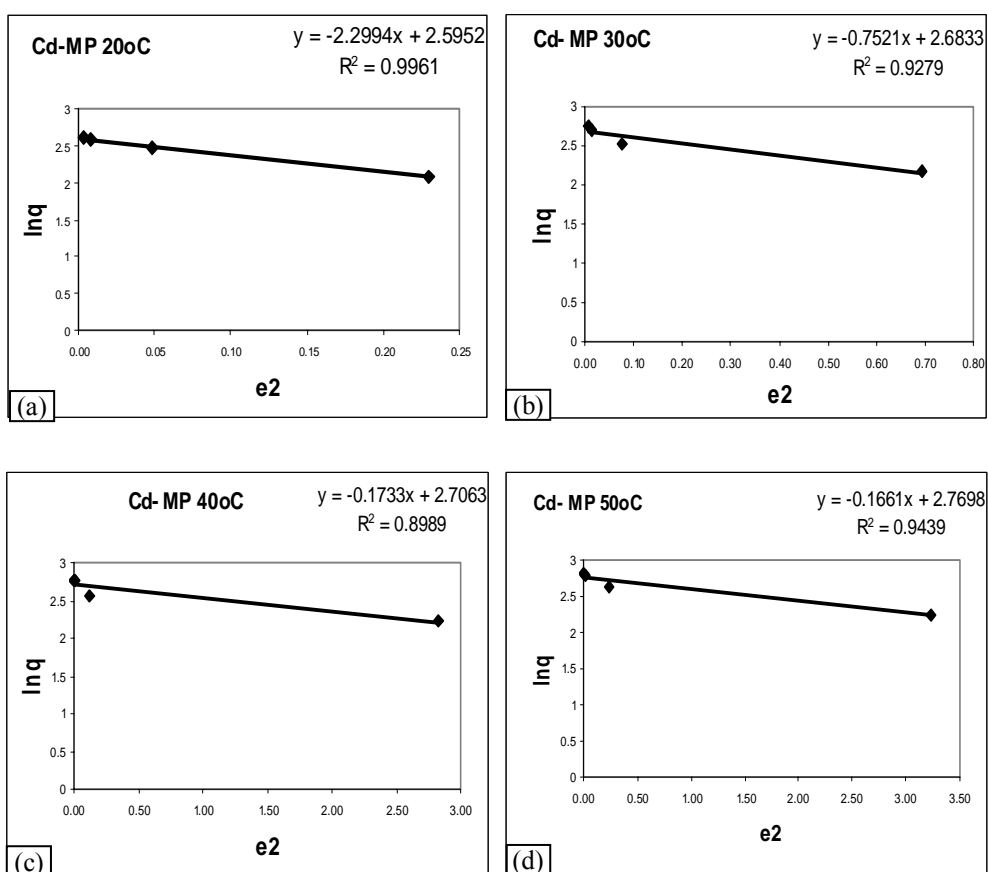


Figure 4.17 (a), (b), (c), (d) Dubinin-Radushkevich plot for cadmium adsorption at 20,30, 40 and 50°C

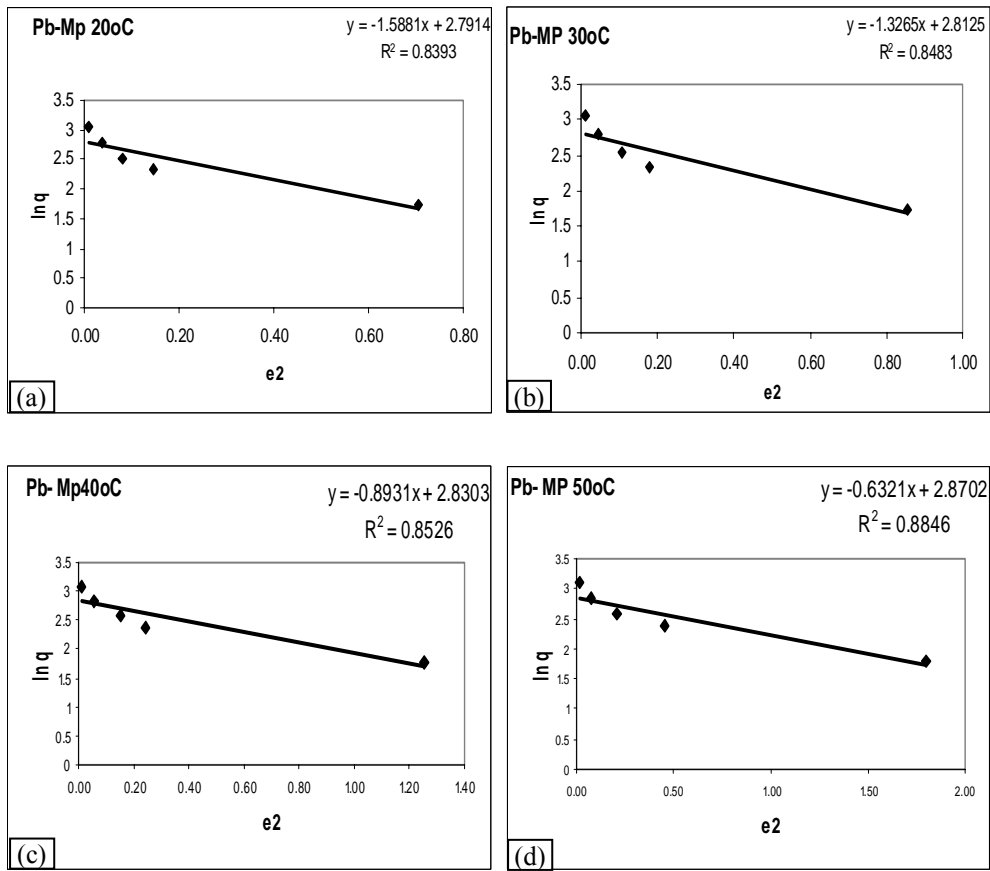


Figure 4.18 (a), (b), (c), (d) Dubinin-Radushkevich plot for lead adsorption at 20,30, 40 and 50°C

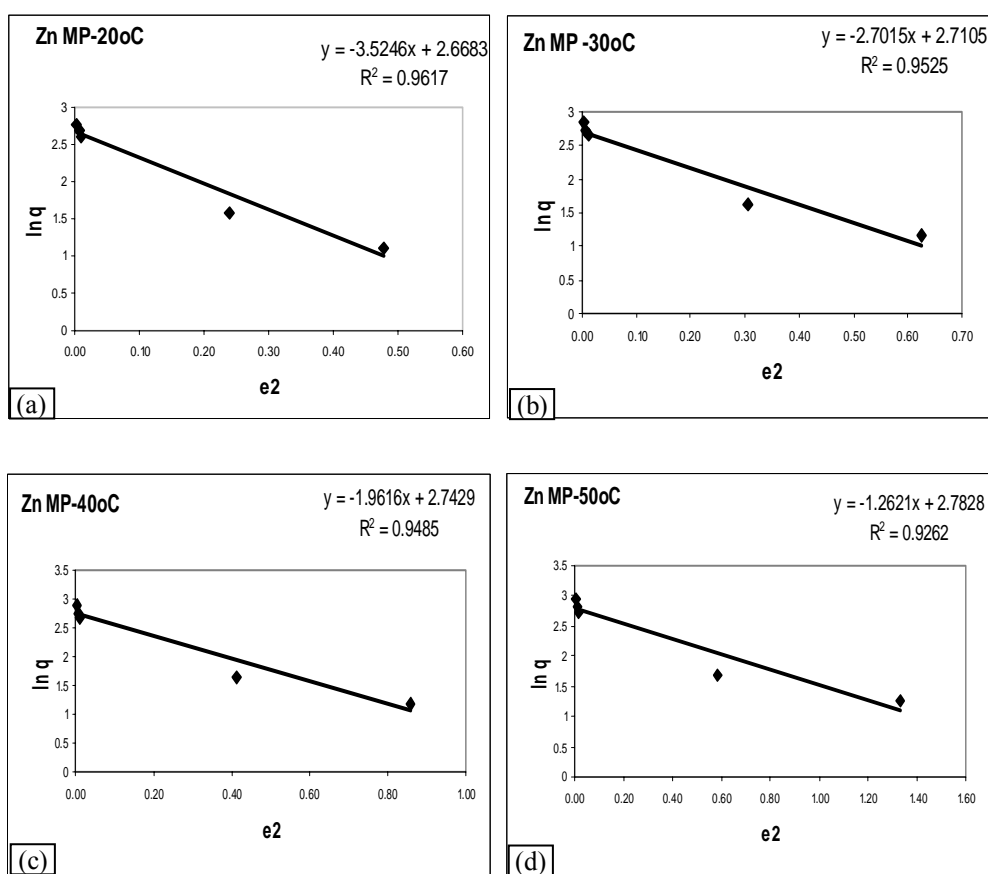


Figure 4.19 (a), (b), (c), (d) Dubinin-Radushkevich plot for zinc adsorption at 20,30, 40 and 50°C

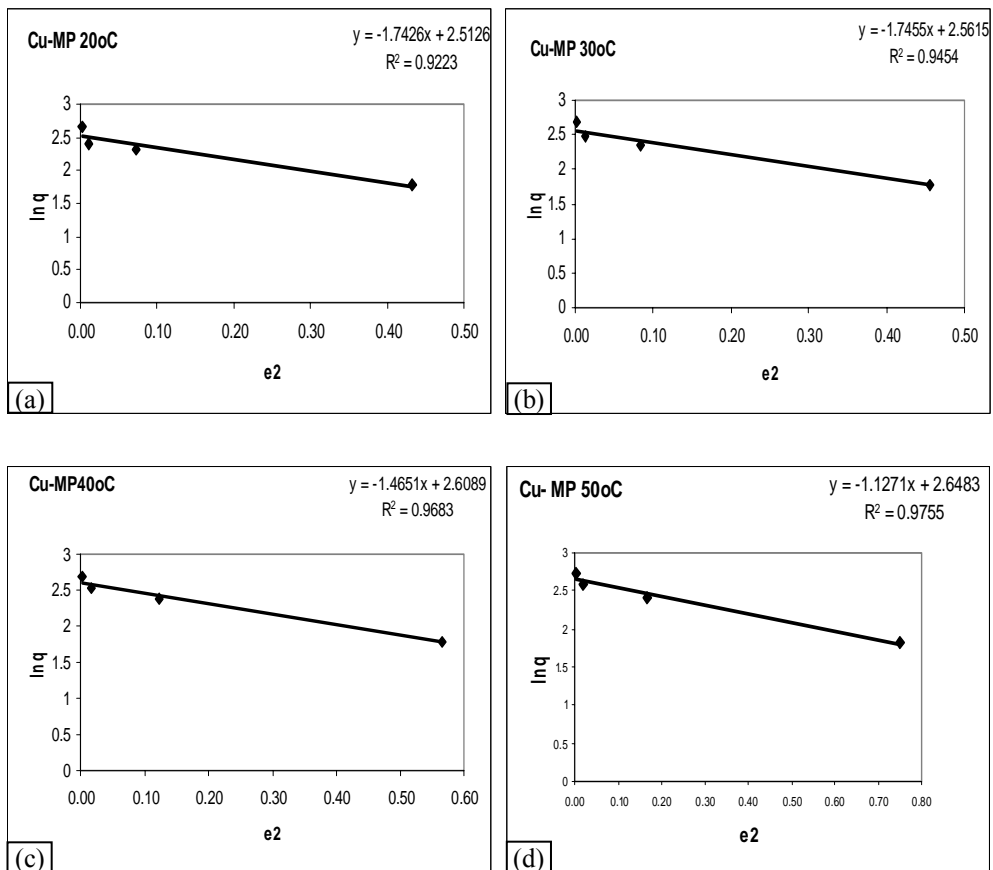


Figure 4.20 (a), (b), (c), (d) Dubinin-Radushkevich plot for copper adsorption at 20,30, 40 and 50°C

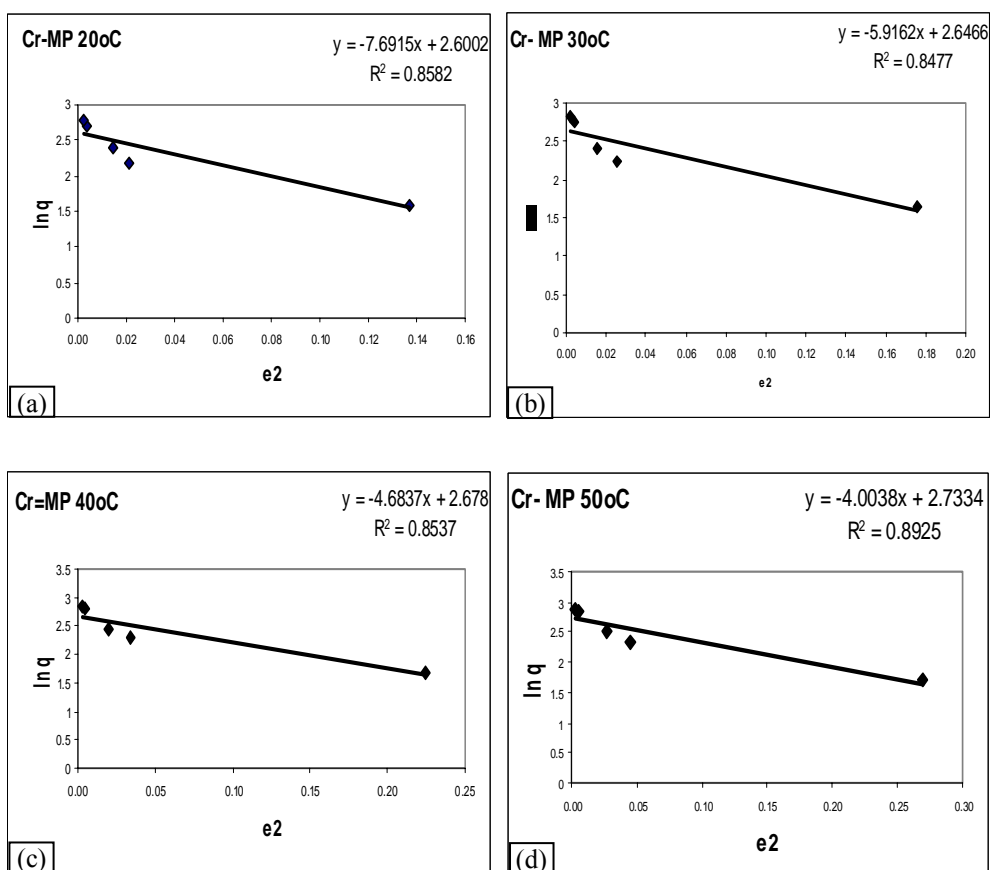


Figure 4.21 (a), (b), (c), (d) Dubinin-Radushkevich plot for chromium adsorption at 20,30, 40 and 50°C

Table 4.1 Isotherm parameters for the adsorption of Cd(II), Pb(II), Zn(II), Cu(II) and Cr(III) onto Mango peel

Heavy Metals	T(K)	R ²	Langmuir model		Freundlich model			Dubinin-Radushkevich		
			q _{max} (mg/g)	b(Lmg ⁻¹)	R ²	1/n	K	R ²	q _{max} (mg/g)	E(kJmol ⁻¹)
Cd(II)	293	0.995	15.08	0.241	0.866	0.251	5.68	0.996	13.40	0.466
	303	0.999	16.72	0.384	0.979	0.226	7.23	0.928	14.63	0.815
	313	0.999	16.67	0.751	0.940	0.179	8.92	0.899	14.97	1.698
	323	0.999	17.30	0.992	0.966	0.172	9.76	0.944	15.95	0.910
Pb(II)	293	0.994	31.05	0.086	0.982	0.579	3.55	0.839	16.29	0.561
	303	0.996	30.40	0.110	0.977	0.565	3.87	0.848	16.65	0.614
	313	0.999	29.50	0.129	0.973	0.532	4.58	0.853	16.95	0.748
	323	0.999	28.25	0.175	0.961	0.496	5.42	0.885	17.64	0.889
Zn(II)	293	0.993	23.47	0.053	0.980	0.627	1.69	0.962	14.42	0.377
	303	0.995	24.50	0.058	0.987	0.617	1.89	0.953	15.03	0.430
	313	0.993	24.57	0.069	0.989	0.597	2.19	0.948	15.53	0.505
	323	0.993	25.25	0.086	0.991	0.565	2.68	0.926	16.16	0.629
Cu(II)	293	0.991	15.30	0.175	0.892	0.284	4.69	0.922	12.33	0.536
	303	0.995	16.00	0.183	0.883	0.297	4.75	0.945	12.95	0.535
	313	0.998	16.13	0.216	0.844	0.285	5.15	0.968	13.58	0.584
	323	0.998	16.40	0.256	0.831	0.276	5.55	0.975	14.13	0.666
Cr(III)	293	0.991	24.80	0.039	0.980	0.561	1.88	0.858	13.46	0.255
	303	0.994	24.39	0.047	0.994	0.540	2.18	0.847	14.10	0.291
	313	0.995	24.69	0.052	0.991	0.529	2.43	0.854	14.52	0.326
	323	0.999	23.90	0.065	0.975	0.518	2.63	0.892	15.38	0.353

4.3.6 Adsorption kinetics

In order to define the adsorption kinetics of heavy metals ions, the kinetic parameters for the adsorption processes were studied for the contact times ranging between 1 to 150 min and first order, second order and intra particle diffusion models were applied to experimental data as shown in Figures 4.22 – 4.28.

The first order kinetic equation is

$$\log(q_e - q) = \log(q_e) - \frac{k_1}{2.303} t \quad (4.1)$$

Where q_e and q are the adsorption capacity at equilibrium and at time t respectively and k_1 is the rate constant of the pseudo first order adsorption process.

Plot of $\log(q_e - q)$ vs. t gives a straight line for first order adsorption kinetics and the rate constant k_1 is computed from the plot.

The sorption data was also studied by second order kinetics

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (4.2)$$

The applicability of this equation can be studied by a plot of t/q vs. t .

Intra particle diffusion was observed using the relationship between specific sorption (q) and the square root of time ($t^{1/2}$). The relation is expressed as follows

$$q = k_d t^{1/2} \quad (4.3)$$

The comparison of experimental sorption capacities (q_{exp}) and the predicted values (q_{cal} , k_1, k_2, k_d , R^2) from pseudo first order, pseudo second order and intra particle diffusion constants are given in Table:4.2 The pseudo first order was not satisfactory to explain the experimental data, whereas the calculated, q_{cal} values derived from the pseudo second order model for sorption of metal ions were very close to the experimental (q_{exp}) values. The second order equation appeared to be the better fitting model than first order and intra particle diffusion equations because it has higher R^2 value (Azouaou 2010; Gupta and Rastogi 2007).

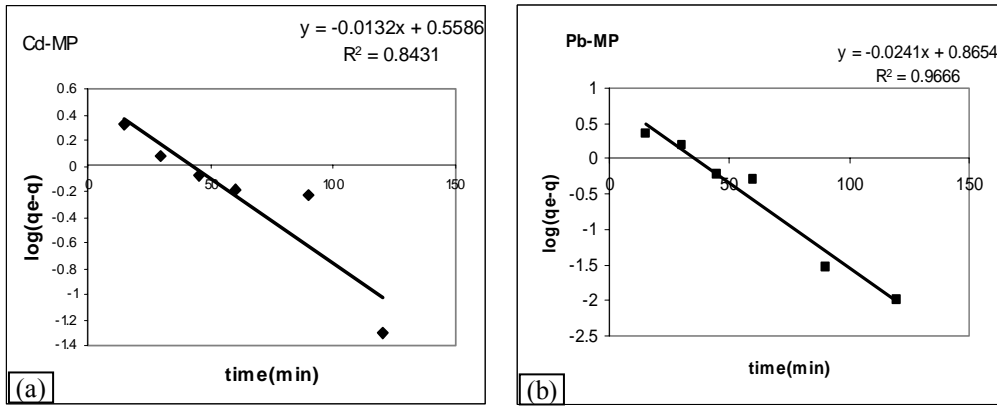


Figure 4.22 (a), (b) First order adsorption kinetics plot of cadmium & lead

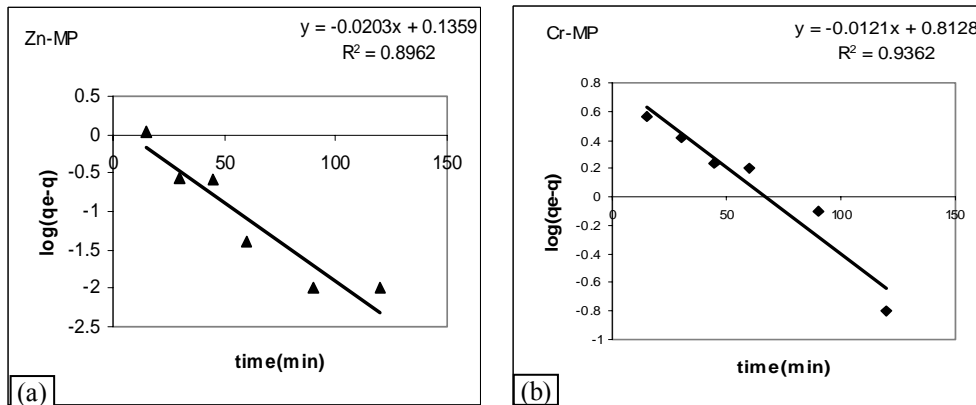


Figure 4.23 (a), (b) First order adsorption kinetics plot of zinc & chromium

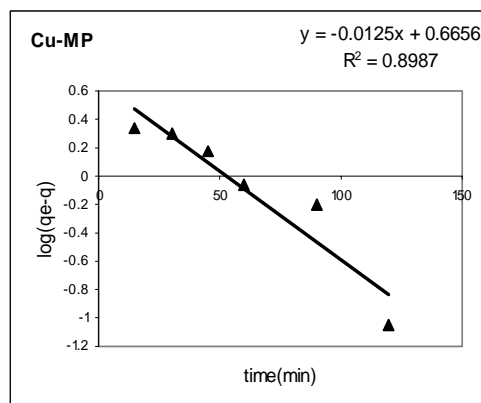


Figure 4.24 First order adsorption kinetics plot of copper

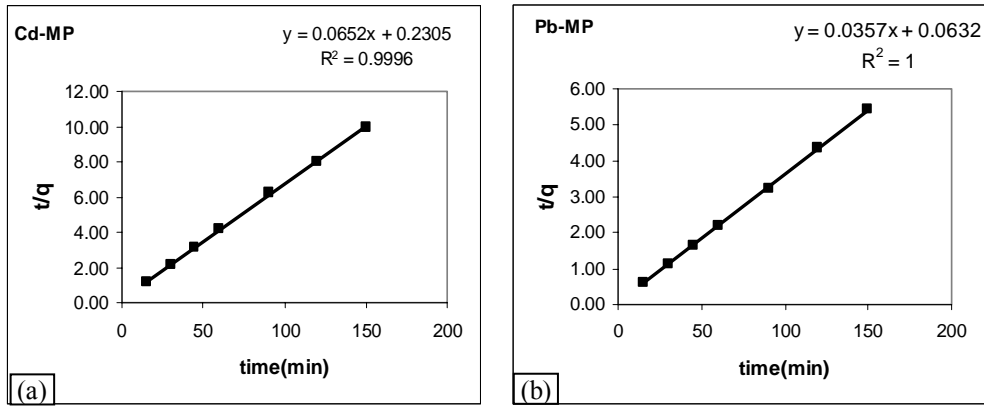


Figure 4.25 (a), (b) Second order adsorption kinetics plot of cadmium & lead

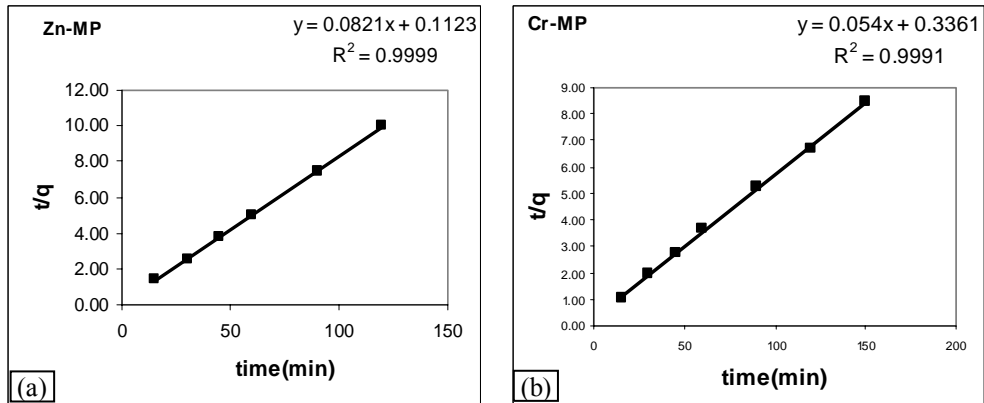


Figure 4.26 (a), (b) Second order adsorption kinetics plot of cadmium & lead

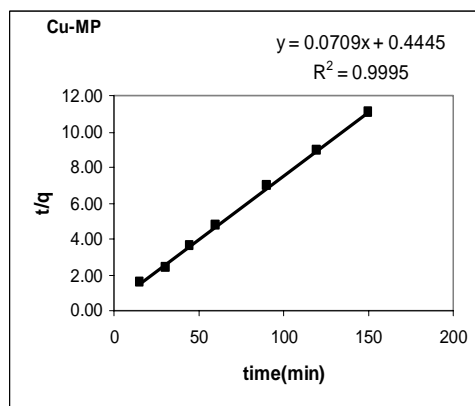


Figure 4.27 Second order adsorption kinetics plot of copper

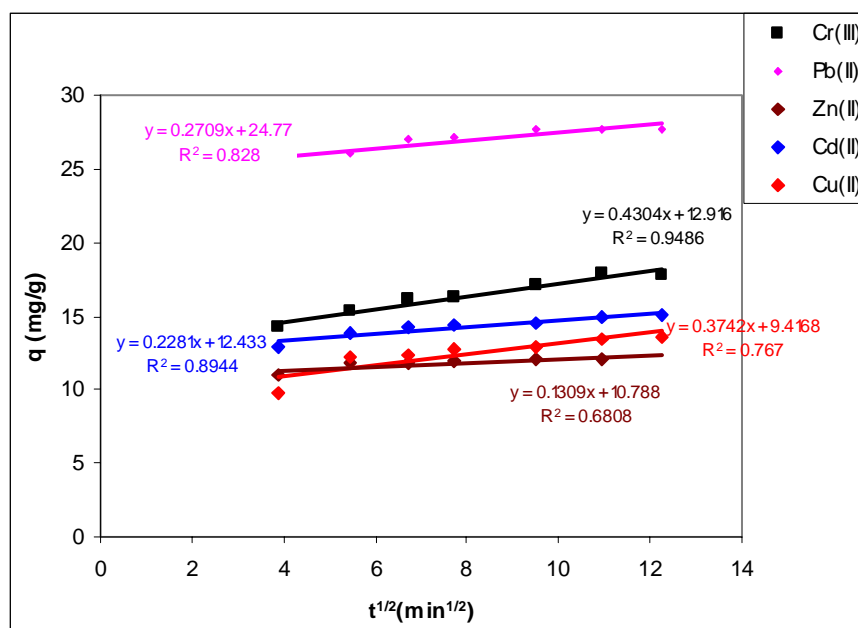


Figure 4.28 Plots for evaluating intra particle diffusion rate constant

Table 4.2 Kinetics parameters for the adsorption of Cd(II), Pb(II), Zn(II), Cr(III) and Cu(II) onto Mango Peel

Heavy Metals	q _{exp} (mg/g)	First order			Second order			Intra Particle diffusion	
		R ²	q _{calc} (mg/g)	k ₁ (min ⁻¹)	R ²	q _{calc} (mg/g)	k ₂ (gmg ⁻¹ min ⁻¹)	k _d (mg ⁻¹ min ^{-1/2})	R ²
Cd(II)	15.05	0.843	3.61	0.030	0.999	15.83	0.018	0.228	0.894
Pb(II)	27.67	0.966	7.33	0.055	1	28.01	0.020	0.271	0.828
Zn(II)	12.03	0.896	1.37	0.047	0.999	12.18	0.060	0.131	0.681
Cr(III)	17.74	0.936	6.49	0.028	0.999	18.52	0.008	0.430	0.948
Cu(II)	13.58	0.898	4.63	0.028	0.999	14.10	0.011	0.374	0.767

4.3.7 Thermodynamic parameters

The changes in Gibbs free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) for the adsorption process were obtained using the following equations

$$\Delta G = -RT \ln b \quad (4.4)$$

$$\ln b = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (4.5)$$

$$\Delta G = \Delta H - T \Delta S \quad (4.6)$$

Where R (8.314 J/mol K) is the gas constant, T (K) the absolute temperature and b (L/mol) the thermodynamic equilibrium constant. As shown in the Figures 4.29 – 4.31 the plots of Gibbs free energy (ΔG) versus temperature was found to be linear.

The results of these thermodynamic calculations are shown in Table 4.3. The negative values the Gibbs free energy for all the five metals show that the adsorption process is spontaneous and that the degree of spontaneity of the reaction increases with increasing temperature (Hao Chen et al., 2010; Mohan and Singh 2002). The overall adsorption process seems to be endothermic ($\Delta H = 38.69, 18.51, 12.63, 12.36, 10.41 \text{ kJmol}^{-1}$ for Cd, Pb, Zn, Cr and Cu respectively). Table 4.3 shows that the ΔS values were positive (i.e. that entropy increases as a result of adsorption). This occurs as a result of redistribution of energy between the adsorbate and adsorbent. Before adsorption occurs, the heavy metal ions near the surface of the adsorbent will be more ordered than in the subsequent adsorbed state and the ratio of free heavy metal ions to ions interacting with the adsorbent will be higher than in the adsorbent state. As a result, the distribution of rotational and translational energy among a small number of molecules increase with increasing adsorption by producing a positive value of ΔS and randomness will increase at the solid solution interface during the process of adsorption. Adsorption is thus likely to occur spontaneously at normal and high temperatures because if $\Delta H > 0$ and $\Delta S > 0$.

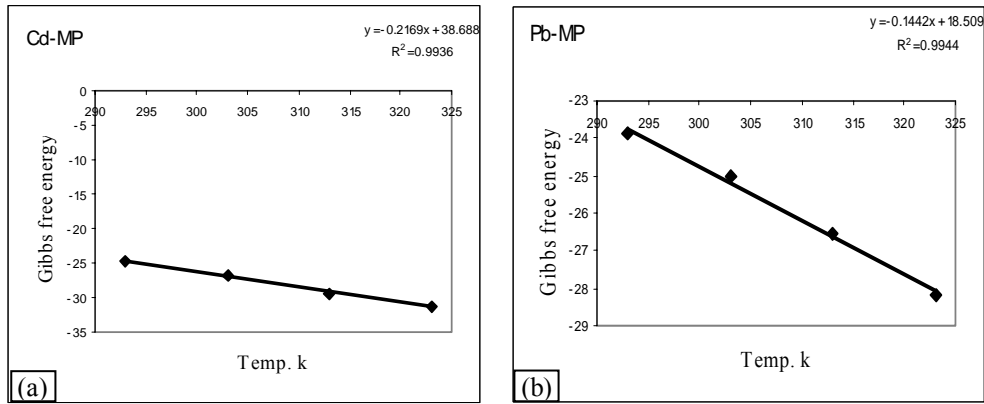


Figure 4.29 (a),(b) Plots of the Gibbs free energy vs. Temperature of cadmium and lead

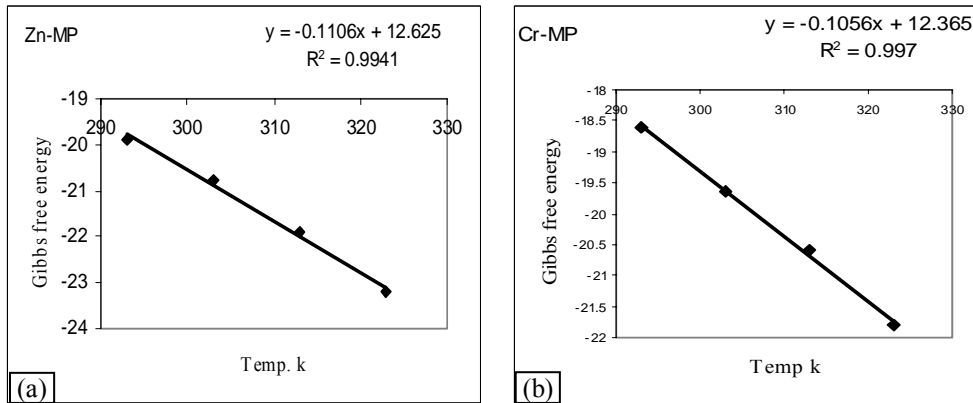


Figure 4.30 Plots of the Gibb's free energy vs. Temperature of zinc and chromium

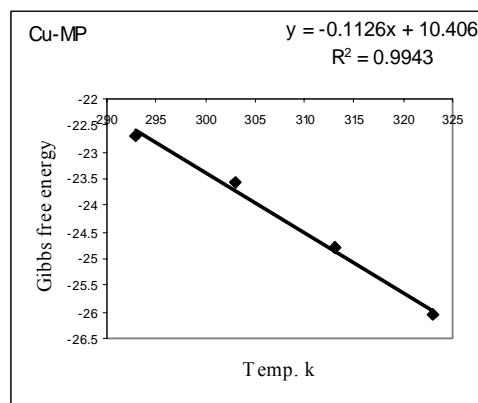


Figure 4.31 Plots of the Gibb's free energy vs. Temperature of copper

Table 4.3 Thermodynamic parameters for the adsorption of Cd(II), Pb(II), Zn(II), Cr(II) and Cu(II) on Mango peel at various temperatures.

Heavy metals	T(K)	b (Lmol ⁻¹)	$\Delta G(\text{kJmol}^{-1})$	$\Delta H(\text{kJmol}^{-1})$	$\Delta S(\text{kJmol}^{-1}\text{K}^{-1})$	R ²
Cd(II)	293	27124.50	-24.86	38.69	0.2169	0.993
	303	43165.40	-26.89			
	313	84386.20	-29.52			
	323	111454.50	-31.21			
Pb(II)	293	18005.70	-23.87	18.51	0.1442	0.994
	303	20720.00	-25.04			
	313	26728.80	-26.53			
	323	36197.80	-28.18			
Zn(II)	293	3498.40	-19.88	12.63	0.1106	0.9941
	303	3818.78	-20.78			
	313	4538.07	-21.91			
	323	5623.50	-23.19			
	293	2059.2	-18.60			
Cr(III)	303	2438.8	-19.65	12.36	0.106	0.997
	313	2686.7	-20.58			
	323	3369.6	-21.81			
Cu(II)	293	11120.55	-22.69	10.41	0.113	0.994
	303	11628.92	-23.58			
	313	13725.94	-24.79			
	323	16267.78	-26.04			

4.3.8 Desorption studies

Desorption efficiency is defined as the percent extraction of heavy metal ions initially loaded onto the biomass. Recovery of metal ions from the loaded adsorbents is necessary for disposal as well as for reuse of adsorbate (Chen et al., 2007). For the desorption experiments, several solvents (acids

and bases) have been used as shown in the Figure 4.32. The studies were carried out using HCl, H₂SO₄, HNO₃, H₂C₂O₄, NaOH and Na₂CO₃ of known concentration of 0.1N with the metal loaded adsorbent. Batch desorption experiments were carried out and the desorption efficiencies are compared in Table 4.4. It can be easily known that desorption efficiency decreases with increasing cycle number due to the decrease of adsorption capacity as shown in Table 4.5. For each adsorption –desorption cycle, new active sites generated by dilute HCl treatment was decreases, resulting in decrease adsorption capacity with the increase in cycle number. Hydrochloric acid showed the maximum desorption efficiency for Pb(II), Cu(II) and Zn(II).

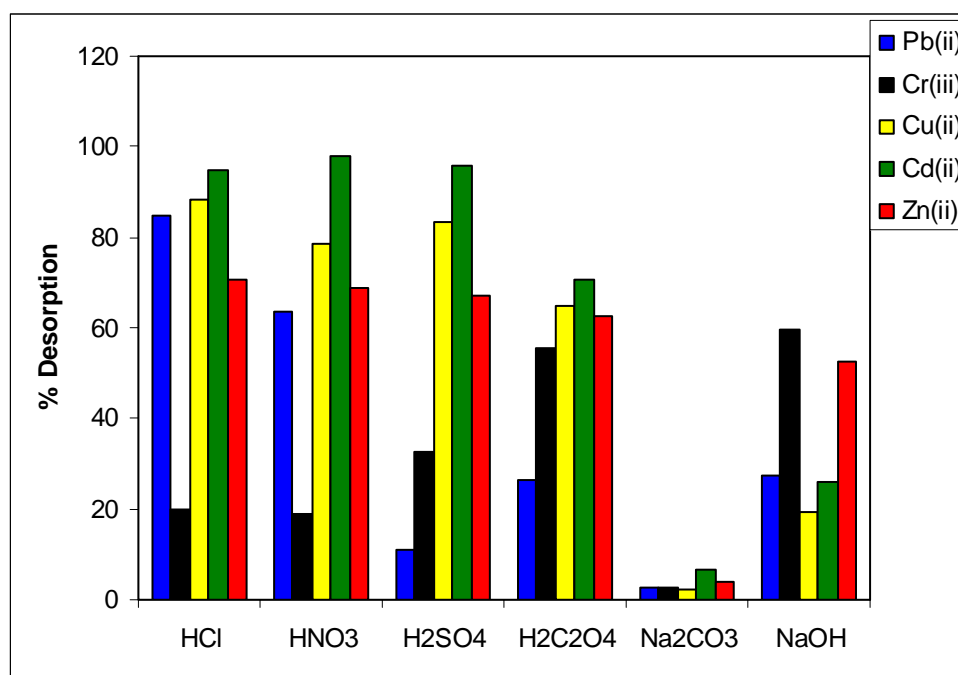


Figure 4.32 Desorption efficiency using various solvents

Table 4.4 Percentage desorption efficiency using various Solvents

Heavy metals	% Adsorption	HCl	HNO ₃	H ₂ SO ₄	H ₂ C ₂ O ₄	Na ₂ CO ₃	NaOH
		%Desorption					
Cd	59.72	94.76	97.80	95.70	70.78	6.52	25.90
Pb	98.22	84.80	63.40	11.18	26.60	2.78	27.40
Zn	55.71	70.60	68.80	67.04	62.86	4.10	52.30
Cr	58.91	19.90	18.80	32.50	55.40	2.45	59.70
Cu	82.93	88.30	78.70	83.30	64.80	2.30	19.25

Table 4.5 Percentage desorption efficiency using 0.1N HCl for various cycles

Cycles	I		II		III		IV		V	
	% adn	% Desn	% adn	% Desn	% adn	% Desn	% adn	% Desn	% adn	% Desn
Cd	74	93	65	82	49	51	44	26	23	21
Pb	89	91	74	78	68	59	50	58	49	56
Zn	66	77	43	34	33	24	26	23	17	22
Cu	86	95	51	67	9	47	6	36	2	31

4.4 Characterization of the adsorbent

Fourier transform infrared spectral analysis was carried out in order to identify the different functional groups present in given samples. The different functional groups which are present in the given samples are OH stretching, CH stretching, C=C stretching and C-O stretching. FT-IR spectrum of given raw mango peel sample shows that the broad and intense peak at 3345.5cm^{-1} was attributed to the stretching of O-H group due to inter- and intramolecular hydrogen bonding of polymeric compounds such as alcohols or phenols. The peak observed at 2918cm^{-1} was associated with the stretching vibrations of C-H bond of methyl, methylene and methoxy groups. The peaks around 1600cm^{-1}

1627 cm^{-1} corresponded to the C=C stretching which might be attributed to the presence of aromatic or olefinic or N-H bending bands. The intense peak at 1000-1031 cm^{-1} corresponded to the C-O stretching of alcohol or carboxylic acid. FTIR spectrum of the given raw mango peel loaded with different metals shows that the peaks at 3345, 2849, 1615, 1024 cm^{-1} (before adsorption) had shifted slightly after binding with metals. This was due to the participation of these functional groups in the binding of metal ions. The shifting of wave number depends on the concentration of metal present in the given sample agreed by the literature survey (Abuzer and Huseyin 2011; Azouaou 2010; Hao Chen et al., 2010). The scanning electron micrograph revealed the surface texture and morphology of the adsorbent is shown in Figure.4.38.

Table 4.6 Comparison of FTIR band positions of raw mango peel (MP) before and after metal ions adsorption in wave number(cm^{-1}).

Assignment	Raw MP	Cd(II)	Pb(II)	Zn(II)	Cr(III)	Cu(II)
O-H stretching	3345.57	3340.68	3341.04	3340.80	3335.06	3339.51
C-H stretching	2849.95	2918.18	2917.01	2918.53	2918.08	2918.02
C=C stretching	1615.74	1633.65	1634.72	1625.14	1627.17	1625.14
C-O stretching	1024.50	1029.37	1030.92	1030.94	1028.50	1030.94

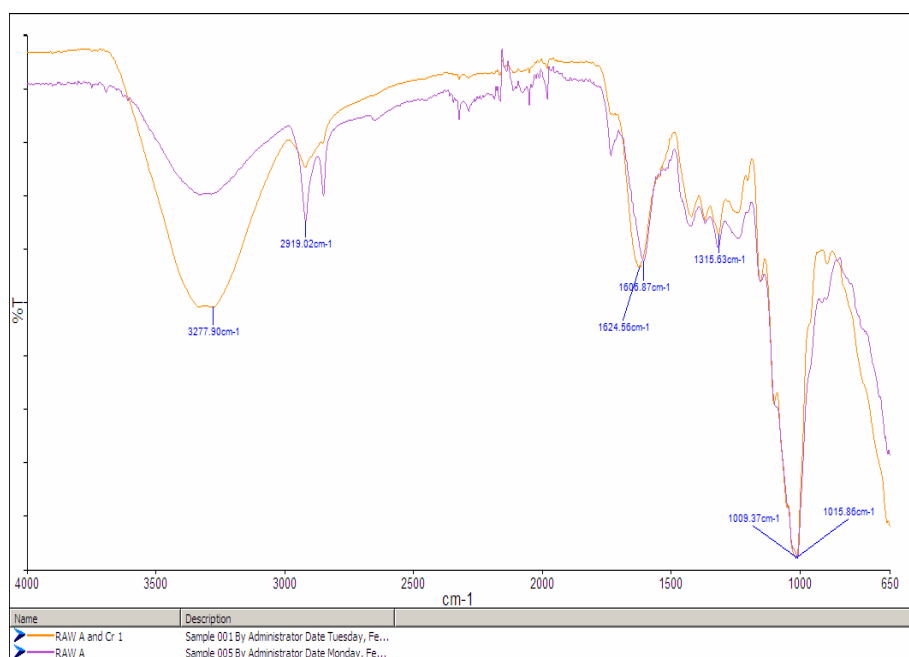
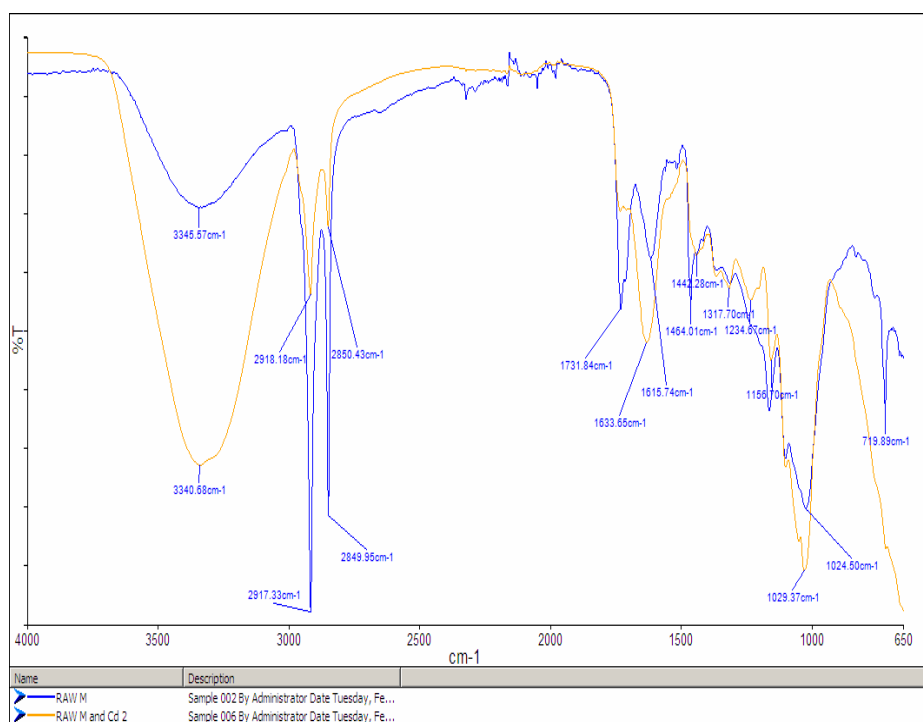


Figure 4.33 FTIR spectra before and after metal ion adsorption on chromium



4.34 FTIR spectra before and after metal ion adsorption on cadmium

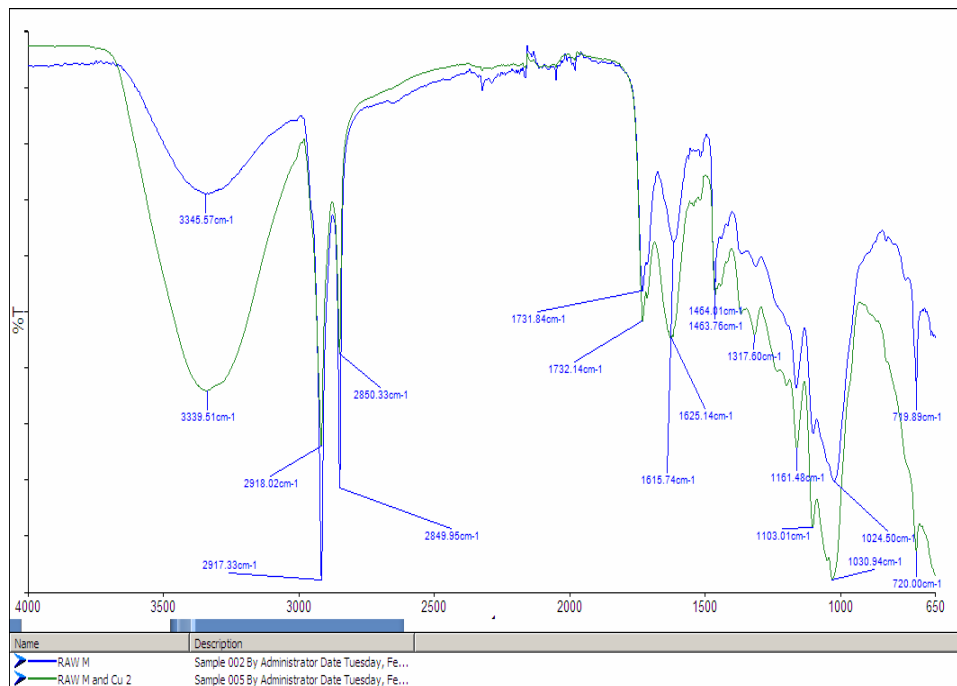


Figure 4.35 FTIR spectra before and after metal ion adsorption on copper

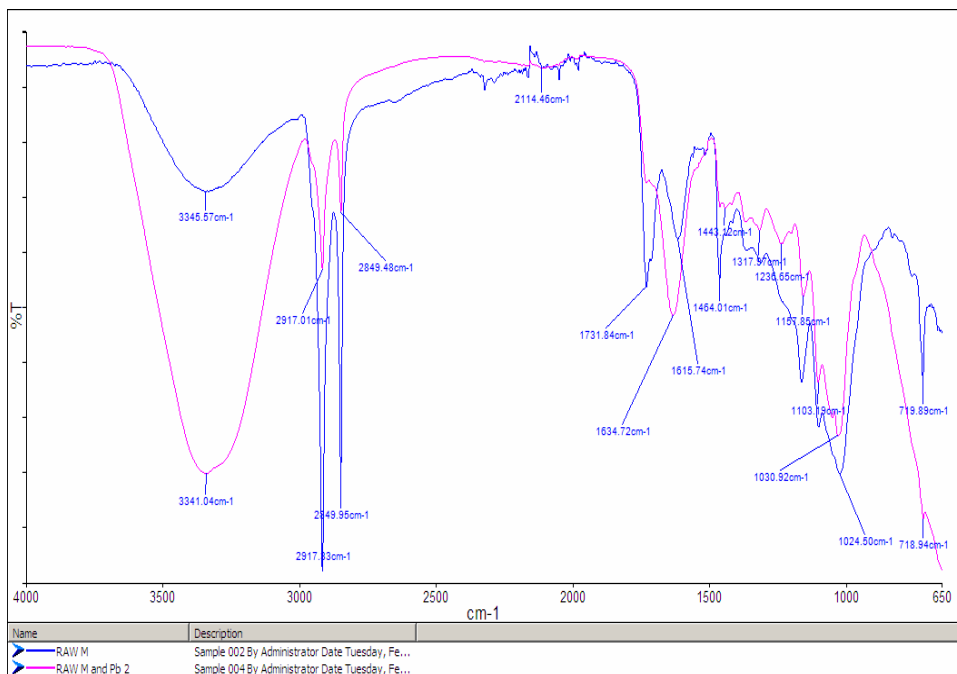


Figure 4.36 FTIR spectra before and after metal ion adsorption on lead

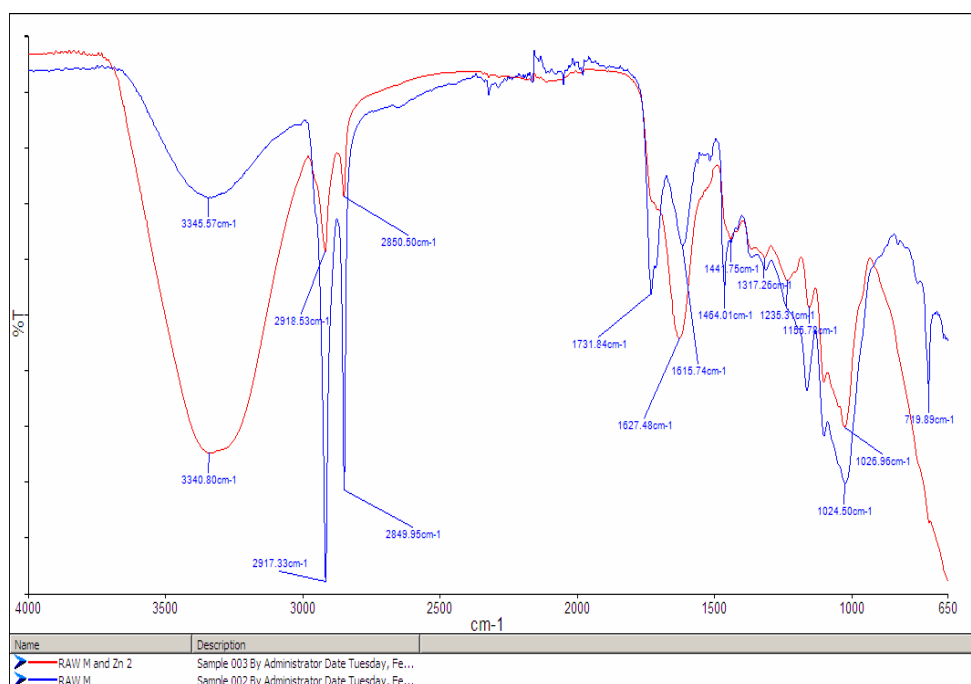


Figure 4.37 FTIR spectra before and after metal ion adsorption on zinc

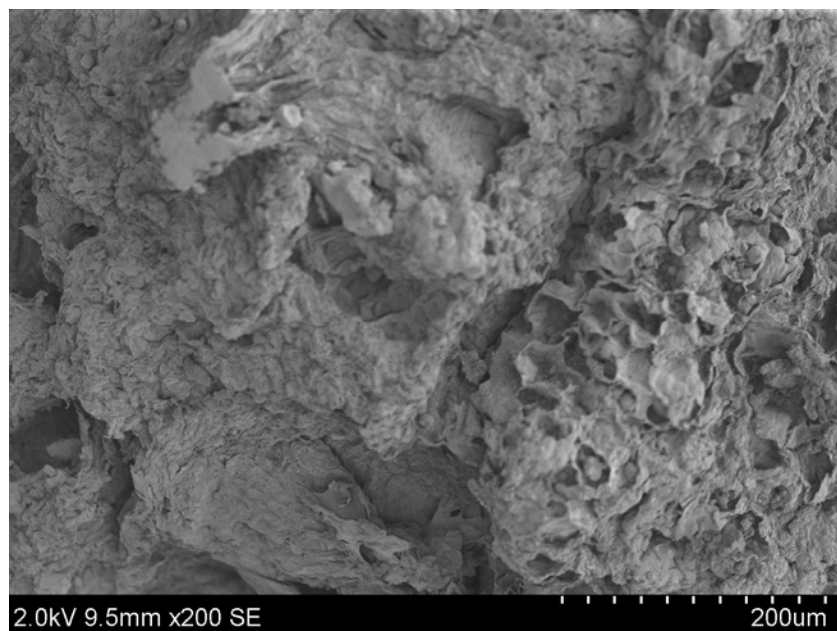


Figure 4.38 Scanning Electron microscopy of mango peel

4.5 Conclusions

This study indicated that mango peel, which is widely available at low cost, can be used as an efficient biosorbent material for removal of Cd(II), Pb(II), Zn(II) Cr(III) and Cu(II) from wastewater. The adsorption isotherms at different temperatures could be well described by the Langmuir Freundlich and Dubinin-Radushkevich isotherm models. Desorption experiments proved that 0.1 N HCl was an efficient desorbent for the recovery of Cu(II), Pb(II) and Zn(II) from biomass. IR spectrum analysis suggested the different functional groups which are present in the given samples are OH stretching, CH stretching, C=C stretching, C-O stretching. The thermodynamic study shows that the adsorption of Cd(II), Pb(II), Zn(II) Cr(III) and Cu(II) were endothermic nature. The negative values of ΔG reveal the feasibility and spontaneous nature of the process.

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ADSORPTION STUDIES USING *ALISMA PLANTAGO AQUATICA*

5.1	Introduction
5.2	Materials and Methods
5.3	Continuous Adsorption Studies in Packed Bed Columns
5.4	Results and Discussion
5.5	Characterization of the Adsorbent
5.6	Continuous study
5.7	Conclusions

5.1 Introduction

Adsorption is one of the physico-chemical processes found to be effective in removing heavy metals from aqueous solution. An adsorbent can be considered as cheap or low cost if it is abundant in nature and requires only a little processing. Such a plant material *Alisma plantago aquatica* was selected for this study.

5.2 Materials and Methods

5.2.1 Adsorbent and reagents preparation

The experiments were carried out using the adsorbent *Alisma plantago aquatica* as shown in Figure 5.1. The adsorbent samples were collected from nearby areas and washed several times with distilled water to remove dust and other impurities. After drying it is ground using domestic mixer and sieved to 250 mesh size in accordance with ASTM method D4749. The sample is washed with distilled water to remove colour and dried in an oven at 70°C for 24 hours. The dried sample was stored in airtight bottles for further use without any chemical or physical treatment.

All reagents used in this study were of analytical grade obtained from Merck Germany. Stock solution of cadmium, lead, zinc, chromium and copper were prepared by metal nitrate salts in double distilled water and the required concentrations were obtained by diluting the stock solution.



Figure 5.1 *Alisma plantago aquatica*



Figure 5.2 Fine grains of dry *Alisma plantago aquatica*

5.2.2 Batch studies

The batch experiments were carried out in 250ml flask with working volume of 100 ml of metal solution. The required dose of adsorbent 0.1g was added to the solution of fixed concentration and flasks were agitated on a temperature controlled incubator shaker at 200rpm. The Metal ion concentrations used were in the range of 10-100mg/l. The pH of the solution was maintained at 5.5 ± 0.5 and the contact time of 120min was used for batch tests. To study the effect of pH, metal solution was adjusted to different pH in the range of (2-7) using either HCl or NaOH solutions. Then, the samples were filtered to remove any fine particles and analyzed for the metal ions using atomic absorption spectrophotometer. The effect of contact time, adsorbent dosage, initial concentration, pH, kinetics and equilibrium parameters were determined. Adsorption isotherm models and thermodynamic parameters were also investigated to know the adsorption behavior.

5.3 Continuous Adsorption Studies in Packed Bed Columns

5.3.1 Preparation of Packed Bed Column

Continuous removal of metal ions by adsorption was studied in a packed bed column made of Borosil glass material with 4cm ID and 40cm height. The packed bed was made from a mixture of dried biomass of *Alisma plantago-aquatica* (12gm) mixed with glass beads (supporting materials). The beds were made for equal heights of 10 cm and with intermittent layer of beads along to provide uniform distribution of the liquid in the bed. Perforated plates at both ends of the packed bed kept the bed in place. Sampling ports were provided at different heights of the column so that samples could be collected to study the effect of bed depth on the adsorption.

5.3.2 Adsorption of Metals in Packed Bed Column

Continuous adsorptions of individual metals were studied by operating

packed bed column in an up flow mode by pumping the desired metal solution using a peristaltic pump. A uniform distribution of the metal solution through the bed was achieved through the distributor system at the bottom of the bed. Photograph of the experimental system is shown in Figure 5.2. Samples were collected from the sampling ports at different heights of the bed at varying intervals of time and were analysed for residual metal concentrations. The metal ion solution at known concentration was passed continuously through the stationary bed of adsorbent (*Alisma plantago aquatica*). The flow rate was regulated with a variable speed pump. Samples were taken from the effluent at timed intervals and analysed for Zn(II) ions as described below. The experiment was continued until a constant concentration of Zn(II) ion was obtained. Experiments were conducted at two flow rates (0.18 and 0.36 l/hr).

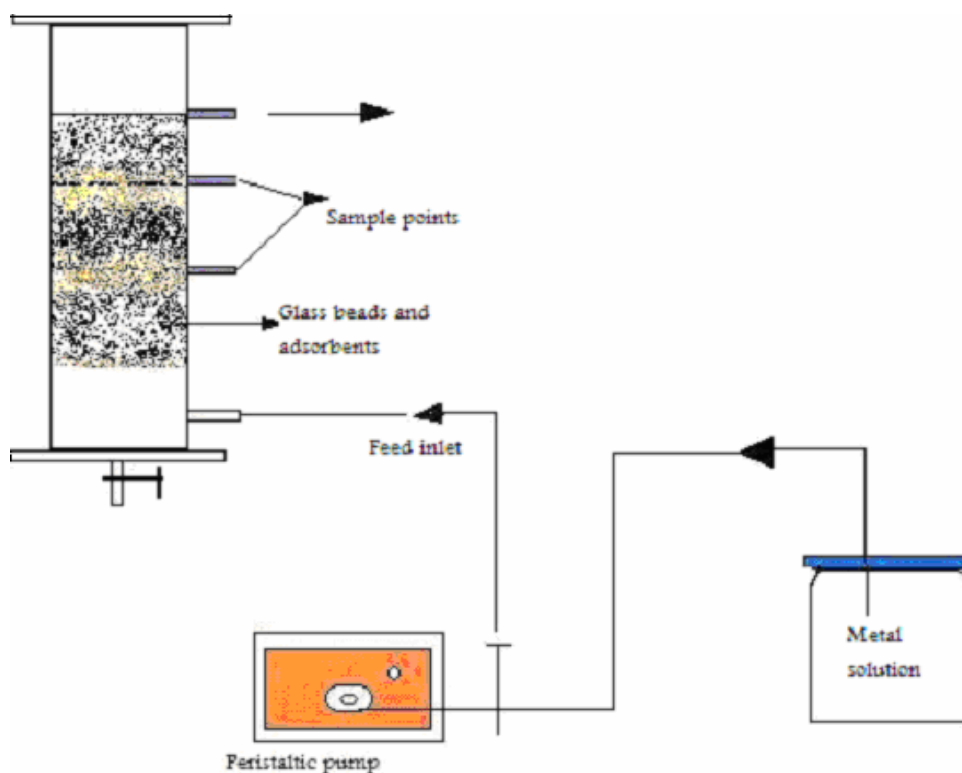


Figure 5.3 Schematic presentation of the packed bed column for continuous adsorption studies



Figure 5.4 Experimental setup of continuous study

5.4 Results and Discussion

Batch studies were carried out in order to determine the effects of some operational parameters on metal ion adsorption. The parameters were the time required for equilibrium, the biomass dose and pH of solution. The uptake of metal ions by the biomass of *Alisma plantago aquatica* was initially evaluated in batch condition.

5.4.1 Effect of contact time

Figure 5.5 shows the dependence of the uptake capacity on the initial metal ions and contact time. The data obtained from the adsorption of Cd(II), Pb(II), Zn(II), Cr(III) and Cu(II) ions onto *Alisma plantago aquatica* showed that the adsorption increased with increasing contact time. The plots in Figure

5.5 show a rapid uptake of Cu(II) ions during the first 5 minutes of agitation, after which the rate of sorption became slower, attaining equilibrium in 60 minutes. Further increase in contact time had negligible effect on the amount of ions adsorbed. The rapid metal uptake was 93.59%, 92.76% and 92.48% for the total sorption of Cu(II) solutions with initial concentration of 5 mg/L, 10 mg/L and 20 mg/L respectively.

The fast initial uptake occurred in the early stage of adsorption was due to the fact that most of the binding sites on mango leaves were free which allowed quick binding of metal ions on the biomass (Gupta et al., 2008). As the binding sites became exhausted, the uptake rate slowed down due to competition for decreasing availability of active sites by metal ions. According to the test results, agitation time was fixed at 120 minutes for the rest of the batch experiment to ensure equilibrium was achieved. The plots of metal uptake as a function of time are single, smooth, and continuous, suggesting the possibility of the formation of monolayer coverage of metal ions at the outer surface of adsorbent (Pimentel et al., 2007). For a fixed concentration of heavy metals and a fixed adsorbent mass, the retention of heavy metals increased with increasing contact time. In addition, the removal efficiencies decreased by about 4-10 % with increasing contact time after equilibrium had been reached. This probably resulted from saturation of adsorbent surface with heavy metals followed by adsorption and desorption process that occur after saturation (Azouaou et al., 2010; Maria Martinez et al., 2006; Mohammad Mehdi et al., 2011).

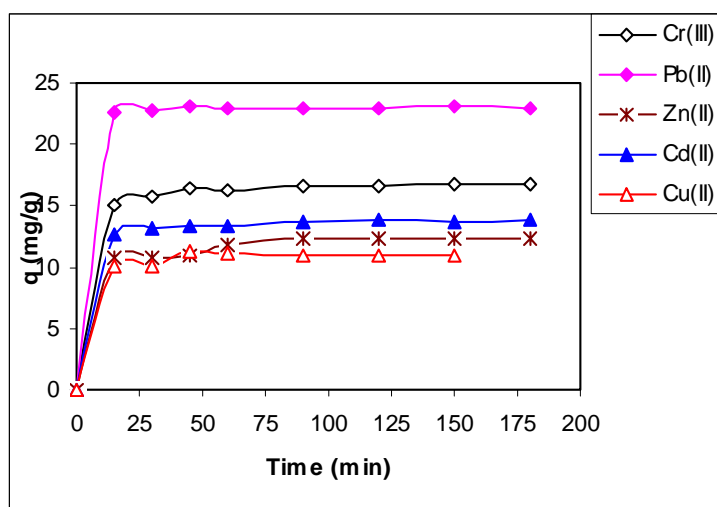


Figure 5.5 Metal uptake capacities at varying time intervals
 (Initial concentration=50ppm, Adsorbent dose=0.3gm/100ml metal solution, temperature =25±2°C, pH=5, Orbital shaking speed=200rpm, Time 180min.)

5.4.2 Effect of Adsorbent dose

The percentage removal of metal ions against adsorbent dosage were plotted and shown in Figure 5.6. It is evident from the plots that the percent removal of metal from the aqueous phase increases with the increase in the adsorbent dosage.(Azouaou et al., 2010; EI-Said et al., 2010; Saifuddin and Kumaran 2005). Percentage removal of metal ions increases as dosage increases from 0.1 to 0.4 gm. Such behavior is obvious because the number of active sites available for metal removal would be more as the amount of the adsorbent increases.

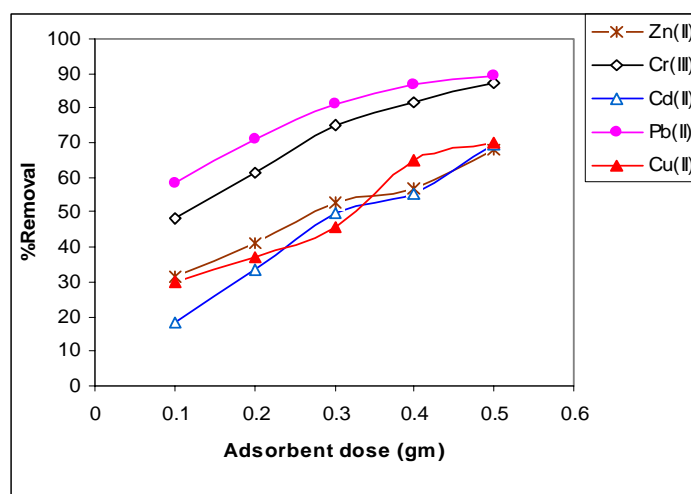


Figure 5.6 Effect of adsorbent dose on metal adsorption

(Initial concentration=50ppm, Adsorbent dose=0.1 to 0.5 gm/100ml metal solution, temperature = $25\pm 2^\circ\text{C}$, pH=5, Orbital shaking speed=200rpm, Time=120min.)

5.4.3 Effect of varying concentration of metal ions

Figure 5.7 shows the graph of percentage removal of metal ions versus different concentrations of heavy metal ions. The percentage of removal of metal ions decreases with increase in concentration of metal ions in the aqueous solution (Azouaou et al., 2010; Mausumi et al., 2006; Mohammad Mehdi et al., 2011).

It is due to an increase in the number of metal ions for the fixed amount of adsorbent. The amount of metal ions adsorbed per unit mass of *Alisma plantago aquatica* increases with the increase in metal ion concentration, which is due to the complete utilization of adsorption surface available which is not the case in low concentrations.

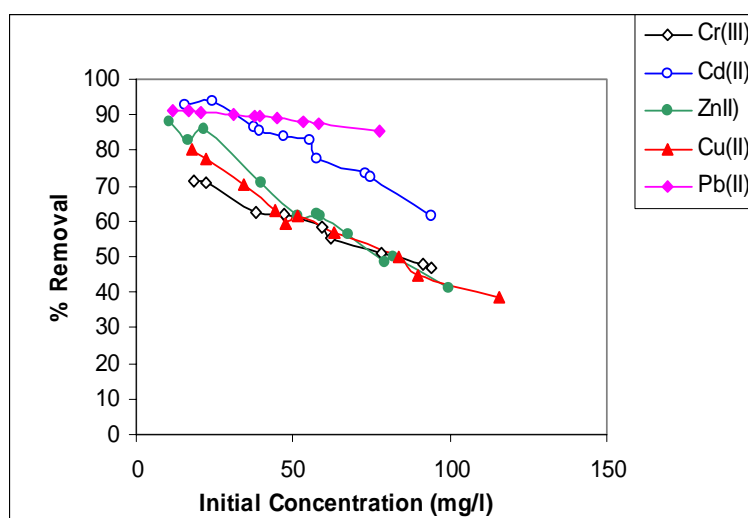


Figure 5.7 Effect of varying concentration of metal ions
 (Initial concentration=10 to 100ppm, Adsorbent dose=0.3gm/100ml metal solution, temperature =25±2°C, pH=5, Orbital shaking speed=200rpm, Time=120min.)

5.4.4 Effect of pH

The pH of the solution is an important parameter affecting adsorption of heavy metal ions. The effect of pH on the adsorption of Cd(II), Pb(II), Zn(II) Cr(III) and Cu(II) by *Alisma plantago aquatica* is showed in Figure 5.8. The maximum removal efficiency for Cd(II) is 96.24% at pH6, 95% for Pb(II) at pH4, 85% for Zn(II) at pH7, 99.8% for Cr(III) at pH6 and 76.7% for Cu(II) at pH5. At low pH values the H⁺ concentration is high and therefore protons can compete with the metal ions for surface sites. At low pH values the metals are present in the solution as Cd²⁺ Pb²⁺ Zn²⁺ Cr³⁺ and Cu²⁺ free cations. When pH increases, there is a decrease in positive surface charge due to the de protonation of the sorbent functional groups, which results in a lower electrostatic repulsion between the positively charged metal ion and the surface of the adsorbent (Azouaou et al., 2010; Babu and Gupta 2008;Gupta and Rastogi 2007). As pH value is higher, more exchangeable

cations contained in the adsorbent can be exchanged with metal ions due to weak competitive adsorption of H^+ ions.

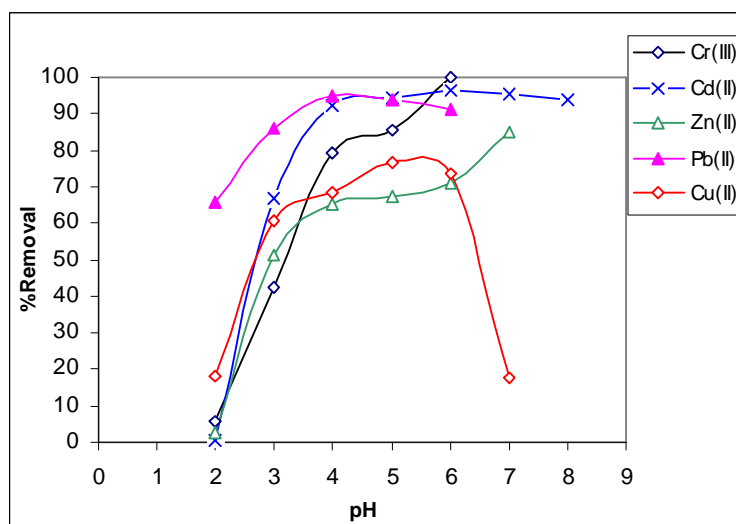


Figure 5.8 Effect of varying pH on metal ions adsorption
(pH = 2 to 8, Initial concentration=50ppm, Adsorbent dose=0.3gm/100ml metal solution, temperature = $25 \pm 2^\circ C$, Orbital shaking speed=200rpm, Time=120min.)

5.4.5 Adsorption isotherms

The equilibrium adsorption isotherms are of fundamental importance in the design of adsorption systems since they indicate how metal ions are partitioned between the adsorbent and liquid phases at equilibrium as a function of metal concentration. When an adsorbent comes into contact with a metal ion solution, the concentration of metal ions on the surface of the adsorbent will increase until a dynamic equilibrium is reached. Widely used sorption isotherms of Langmuir, Freundlich and Dubinin-Radushkevich were used to fit the experimental data. The values of the parameters, correlation coefficients (R^2) are summarized in Table 5.1.

The maximum monolayer adsorption capacity (q_m) was calculated from Langmuir model. The results of this study indicated that *Alisma plantago aquatica* had remarkable potential for the removal of Cd(II), Pb(II), Zn(II) Cr(III) and Cu(II) ions from aqueous solution. In view of the values of the linear regression coefficients, Langmuir model fit very well to the sorption data in the studied concentration range as shown in Figures 5.9 – 5.23. Langmuir constants related to the sorption capacity and energy of adsorption, The Langmuir isotherm assumes a homogeneous surface and a constant sorption potential. Dubinin-Radushkevich (D-R) isotherm assumes only a homogeneous surface (Azouaou et al., 2010; Can and Jianlong 2007; Hao Chen et al., 2010).

The Langmuir isotherm constants do not explain the chemical or physical properties of the adsorption process. However, the mean adsorption energy (E) calculated from the D-R isotherm provides important information about these properties. For $E < 8 \text{ kJmol}^{-1}$, physisorption dominates the sorption mechanism. If E is between 8 and 16 kJmol^{-1} , ion-exchange is the dominant factor. If $E > 16 \text{ kJmol}^{-1}$, sorption is dominated by particle diffusion. In this study the adsorption energies are less than 2 kJmol^{-1} suggesting that the sorption process was dominated by physical forces at all studied temperatures.

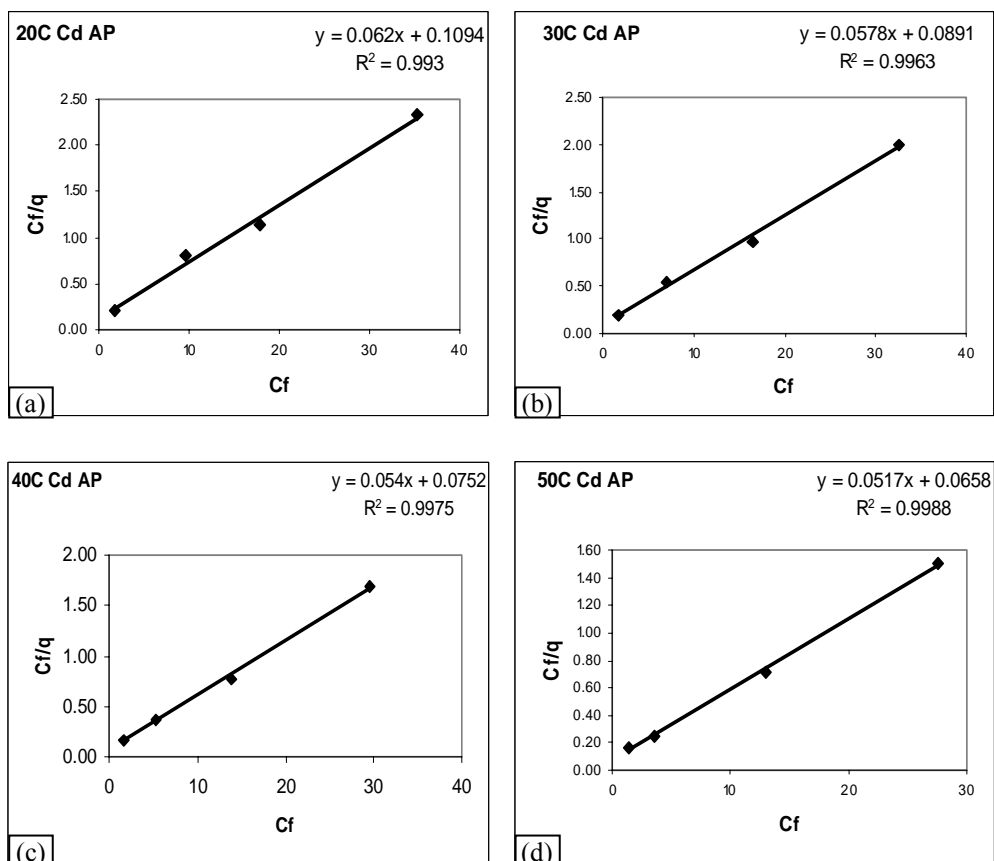


Figure 5.9 (a), (b), (c), (d) Langmuir plot for cadmium adsorption at 20, 30, 40 and 50°C

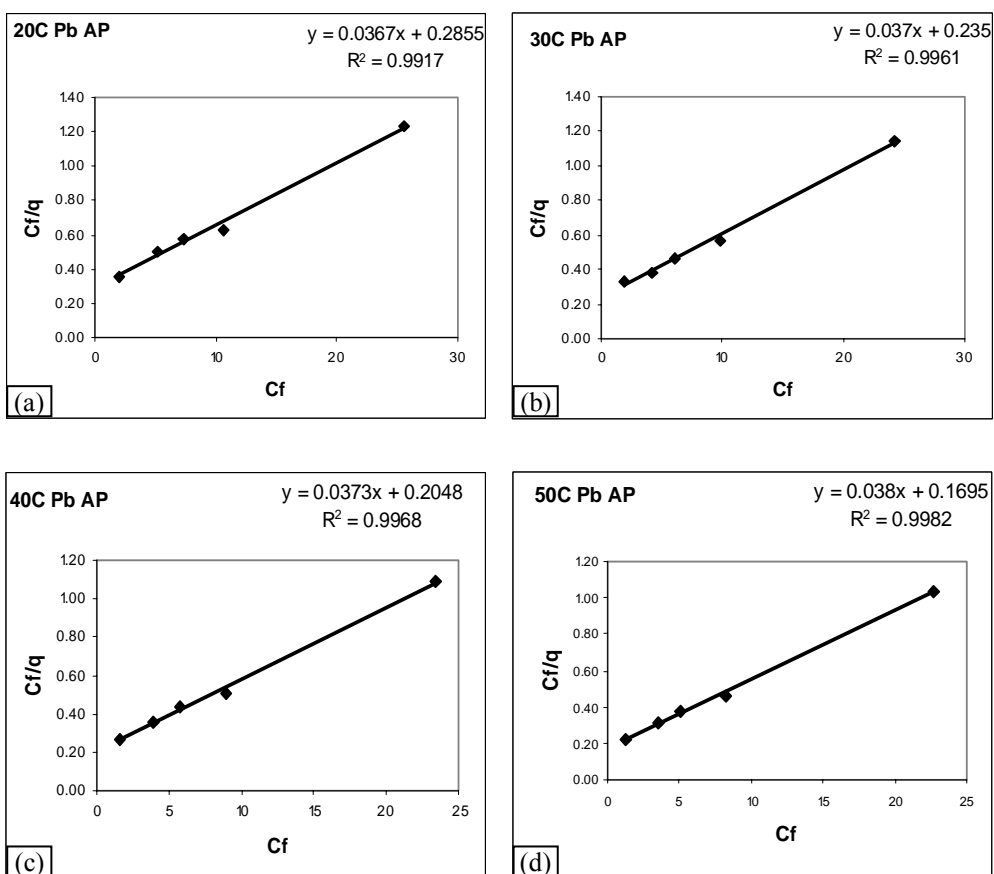


Figure 5.10 (a), (b),(c),(d) Langmuir plot for lead adsorption at 20,30,40 and 50°C

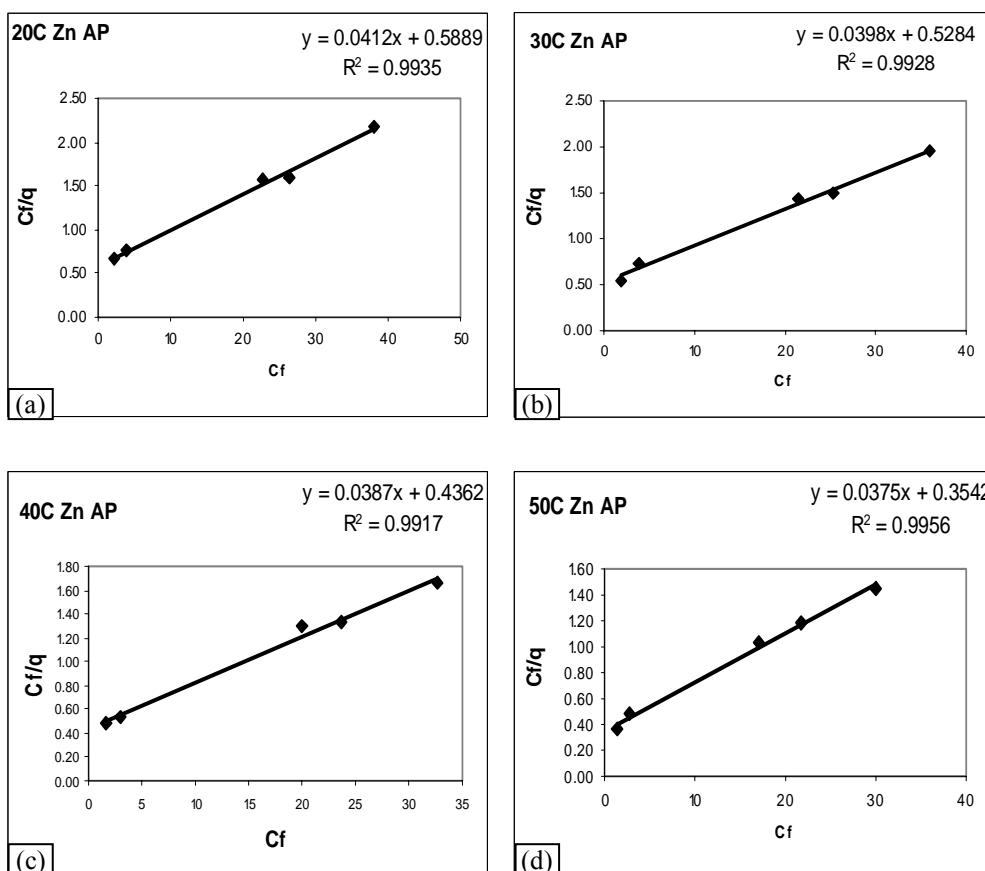


Figure 5.11 (a), (b),(c),(d) Langmuir plot for zinc adsorption at 20,30,40 and 50°C

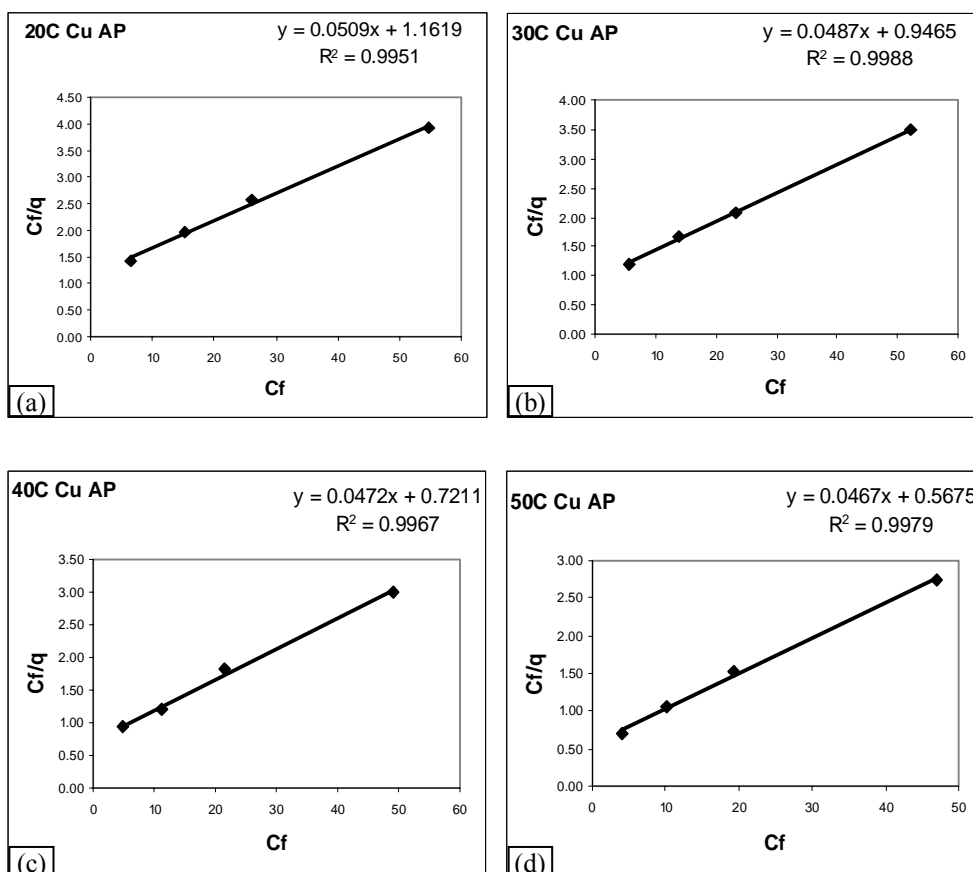


Figure 5.12 (a), (b),(c),(d) Langmuir plot for copper adsorption at 20,30,40 and 50°C

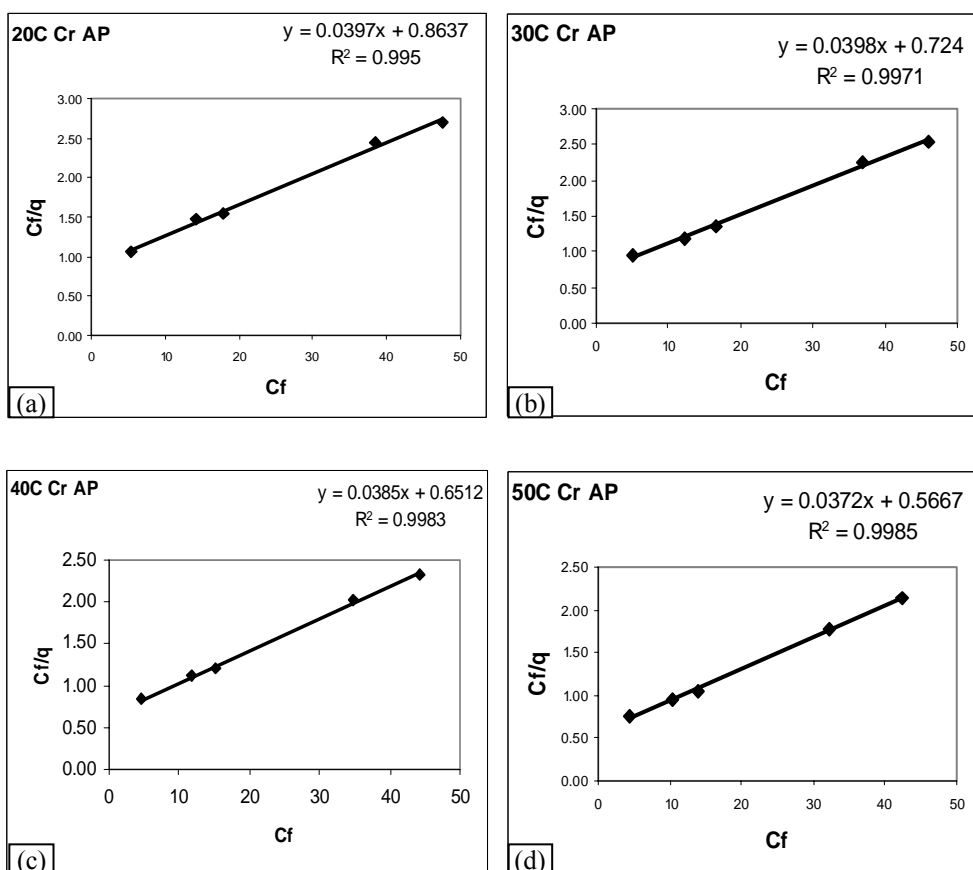


Figure 5.13 (a), (b),(c),(d) Langmuir plot for chromium adsorption at 20,30,40 and 50°C

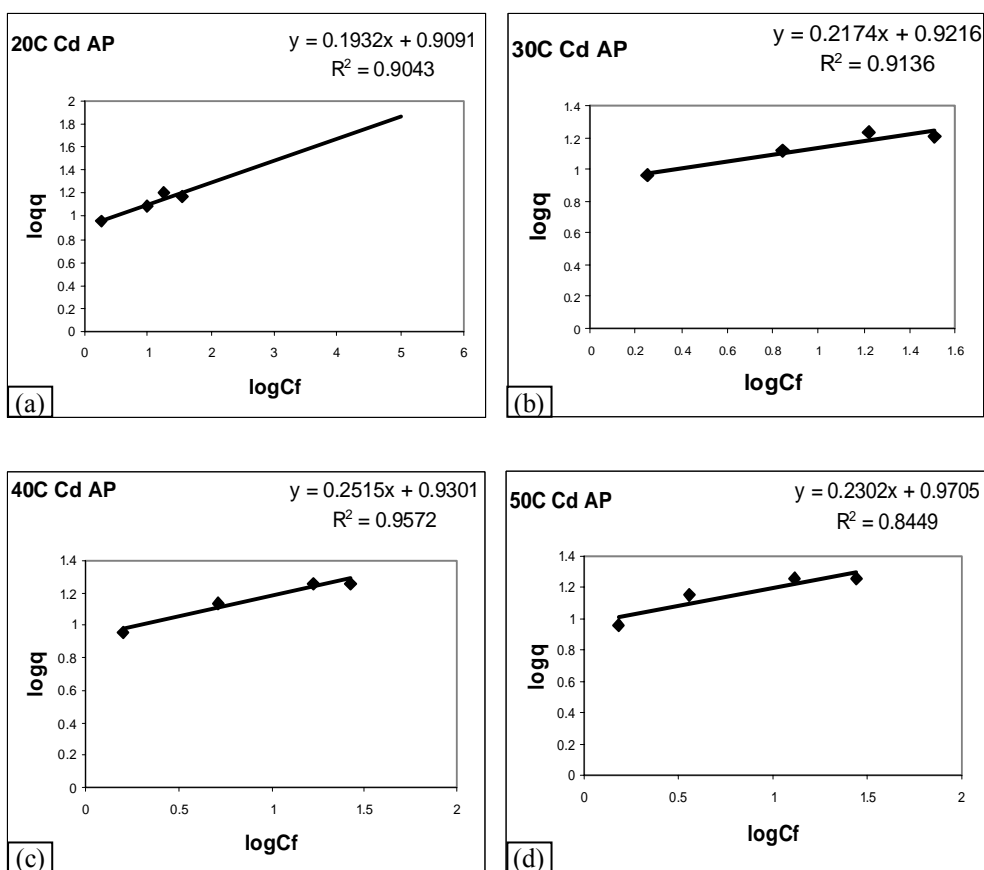


Figure 5.14 (a), (b), (c), (d) Freundlich plot for cadmium adsorption at 20,30, 40 and 50°C

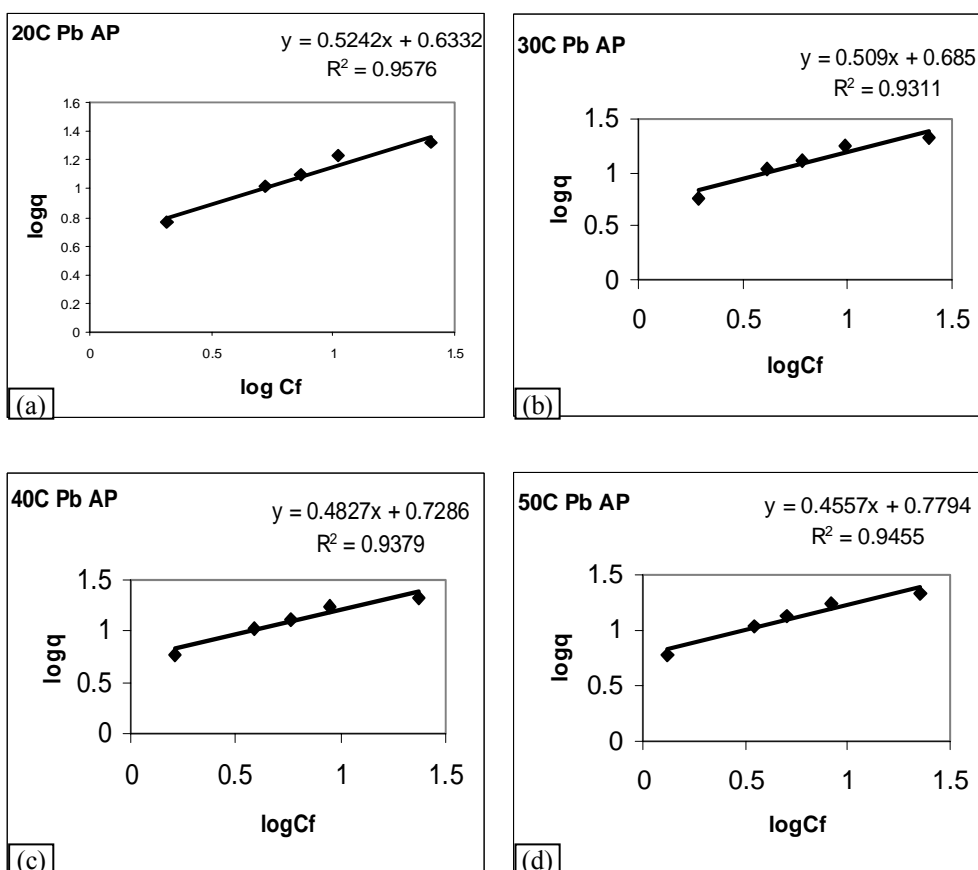


Figure 5.15 (a), (b), (c), (d) Freundlich plot for lead adsorption at 20,30, 40 and 50°C

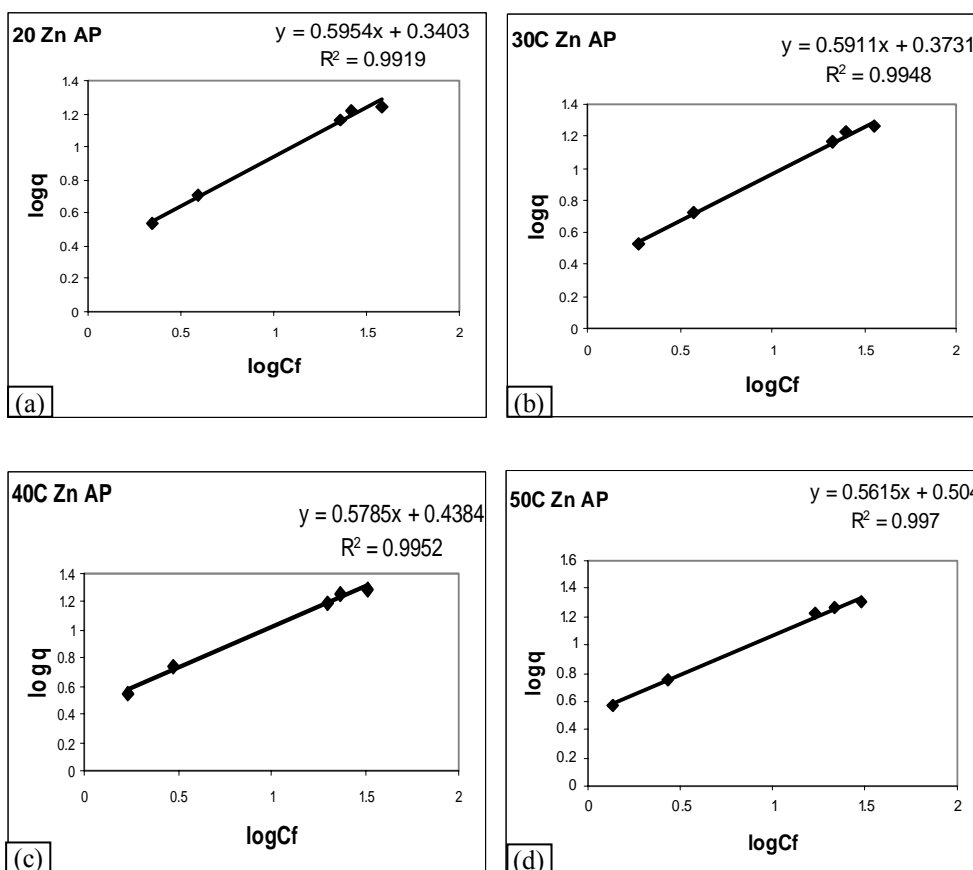


Figure 5.16 (a), (b), (c), (d) Freundlich plot for zinc adsorption at 20,30, 40 and 50°C

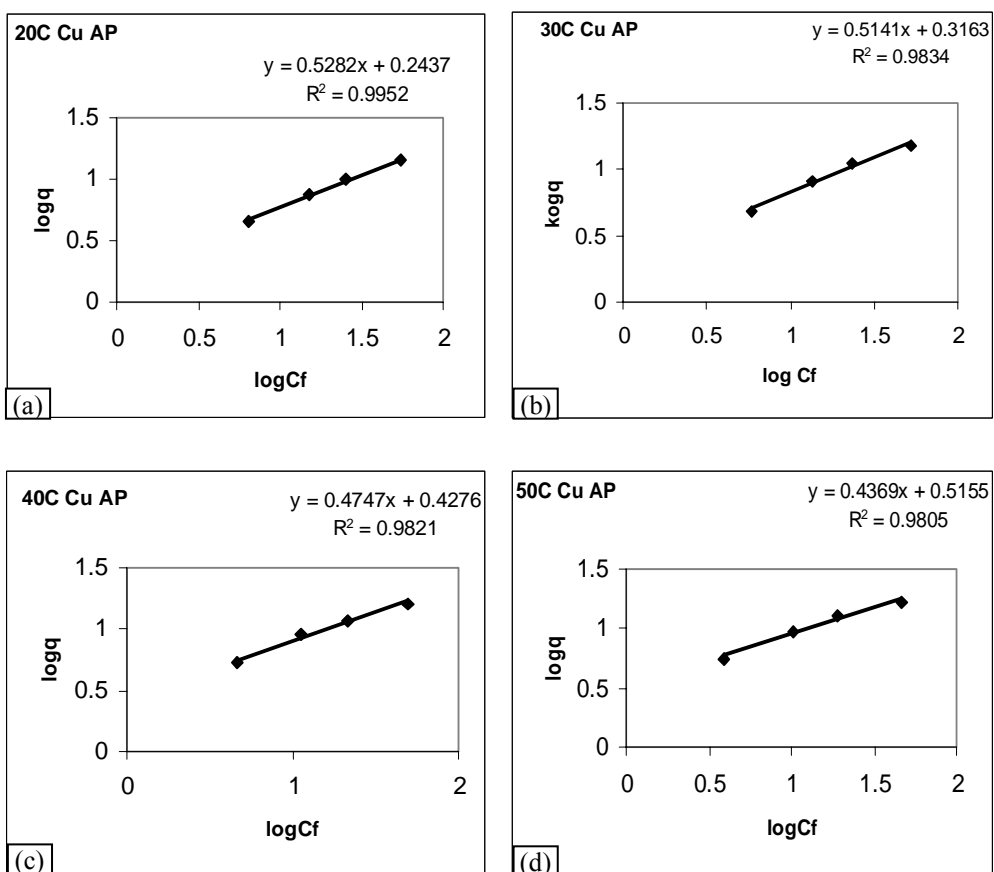


Figure 5.17 (a), (b), (c), (d) Freundlich plot for copper adsorption at 20,30, 40 and 50°C

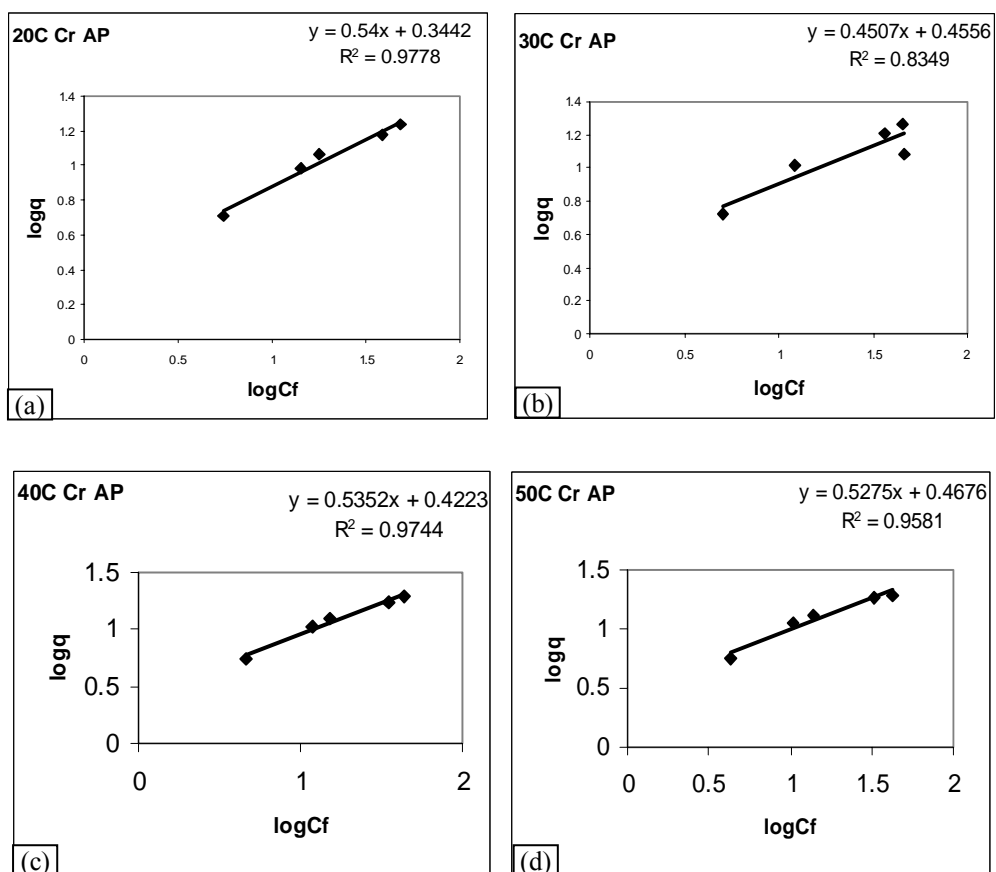


Figure 5.18 (a), (b), (c), (d) Freundlich plot for chromium adsorption at 20,30,40 and 50°C

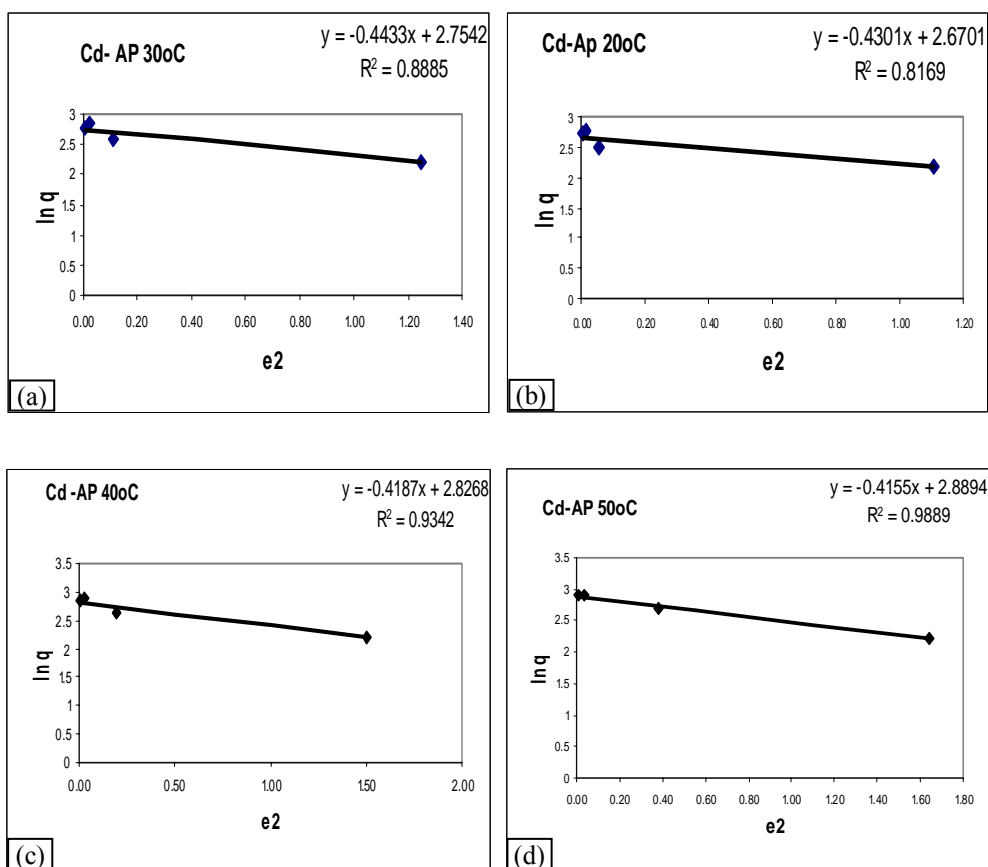


Figure 5.19 (a), (b),(c), (d) Dubinin-Radushkevich plot for cadmium adsorption at 20,30,40 and 50°C

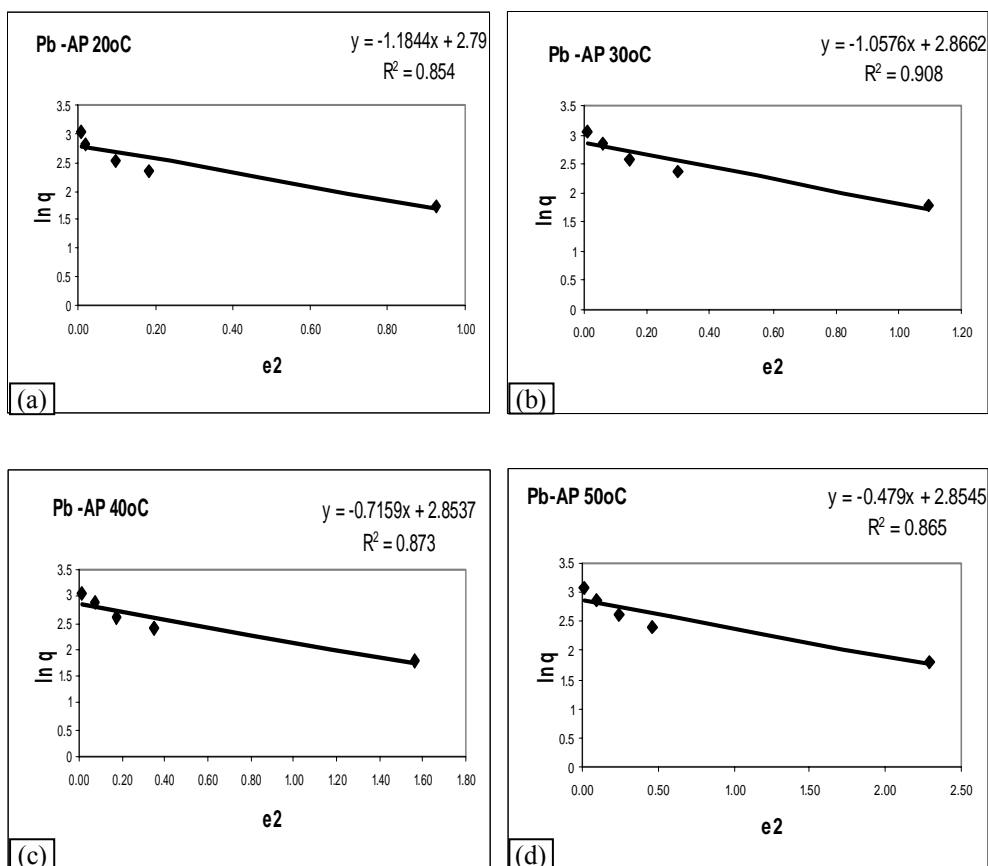


Figure 5.20 (a), (b).(c), (d) Dubinin-Radushkevich plot for lead adsorption at 20,30, 40 and 50°C

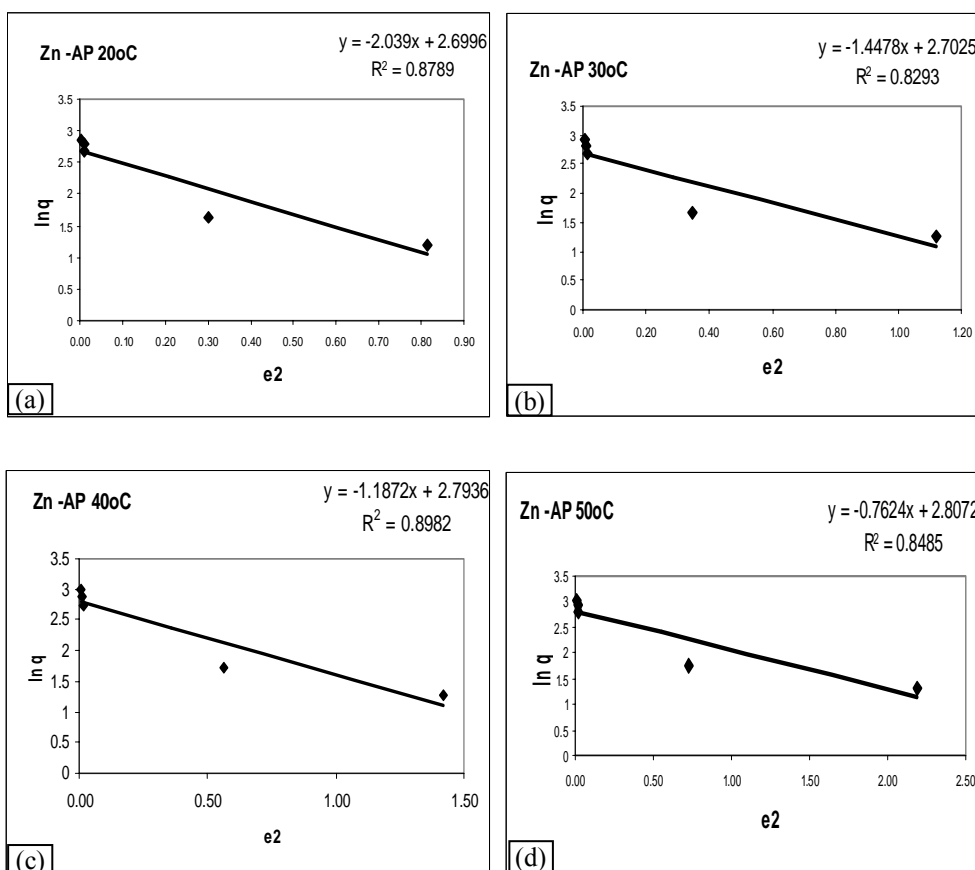


Figure 5.21 (a), (b),(c), (d) Dubinin-Radushkevich plot for zinc adsorption at 20,30, 40 and 50°C

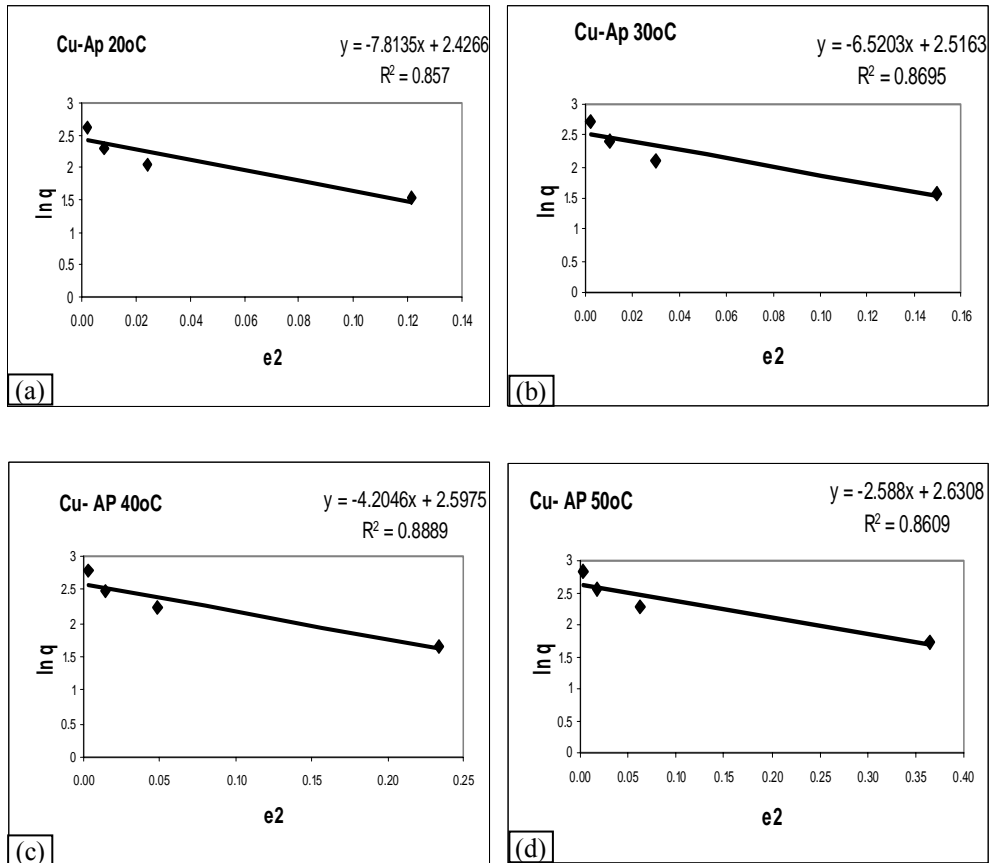


Figure 5.22 (a), (b),(c), (d) Dubinin-Radushkevich plot for zinc adsorption at 20,30, 40 and 50°C

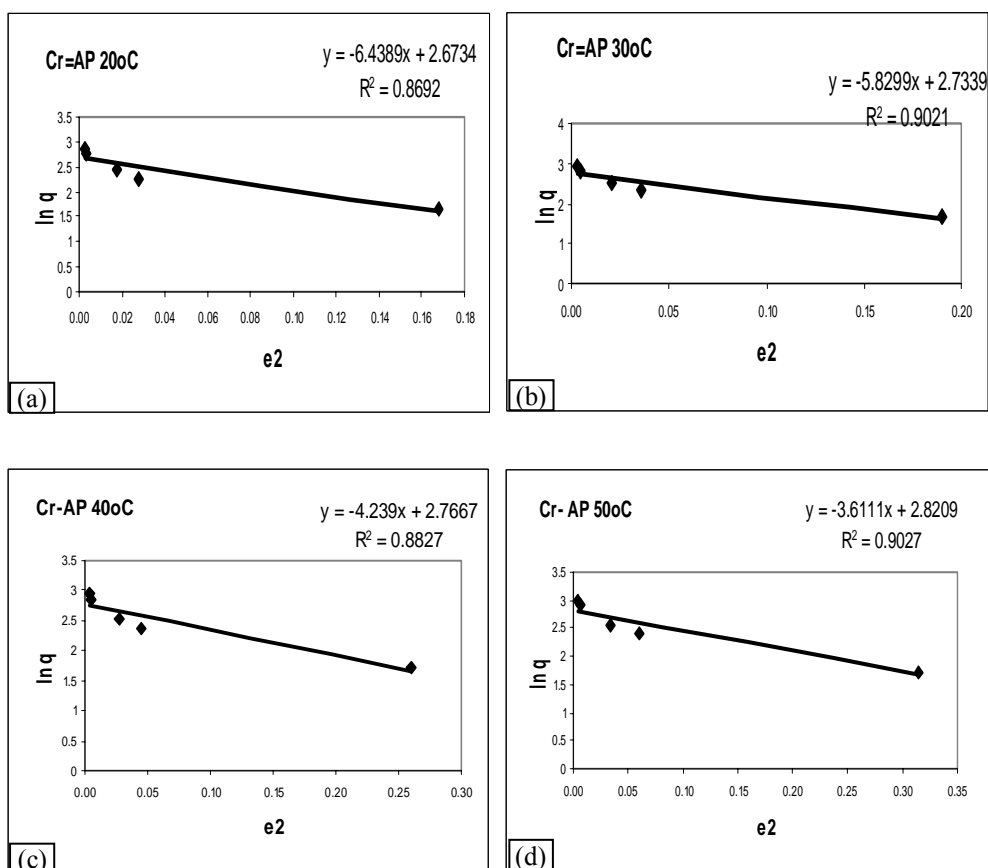


Figure 5.23 (a), (b),(c),(d)Dubinin-Radushkevich plot for chromium adsorption at 20,30,40 and 50°C

Table 5.1 Isotherm parameters for the adsorption of Cd(II), Pb(II),Zn(II) Cr(III) and Cu(II) on *Alisma Plantago Aquatica*

Heavy Metals	T(K)	R ²	Langmuir model		Freundlichmodel			Dubinin-Radushkevich		
			q _{max} (mg/g)	b(Lmg ⁻¹)	R ²	1/n	K	R ²	q _{max} (mg/g)	E(kJmol ⁻¹)
Cd(II)	293	0.993	16.13	0.567	0.904	0.193	8.11	0.817	14.44	1.078
	303	0.996	17.30	0.649	0.991	0.225	7.87	0.888	15.71	1.062
	313	0.997	18.52	0.718	0.957	0.251	8.51	0.934	16.89	1.093
	323	0.999	19.34	0.786	0.845	0.230	9.34	0.989	17.98	1.096
Pb(II)	293	0.992	27.24	0.128	0.957	0.523	4.30	0.854	16.29	0.649
	303	0.996	27.02	0.157	0.931	0.510	4.84	0.908	17.57	0.687
	313	0.997	26.80	0.182	0.938	0.483	5.35	0.873	17.35	0.836
	323	0.998	26.32	0.224	0.945	0.456	6.02	0.865	17.36	1.022
Zn(II)	293	0.993	24.27	0.069	0.992	0.595	2.18	0.879	14.87	0.495
	303	0.993	25.12	0.075	0.994	0.591	2.36	0.829	14.92	0.587
	313	0.992	25.83	0.089	0.995	0.578	2.74	0.898	16.34	0.648
	323	0.995	26.67	0.106	0.997	0.562	3.19	0.848	16.56	0.809
Cu(II)	293	0.995	19.65	0.044	0.995	0.529	1.75	0.857	11.32	0.253
	303	0.998	20.53	0.052	0.983	0.515	2.07	0.869	12.38	0.277
	313	0.997	21.18	0.065	0.982	0.473	2.67	0.889	13.43	0.345
	323	0.998	21.41	0.082	0.980	0.438	3.27	0.861	13.88	0.439
Cr(III)	293	0.995	25.19	0.046	0.977	0.540	2.21	0.869	14.49	0.278
	303	0.997	25.13	0.055	0.835	0.450	2.85	0.902	15.39	0.293
	313	0.998	25.97	0.059	0.974	0.534	6.82	0.883	15.91	0.343
	323	0.999	26.88	0.065	0.958	0.529	2.93	0.903	16.79	0.372

5.4.6 Adsorption kinetics

To study the adsorption kinetics of Cd(II), Pb(II),Zn(II) Cr(III) and Cu(II) on *Alisma plantago aquatica* first order kinetics and second order kinetics were applied to the batch experimental data as shown in Figure 5.24 – 5.30. The kinetics in most cases follows the first order rate equation (Azouaou 2010; Gupta and Rastogi 2007). The obtained correlation coefficient values $R^2 > 0.99$ indicate that all the metal ions sorption on *Alisma plantago*

aquatica proceeds followed the pseudo second order equation. The values of the first order, second order and intra particle diffusion kinetic models are tabulated in the Table 5.2.

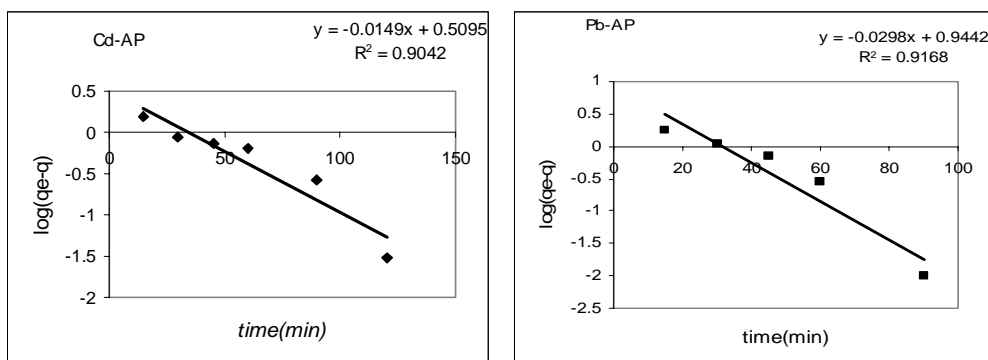


Figure 5.24 (a), (b) First order adsorption kinetics plot of cadmium & lead

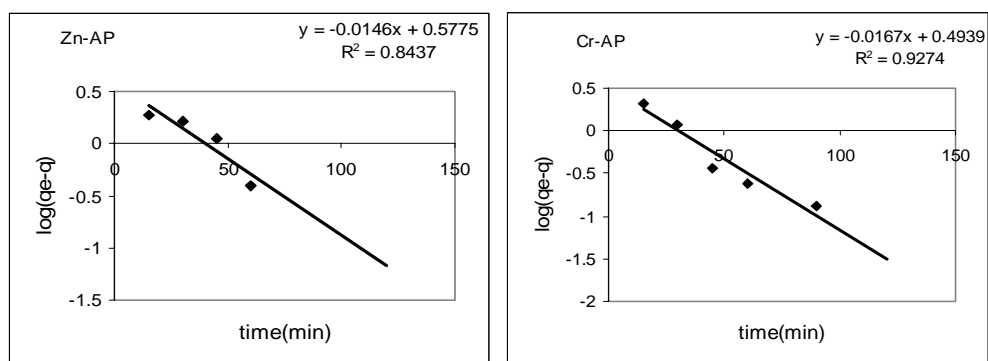


Figure 5.25 (a), (b) First order adsorption kinetics plot of zinc & chromium

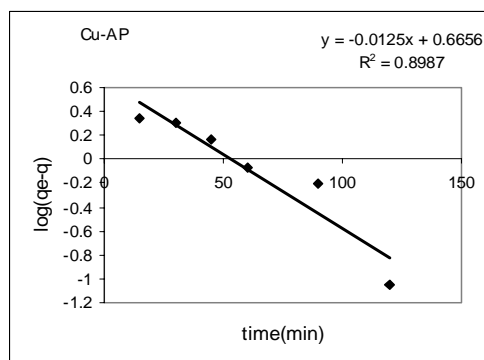


Figure 5.26 First order adsorption kinetics plot of copper

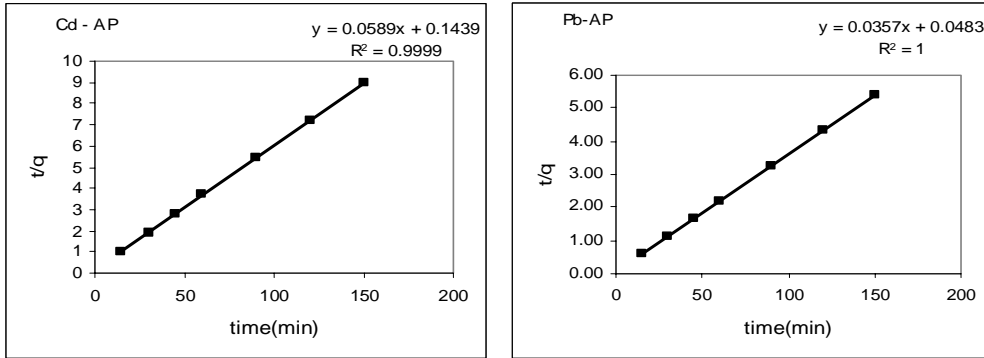


Figure 5.27 (a), (b) Second order adsorption kinetics plot of cadmium & lead

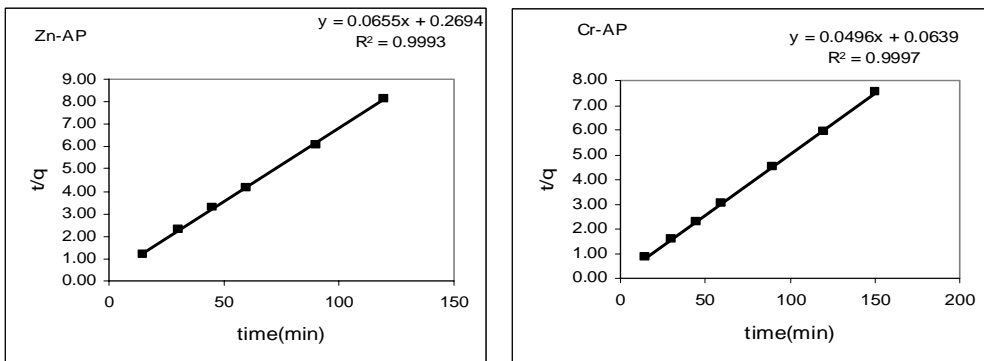


Figure 5.28 (a), (b) Second order adsorption kinetics plot of zinc & chromium

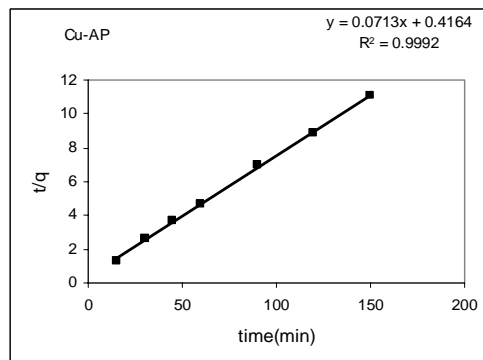


Figure 5.29 Second order adsorption kinetics plot of copper

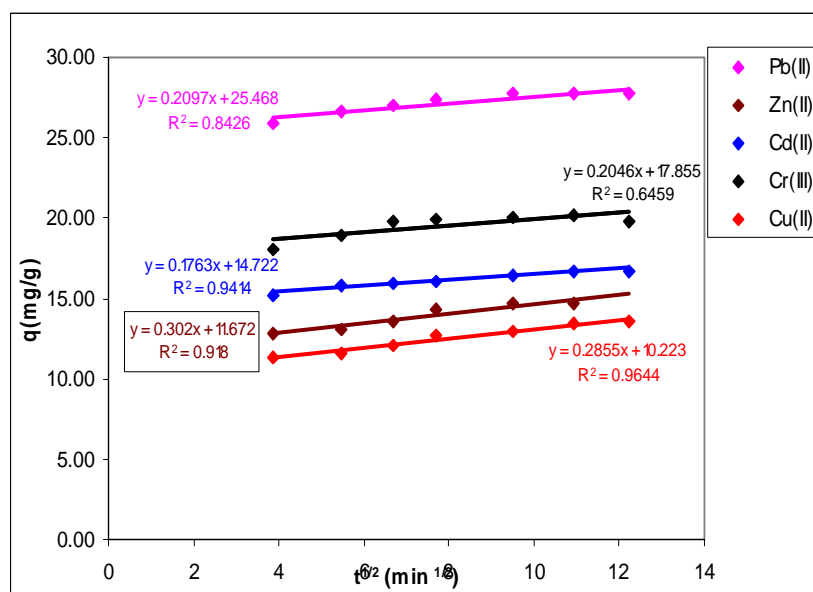


Figure 5.30 Plots for evaluating intra particle diffusion rate constant

Table 5.2 Kinetics parameters for the adsorption of Cd(II), Pb(II), Zn(II), Cr(III) and Cu(II) onto *Alisma Plantago Aquatica*

Heavy Metals	q _{exp} (mg/g)	First order			Second order			Intra Particle diffusion	
		R ²	q _{calc} (mg/g)	k ₁ (min ⁻¹)	R ²	q _{calc} (mg/g)	k ₂ (gmg ⁻¹ min ⁻¹)	k _d (mg ⁻¹ min ^{-1/2})	R ²
Cd(II)	16.73	0.904	3.23	0.034	0.999	16.98	0.024	0.176	0.941
Pb(II)	27.71	0.917	8.79	0.068	1	28.01	0.026	0.209	0.842
Zn(II)	14.73	0.844	3.78	0.033	0.999	15.27	0.016	0.302	0.918
Cr(III)	20.13	0.927	3.12	0.038	0.999	20.16	0.038	0.205	0.646
Cu(II)	13.56	0.898	4.63	0.028	0.999	14.02	0.012	0.285	0.964

5.4.7 Thermodynamic parameters

The experiments were conducted at different temperatures (20, 30, 40, 50°C). The thermodynamic parameters such as change in standard free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) can be determined using the equations. R is (8.314 J/molK) is the gas constant, T(K) the absolute temperature and b (L/mol) the thermodynamic equilibrium constant. The values

of enthalpy and entropy were obtained from the slope and intercept of the plots as shown in Figures 5.31 – 5.33. Positive values of ΔH indicate that the adsorption of metal ions on the adsorbent is endothermic ($\Delta H = 8.42, 14.46, 11.36, 8.95, 16.76 \text{ kJmol}^{-1}$ for Cd, Pb, Zn, Cr and Cu respectively). The negative values of ΔG reveal the feasibility and spontaneous nature of the process. Here Cd(II), and Pb(II) are more spontaneous process compared to other metals. This result also shows that the adsorption capacity of *Alisma plantago aquatica* for all metals increases with increasing temperature. The ΔS values are very small that means the entropic change occurring during adsorption process is negligible (Hao Chen et al., 2010; Mohan and Singh 2002)

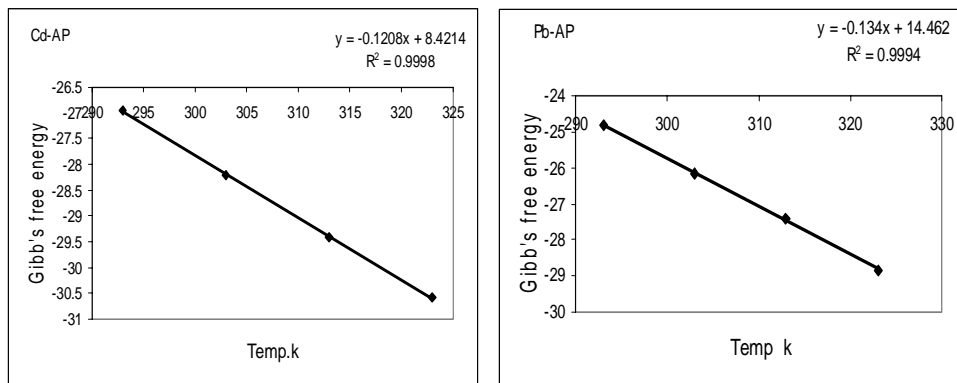


Figure 5.31 (a),(b) Plots of the Gibbs free energy vs. Temperature of cadmium and lead

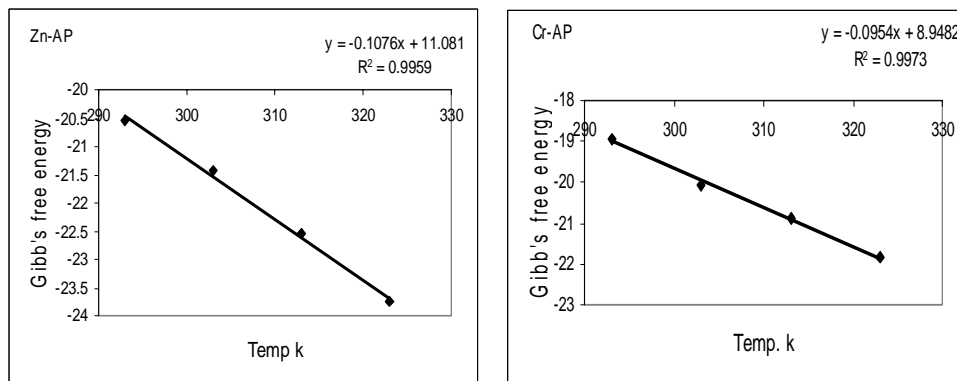


Figure 5.32 (a),(b) Plots of the Gibbs free energy vs. Temperature of zinc and chromium

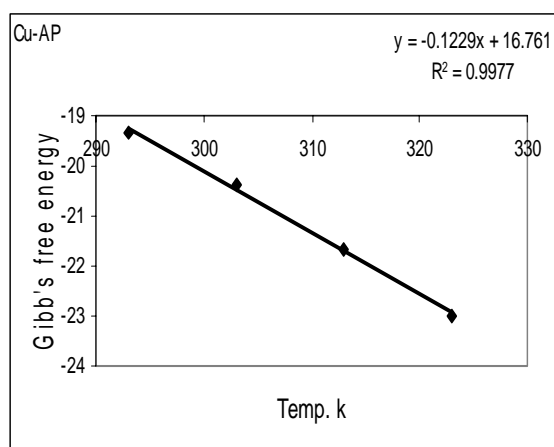


Figure 5.33 Plots of the Gibbs free energy vs. Temperature of copper

Table 5.3 Thermodynamic parameters for the adsorption of Cd(II), Pb(II), Zn(II) Cr(III) and Cu(II) on *Alisma Plantago Aquatica* at various temperatures.

Heavy metals	T(K)	b (Lmol ⁻¹)	$\Delta G(\text{kJmol}^{-1})$	$\Delta H(\text{kJmol}^{-1})$	$\Delta S(\text{kJmol}^{-1}\text{K}^{-1})$	R ²
Cd(II)	293	63702.8	-26.95	8.421	0.1208	0.9998
	303	72954.1	-28.21			
	313	80710.4	-29.40			
	323	88354.3	-30.58			
Pb(II)	293	26521.6	-24.81	14.462	0.1340	0.9994
	303	32530.4	-26.17			
	313	37710.4	-27.42			
	323	46412.8	-28.85			
Zn(II)	293	4570.76	-20.53	11.364	0.1086	0.9959
	303	4904.25	-21.41			
	313	5800.10	-22.55			
	323	6918.30	-23.74			
Cr(III)	293	2392	-18.95	8.9482	0.0954	0.9973
	303	2860	-20.05			
	313	3068	-20.89			
	323	3411	-21.85			
Cu(II)	293	2783.50	-19.32	16.760	0.123	0.9977
	303	3272.83	-20.39			
	313	4130.75	-21.67			
	323	5230.16	-22.99			

5.4.8 Desorption studies

A desorption study is also important since it is useful in the recycling of the adsorbent and recovery of metal. In order to know the nature of adsorption i.e., physical, chemical or both, desorption study was carried out. The studies were carried out using HCl, H₂SO₄, HNO₃, H₂C₂O₄, NaOH and Na₂CO₃ of known concentration of 0.1N with the metal loaded adsorbent. For the desorption experiments, several solvents (acids and bases) have been used as shown in the Figure 5.34. Batch desorption experiments were carried out and the desorption efficiencies are compared in Table 5.4. Hydrochloric acid showed the maximum desorption efficiency for Pb(II), Cu(II) and Zn(II). %Desorption efficiency using 0.1N HCl for various cycles is shown in Table 5.5. It is observed from Table 5.5 that adsorption capacity decreases gradually with the increase of cycle number. The desorption of adsorbed metal ions on adsorbent resulted about 90% thereby indicating the process of adsorption physical in nature. For each adsorption –desorption cycle, new active sites generated by dilute HCl treatment was decreases, resulting in decrease adsorption capacity with the increase in cycle number. Table 5.5 also shows that desorption capacity change evidently in the whole regeneration studies. It can be easily known that desorption efficiency decreases with increasing cycle number due to the decrease of adsorption capacity. In general Cd²⁺ Pb²⁺ Zn²⁺ and Cu²⁺ loaded *Alisma Plantago Aquatica* can be easily desorbed by selecting HCl as a regenerant.

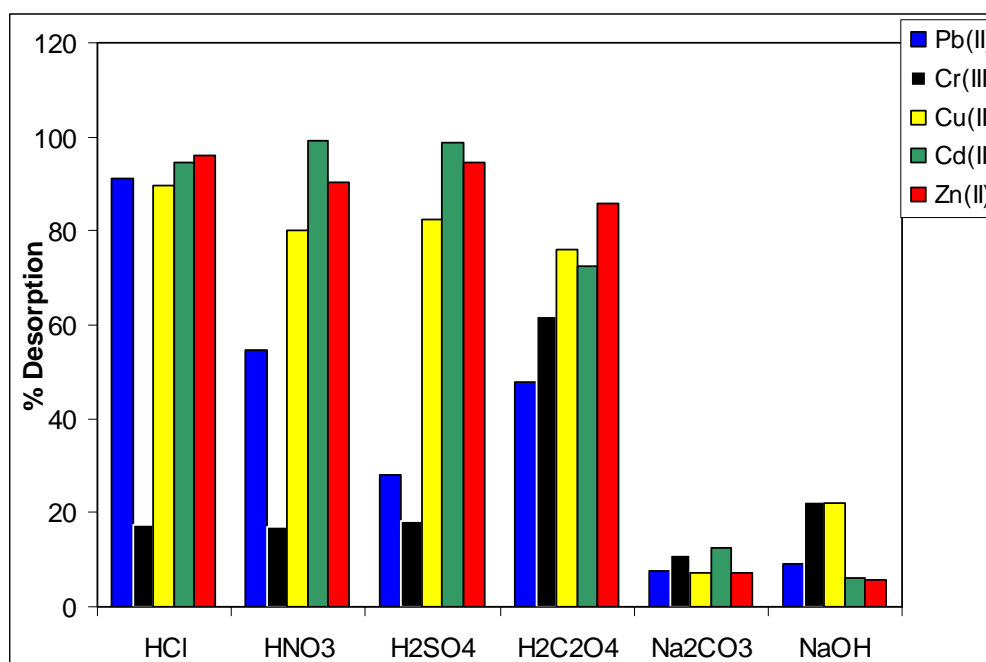


Figure 5.34 Desorption efficiency using various solvents

Table 5.4 Percentage desorption efficiency using various Solvents

Heavy metals	% Adsorption	HCl	HNO ₃	H ₂ SO ₄	H ₂ C ₂ O ₄	Na ₂ CO ₃	NaOH
		%Desorption					
Cd	80.96	94.71	98.96	98.56	72.45	12.52	6.11
Pb	98.22	91.26	54.57	28.00	47.93	7.68	8.94
Zn	53.42	95.89	90.42	94.46	85.64	7.13	5.68
Cr	83.46	17.52	17.19	18.38	61.75	11.09	22.23
Cu	85.42	89.49	80.32	82.25	75.83	7.13	22.14

Table 5.5 %Desorption efficiency using 0.1N HCl for various cycles

Cycles	I		II		III		IV		V	
	% adn	% Desn	% adn	% Desn	% adn	% Desn	% adn	% Desn	% adn	% Desn
Cd	77	96	74	86	55	73	38	63	19	26
Pb	97	93	86	84	68	73	67	73	66	68
Zn	87	79	51	45	44	25	29	23	16	22
Cu	90	93	28	63	11	49	5	43	4	42

5.5 Characterization of the adsorbent

Fourier transform infrared spectral analysis was carried out in order to identify the different functional groups present in the given samples as shown in Figures 5.35 – 5.39. The different functional groups which are present in the given samples are OH stretching, CH stretching, C=C stretching, C-O stretching. FTIR spectrum of given raw *Alisma Plantago Aquatica* sample shows a broad and intense peak at 3330.18cm^{-1} which can be attributed to the stretching of O-H group due to inter- and intramolecular hydrogen bonding of polymeric compounds such as alcohols or phenols. The peak observed at 2918cm^{-1} was associated with the stretching vibrations of C-H bond of methyl, methylene and methoxy groups. The peaks around $1600\text{-}1627\text{cm}^{-1}$ corresponded to the C=C stretching which might be attributed to the presence of aromatic or olefinic or N-H bending bands. The intense peak at $1000\text{-}1031\text{cm}^{-1}$ corresponded to the C-O stretching of alcohol or carboxylic acid. FTIR spectrum of the given raw *Alisma Plantago Aquatica* loaded with different metals shows that the peaks at $3330, 2918, 1606, 1009\text{ cm}^{-1}$ (before adsorption) had shifted lightly after binding with metals as shown in the Table 5.6. This was due to the participation of these functional groups in the binding of metal ions. It was also noted that shifting of wave number depends on the concentration of the metal present in the given sample agreed by literature survey (Abuzer and Huseyin 2011; Azouaou 2010; Hao Chen et al., 2010)

The scanning electron micrograph revealed the surface texture and morphology of the adsorbent is showed in Figure 5.40. The surface area of the adsorbent was observed to be $0.4643\text{m}^2/\text{g}$ by BET method.

Table 5.6 Comparison of FTIR band positions of raw *Alisma Plantago Aquatica* (AP) before and after metal ions adsorption in wave number(cm^{-1}).

Assignment	Raw AP	Cd(II)	Pb(II)	Zn(II)	Cr(III)	Cu(II)
O-H stretching	3330.18	3334.80	3337.47	3334.31	3277.90	3336.07
C-H stretching	2918.70	2921.93	2918.75	2921.66	2926.02	2920.61
C=C stretching	1606.90	1627.14	1627.02	1614.77	1624.56	1627.93
C-O stretching	1009.48	1029.59	1031.65	1031.33	1015.86	1011.23

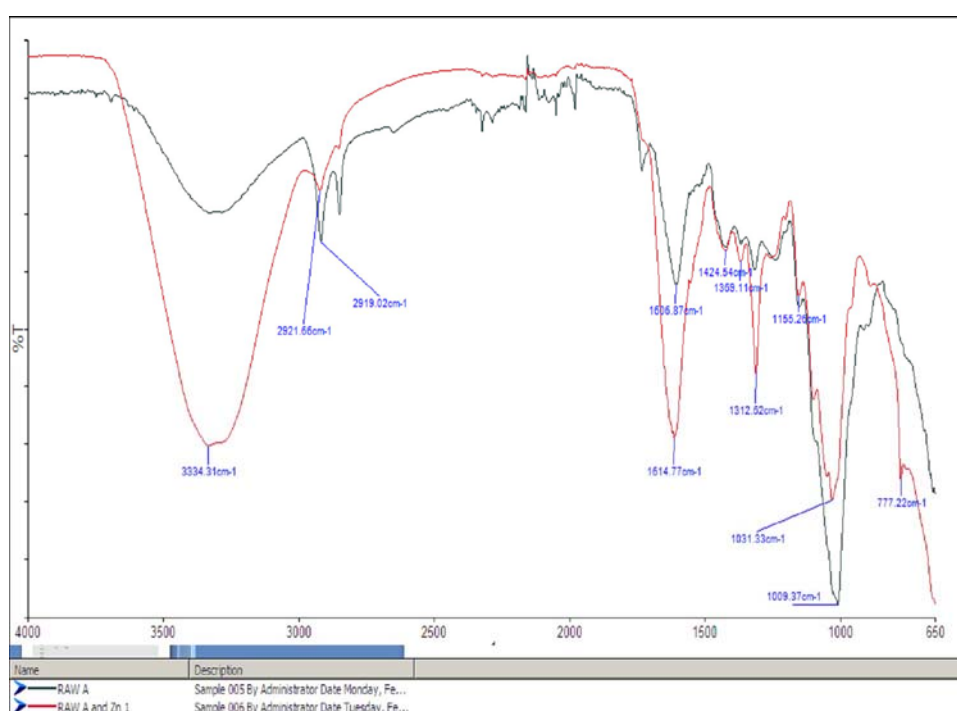


Figure 5.35 FTIR spectra of AP before and after adsorption on Zn(II)

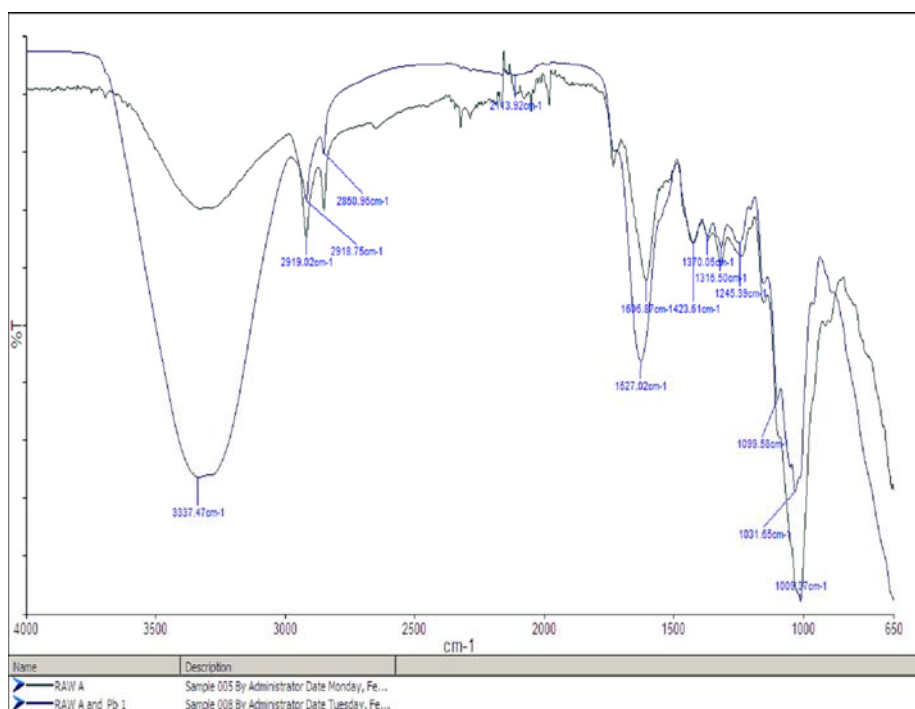


Figure:5.36 FTIR spectra of AP before and after adsorption on Pb(II)

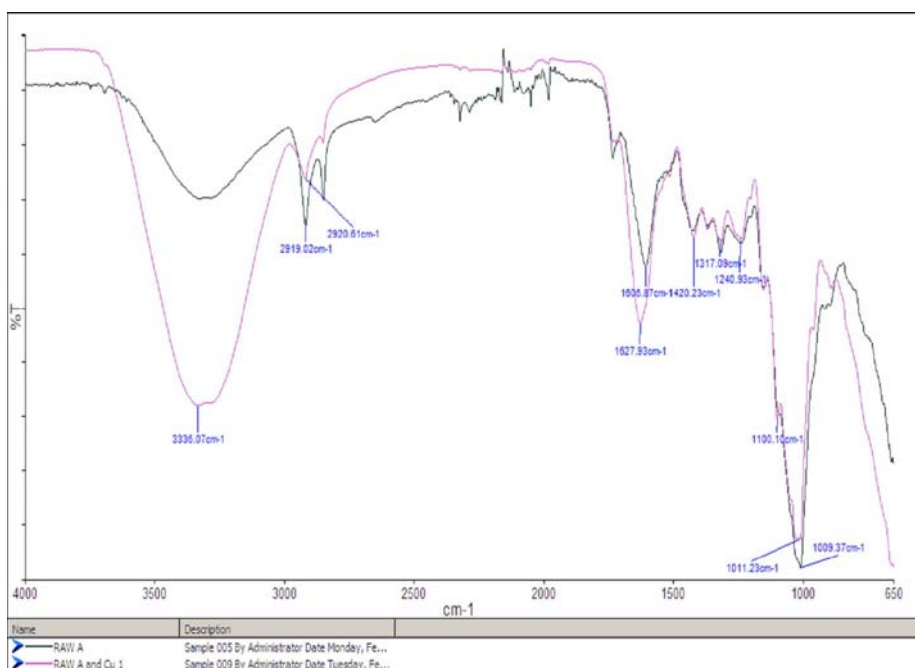


Figure 5.37 FTIR spectra of AP before and after adsorption on Cu(II)

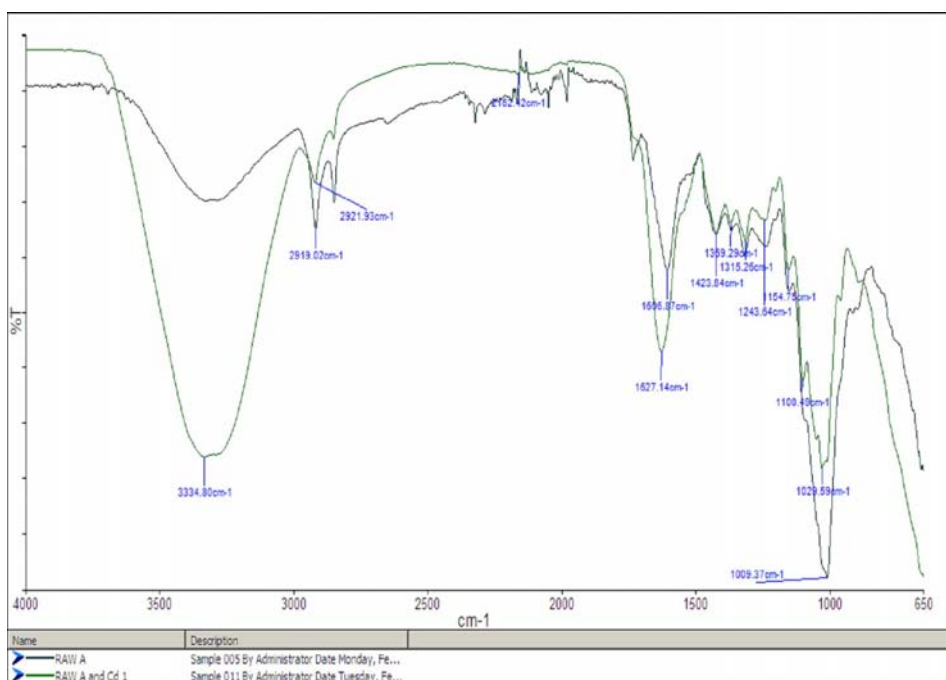


Figure 5.38 FTIR spectra of AP before and after adsorption on Cd(II)

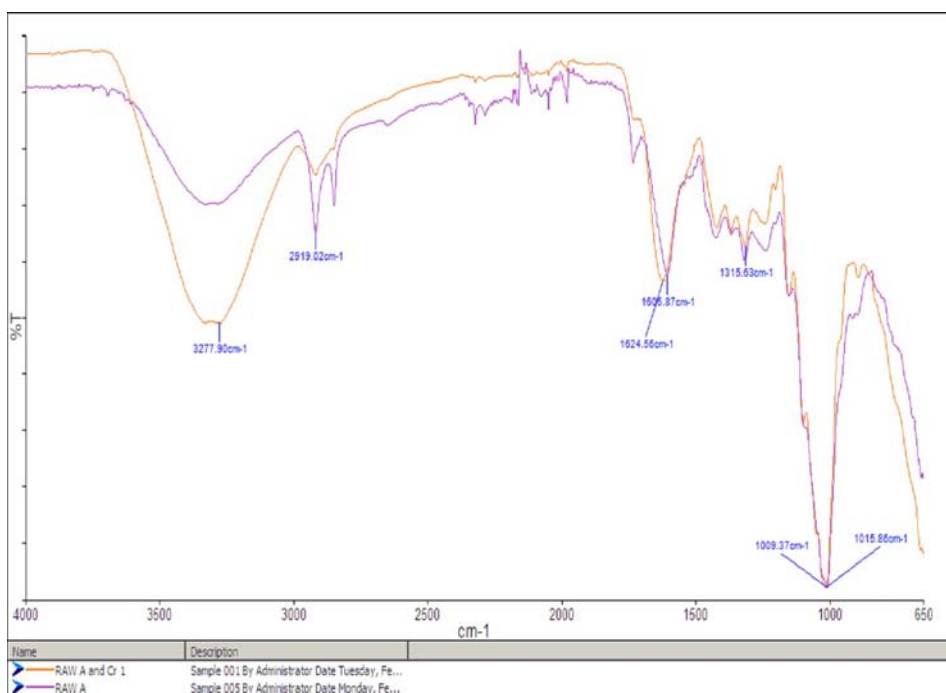


Figure 5.39 FTIR spectra of AP before and after adsorption on Cr(III)



Figure 5.40 Scanning Electron microscopy of *Alisma Plantago Aquatica*

5.6 Continuous study

A continuous fixed bed study was carried out using *Alisma Plantago Aquatica* as an adsorbent for the removal of zinc. In column operation, rate of adsorption depends on the concentration of metal in the solution being treated. As the adsorbent is continuously in contact with fresh metal bearing solution, the concentration of the solution in contact with a given layer of adsorbent in the column is relatively constant. The performance of packed bed column was analyzed using the effluent concentration versus time curves. For adsorption, the plot is usually referred to as the breakthrough curve.

The relative concentration of metal ions in treated effluent was plotted as a function of time in the form of breakthrough curves as illustrated by representative data in Figures.5.41 to 5.42. As the flow rate increases, the breakthrough curves become steeper and the breakpoint time decreases. The

flow rate affects the slope of the linear part of the breakthrough curve. Saturation time is also greatly affected by the flow rate. As flow rate is increased, the time required for breakthrough point of zinc uptake decreased. At lower inlet zinc concentration the treated volume was greater.

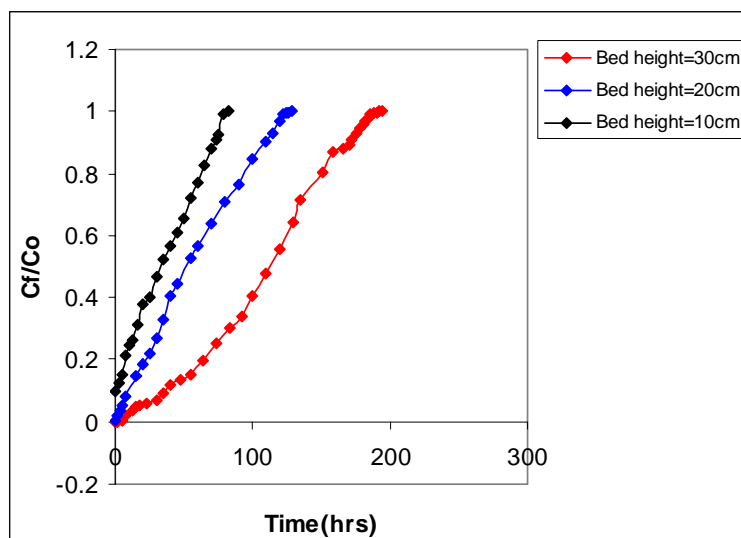


Figure 5.41 Breakthrough curves at different bed depths for zinc adsorption. Flow rate 3ml/min, $C_o = 10\text{mg/l}$

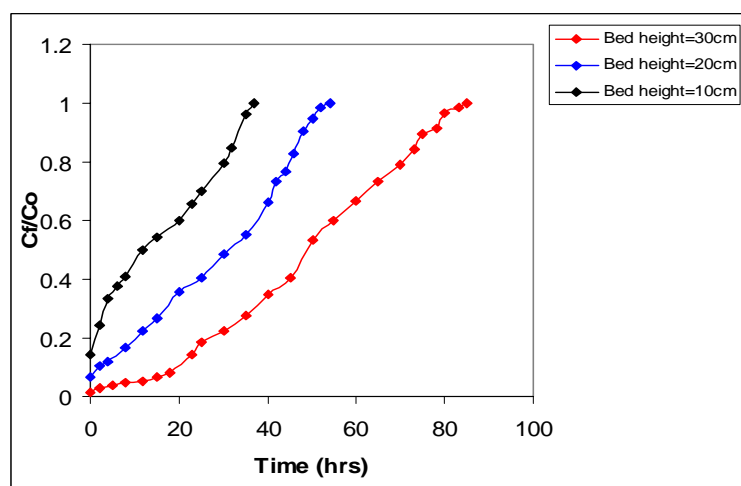


Figure 5.42 Breakthrough curves at different bed depths for zinc adsorption. Flow rate 6ml/min, $C_o = 10\text{mg/l}$

5.6.1 Mathematical description

The performance of packed beds is described through the concept of the breakthrough curve. The time for breakthrough appearance and the shape of the breakthrough curve are very important characteristics for determining the operation and the dynamic response of an adsorption column.

The breakthrough curves show the loading behavior of zinc to be removed from solution in a fixed bed and is usually expressed in terms of the adsorbed zinc concentration (C_{ad}) = inlet zinc concentration (C_o) – outlet zinc (C_f)

The maximum (equilibrium) capacity of the column for given feed concentration is equal to the area under the plot of the adsorbed metal ion concentration C_{ads} versus time or the area behind the breakthrough curve. The amount of metal that remains in the effluent, C_{eq} , is the area under the breakthrough curve as shown in Figures 5.43 to 5.48.

$$C_{max} = Q \int_{t=0}^{t=t_{total}} C_{ad} dt \quad (5.1)$$

$$W = QC_o t_{total} \quad (5.2)$$

$$Y = \frac{C_{max}}{W} 100 \quad (5.3)$$

In the first stage of removal studies in the continuous flow fixed column with *Alisma Plantago Aquatica*, the flow rate was changed from 3ml/min to 6ml/min. and the zinc concentration in the feed was kept constant at 10ppm. From the Table 5.7 at the lowest flow rate of 3ml/min, relatively higher uptake capacity values were observed. In general the total adsorbed zinc quantity, maximum zinc uptake and zinc removal percentage values decreased with increasing flow rate.

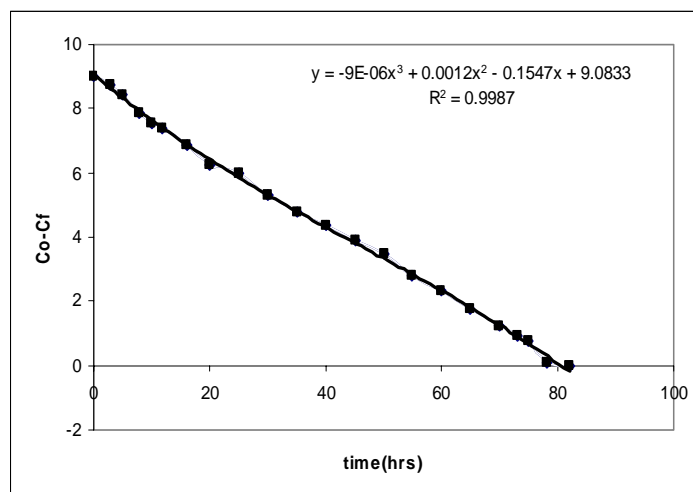


Figure 5.43 Plots of zinc adsorbed against time for flow rate of 3ml/min, bed depth of 10cm and concentration = 10mg/l

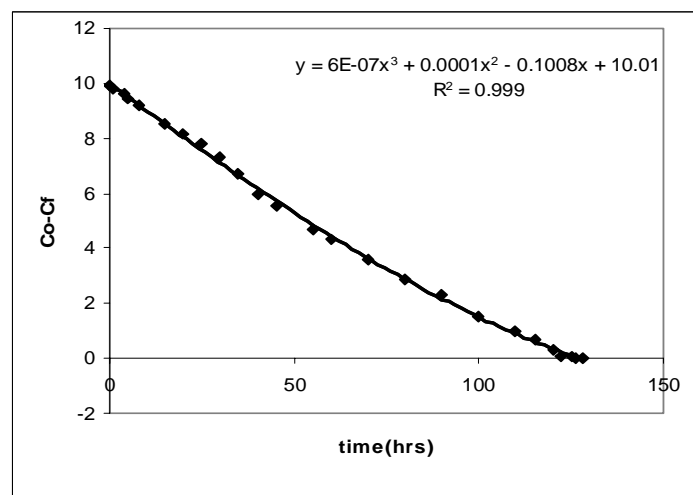


Figure 5.44 Plots of zinc adsorbed against time for flow rate of 3ml/min, bed depth of 20cm and concentration = 10mg/l

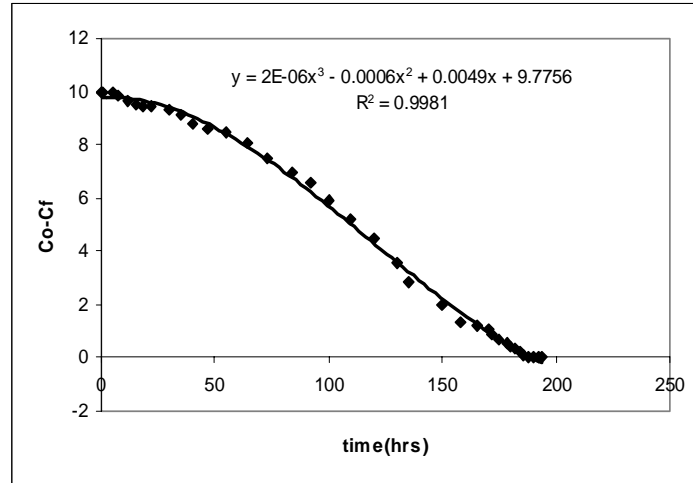


Figure 5.45 Plots of zinc adsorbed against time for flow rate of 3ml/min, bed depth of 30cm and concentration = 10mg/l

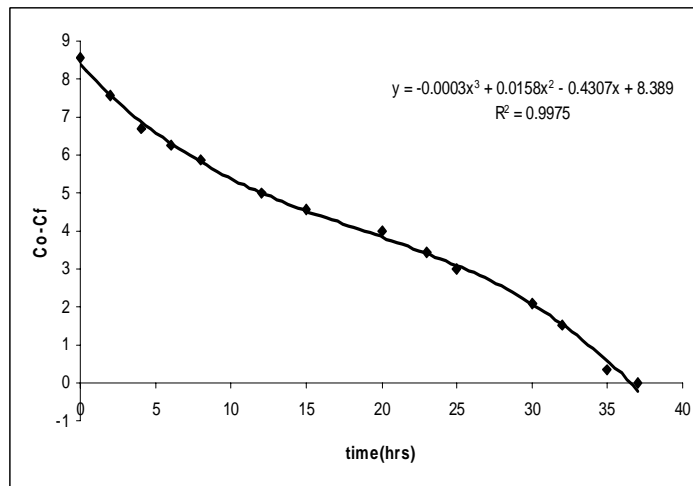


Figure 5.46 Plots of zinc adsorbed against time for flow rate of 6ml/min, bed depth of 10cm and concentration = 10mg/l

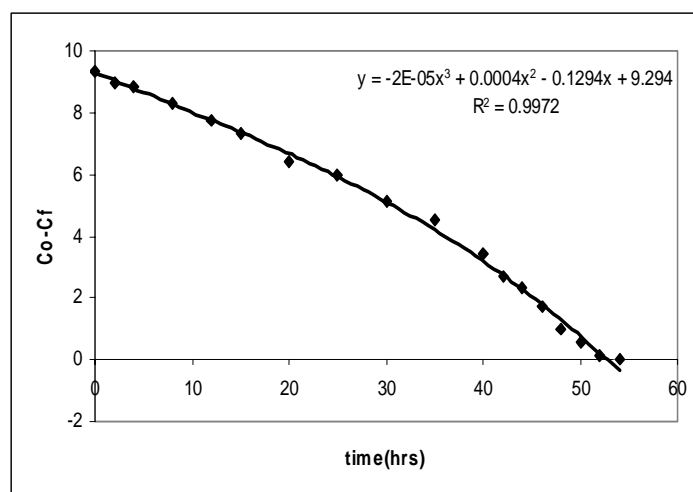


Figure 5.47 Plots of zinc adsorbed against time for flow rate of 6ml/min, bed depth of 20cm and concentration = 10mg/l

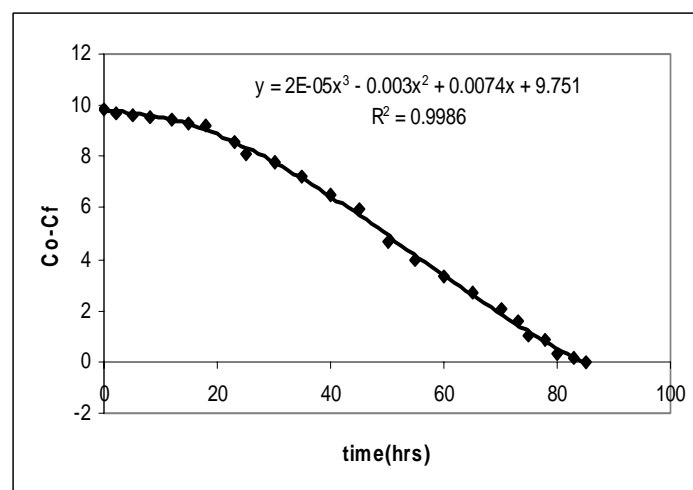


Figure 5.48 Plots of zinc adsorbed against time for flow rate of 6ml/min, bed depth of 30cm and concentration = 10mg/l

Table 5.7 Effect of flow rate and bed depth on the adsorption of Zn(II) by *Alisma Plantago Aquatica*

Flow rate (ml/min)	Conc. (mg/l)	Bed depth (cm)	Maximum equilibrium capacity(mg)	Metal loading(mg)	Uptake capacity (mg/gm)	Yield (%)
3	10	10	62.0	147.6	15.5	42.0
		20	101.8	230.4	12.7	44.2
		30	223.0	349.2	18.6	63.8
6	10	10	51.1	133.2	12.8	38.3
		20	105.0	194.4	13.1	54.0
		30	180.9	306.0	15.1	59.1

5.6.2 Application of the Adams -Bohart and Wolborska models

The fundamental equations describing the relationship between C/C_0 and t in flowing systems were established by Adams -Bohart and Wolborska models. Adams –Bohart model is used for the description of the initial part of the breakthrough curve and is given by the following equations, with parameters k and N_0 .

$$\ln \frac{C}{C_0} = kC_0 t - kN_0 \frac{Z}{U_0} \quad (5.4)$$

Where C is the solute concentration (mg/l); Z the bed depth (cm); k the kinetic constant (l/mg hr); U_0 the linear flow rate (cm/hr), defined as the ratio of the flow rate Q (ml/hr) to the cross sectional area A (cm²) and N_0 the saturation concentration (mg/l).

Wolborska model is also used for the description of adsorption dynamics using mass transfer equations for diffusion mechanisms in the range of the low concentration breakthrough curve. The following relationship describes the concentration distribution in the bed for the low concentration region.

$$\ln \frac{C}{C_o} = \frac{\beta C_o}{N_o} t - \frac{\beta Z}{U_o} \quad (5.5)$$

Where β is the coefficient of the external mass transfer (1/hr). The expression of the Wolborska solution is equivalent to the Adams – Bohart relation if the coefficient k is equal to β/N_o .

Both the model expression can be linearized to give a relationship between $\ln (C/C_o)$ and time as shown in the Figures 5.49 – 5.50 from which the model parameters can be calculated. It was observed that the model predictions agreed very closely with experimental data giving a linear relationship up to 50% breakthrough, for all breakthrough curves ($R^2 > 0.9$). The model parameters, rate constant (k) or mass transfer coefficient (β) and the adsorption capacity (N_o) were calculated from the slope and intercept of the lines respectively. The values of the Adams -Bohart and Wolborska model parameters corresponding to the experimental conditions and determination coefficient (R^2) are given in the Table 5.8

The values shown in the Table 5.8 was obtained after applying the respective model equations to the experimental data for varying bed depths zinc adsorption column. However Adams -Bohart and Wolborska model predictions of N_o matched well. Although the Adams -Bohart and Wolborska model provides a simple and comprehensive approach to running and evaluating adsorption column tests, its validity is limited to the range of conditions used.

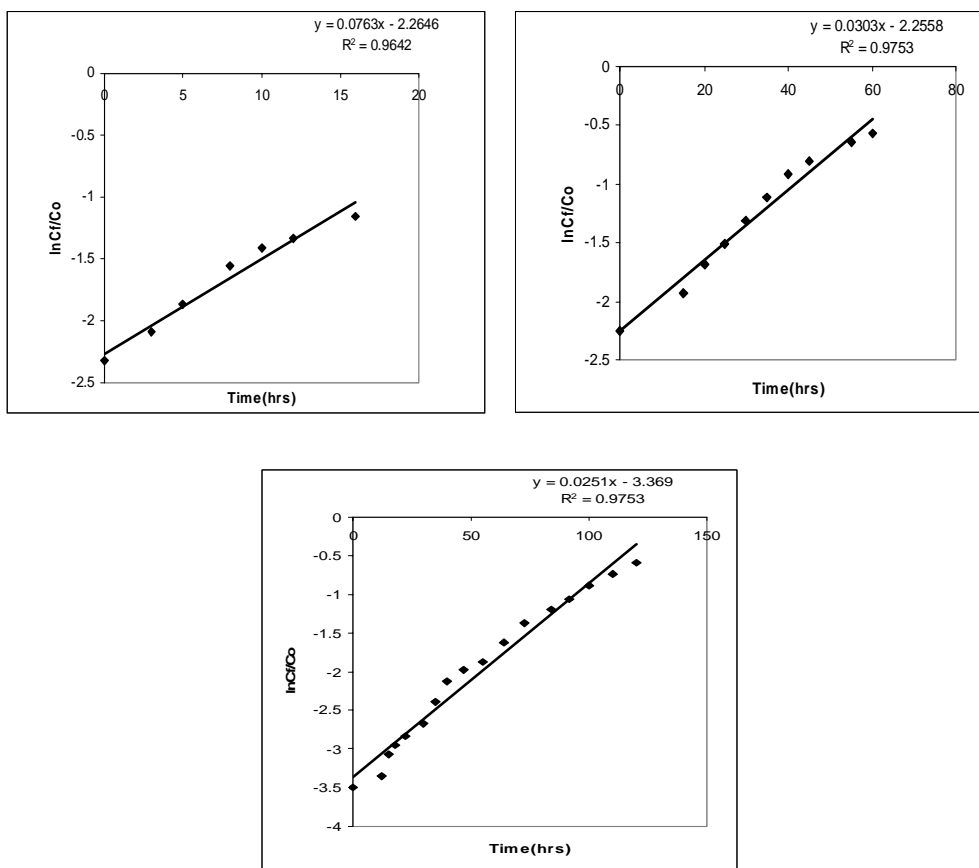


Figure 5.49 Plots of $\ln(C_f/C_o)$ against time for flow rate of 3ml/min and bed depth (a) 10cm (b) 20cm (c) 30cm and conc. 10mg/l

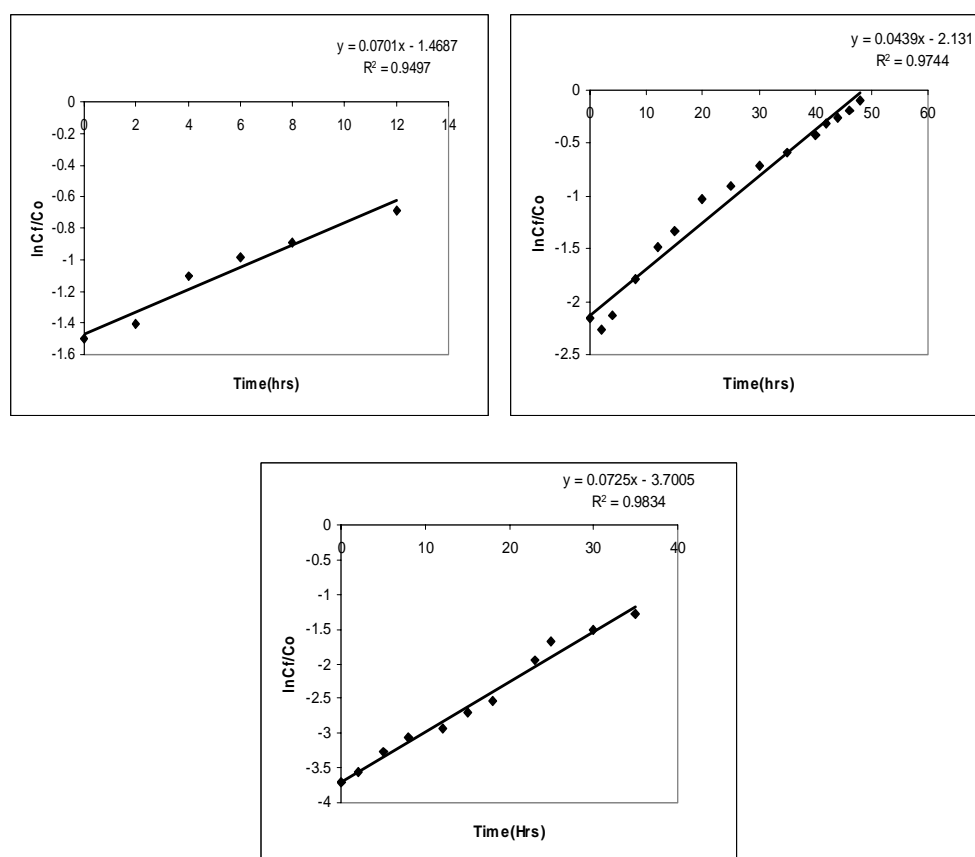


Figure 5.50 Plots of $\ln(C_t/C_0)$ against time for flow rate of 6ml/min and bed depth (a) 10cm (b) 20cm (c) 30cm and conc. 10mg/l

Table 5.8 Adams -Bohart and Wolborska model parameters corresponding to experimental conditions

Flow rate (ml/min)	Conc (mg/l)	Bed depth (cm)	Adams -Bohart		Wolborska		R ²
			N ₀ (mg/l)	k (l/mg hr)	β (1/hr)	N ₀ (mg/l)	
3	10	10	425.32	0.00763	3.245	425.30	0.9642
		20	533.42	0.00303	1.616	533.33	0.9753
		30	641.14	0.00251	1.609	641.03	0.9753
6	10	10	597.20	0.00701	4.18	597.20	0.9497
		20	695.60	0.00439	3.05	695.44	0.9744
		30	487.62	0.00725	3.53	486.89	0.9834

5.7 Conclusions

The present study on removal of Cd(II), Pb(II), Zn(II) Cr(III) and Cu(II) from aqueous solution using naturally available material *Alisma plantago aquatica* was carried out in batch experiment. The operational parameters like pH has significant effect on the removal efficiency. Kinetics data were best modeled by second order kinetics equation. The negative values of ΔG reveal the feasibility and spontaneous nature of the process. Equilibrium models like Langmuir, Freundlich and Dubinin-Radushkevich isotherm models were used for the study and equilibrium data. The breakthrough curves for packed column adsorption of zinc ions by *Alisma plantago aquatica* were plotted at various flow rates. The Adams – Bohart and Wolborska models were applied to experimental data.

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CONCLUSIONS

6.1	Conclusion of the Thesis
6.2	Scope of the Further Research

6.1 Conclusions of the Thesis

The batch study on heavy metal removal by adsorption using mango peel and *Alisma plantago aquatica* were carried out in batch shake flasks. The major findings of the study are discussed in this section.

- Batch studies on cadmium, lead, zinc, chromium and copper removal showed significant effects of the variables adsorbent dose, contact time, initial metal concentration, pH etc. The results provide a good indication of the different operating conditions that would be required for efficient removal of each heavy metal from aqueous solution.
- pH is a significant factor in adsorption processes since it causes electrostatic changes in the solution. The maximum removal efficiency for Cd(II) is 96.24% at pH 6, 95% for Pb(II) at pH 4, 85% for Zn(II) at pH 7, 99.8% for Cr(III) at pH 6 and 76.7% for Cu(II) at pH 5 were obtained for *Alisma plantago aquatica*. Removal of metal were 83.47% Cd(II) at pH 6, 94.93% Pb(II) at pH 4, 86.69% Zn(II) at pH 7, 79.32% Cr(III) at pH 6 and 82.82% Cu(II) at pH 5 for mango peel.

- Langmuir, Freundlich and Dubinin-Radushkevich (D-R) isotherms were observed to fit the equilibrium data and the model parameters were calculated at various temperatures using linearized equations.
- Langmuir isotherm model ($R^2 \approx 1$) is in good agreement with the experimental data as compared to Freundlich and D-R models.
- Kinetics data were best modeled by a pseudo second order kinetics equation.
- The desorption study was also carried out and showed that the hydrochloric acid (HCl) 0.1N is the best extractant.
- The thermodynamic constants, ΔG , ΔH and ΔS of the adsorption process showed that adsorption of Cd(II), Pb(II), Zn(II) Cr(III) and Cu(II) were endothermic and spontaneous.
- The breakthrough curves for packed column adsorption of zinc ions by *Alisma plantago aquatica* were plotted at various flow rates. The results showed that the adsorption of zinc is dependent on flow rate. The zinc removal yield decreased with increasing flow rate.
- The Adams – Bohart and Wolborska models were applied to experimental data obtained from dynamic studies performed on fixed column to predict the breakthrough curves and to determine the column kinetic parameters. The region of the breakthrough was defined by the Adams – Bohart and Wolborska model at all flow rates. The model constants belonging to each model were determined by linear and non – linear regression techniques and were proposed for the use in column design.

6.2 Scope for Future Research

The technology, which uses locally available plant waste material like mango peel, and *Alisma plantago aquatica* is extremely low cost, effective and viable.

Following are the scope for future research:

- To explore the possibilities, modifications / pretreatment of adsorbent to improve its adsorption capacity.
- Studies with actual industrial wastewater to evaluate parameters for field applications.

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A.1 Estimation of concentration of Cadmium, lead, zinc, chromium and copper

The concentration of Cadmium, lead, zinc, chromium and copper were measured by determining the absorbance using an Atomic Absorption Spectrophotometer. The concentrations were read out from a standard plot shown in Figure (A.1-5). For the preparation of standard plot samples of different concentrations of Cadmium, lead, zinc, chromium and copper were prepared from stock solution of 100ppm by appropriate dilution. Absorbance of the samples were measured and plotted as in Figure (A.1-5)

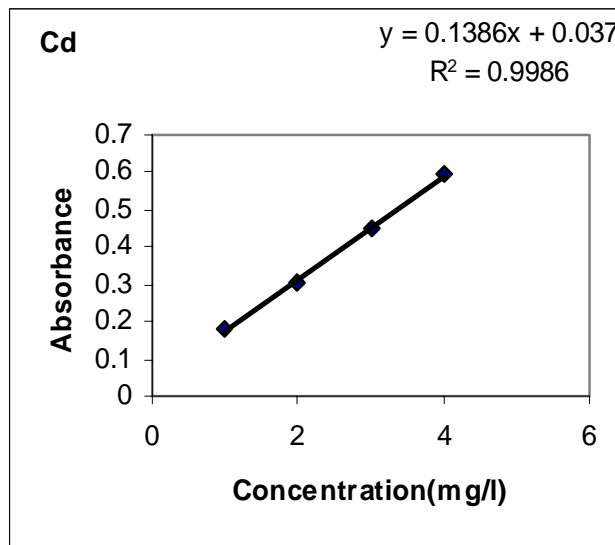


Figure A.1 Standard plot between concentration of cadmium and absorbance.

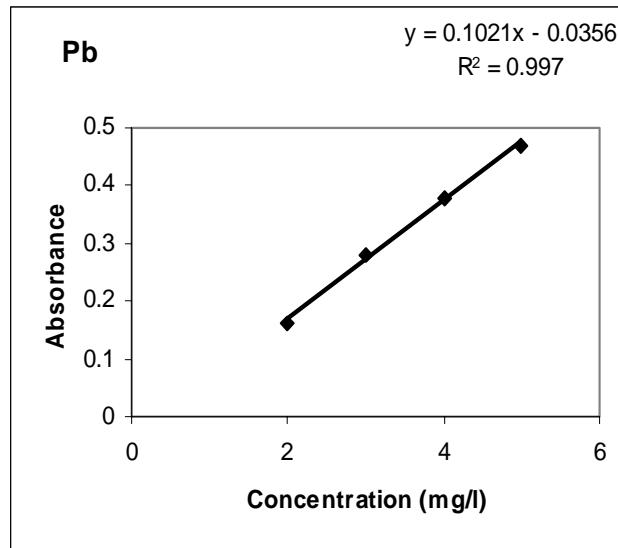


Figure A.2 Standard plot between concentration of lead and absorbance.

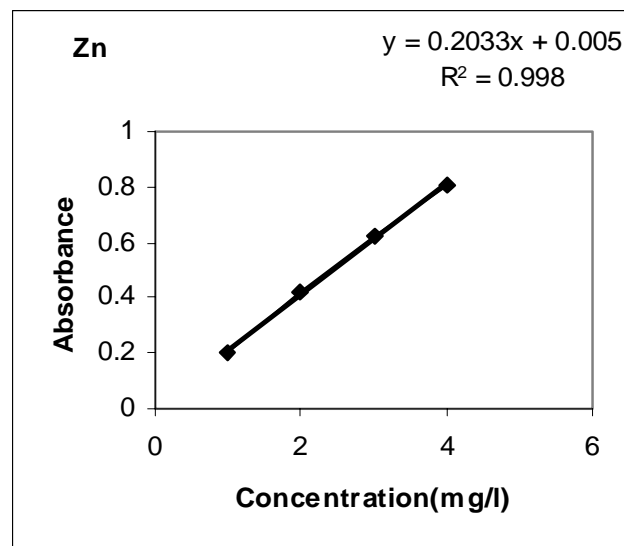


Figure A.3 Standard plot between concentration of zinc and absorbance.

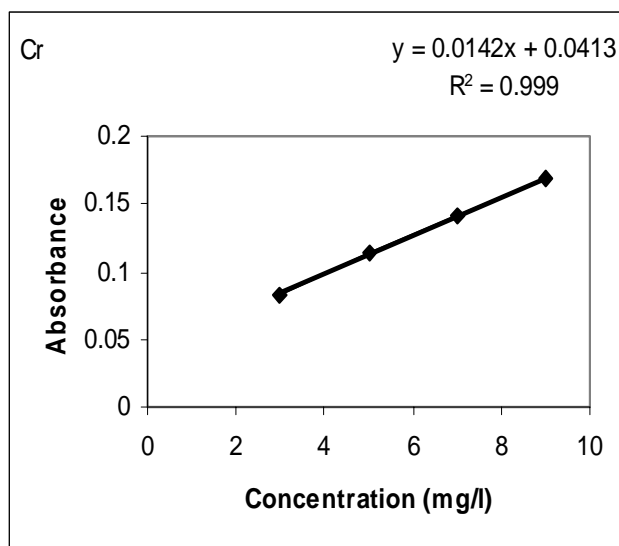


Figure A.4 Standard plot between concentration of chromium and absorbance.

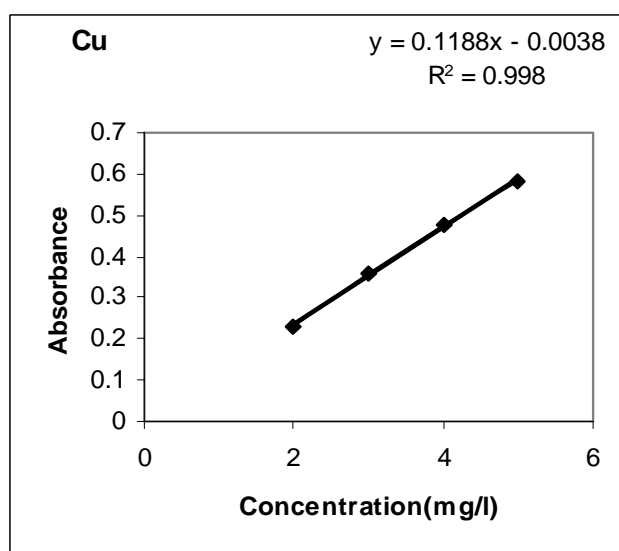


Figure A.5 Standard plot between concentration of copper and absorbance.

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List of Publications

Journals

E.R.Ushakumary and G.Madhu(2013) 'Removal of Cadmium, Chromium , Copper, Lead and Zinc ions by *Alisma Plantago Aquatica* ' International Journal of Environment and Waste Management (Accepted)

Conferences

Ushakumary.E.R, Madhu.G 'Adsorption of Cr(VI) using Natural Adsorbent' Twenty fifth National Convention of Chemical Engineers & National seminar on Energy for a sustainable society October 9-10, 2009.

Ushakumary.E.R, Madhu.G 'Kinetic and Optimization Studies Using *Alisma plantago aquatica* for the Removal of Chromium (VI) from Aqueous Solution' International Conference on Materials for Future ICMF – 2011, February 23-25, Government Engineering College, Thrissur, India.

Ushakumary.E.R, Madhu.G 'Optimization of process parameters for the biosorption of Cr(VI) ions by mango peelings using response surface methodology' International Conference on Recent Advances in Chemical Engineering and Technology(RACET 2011) March 10-12, Kochi, India.

Ushakumary.E.R, Madhu.G 'Waste Water Treatment Using Natural Adsorbent' Second National Technological Congress NATCON 2012, February 9-10, Government Engineering College, Thrissur, India.

Ushakumary.E.R, Madhu.G 'Studies on Zinc (II) Adsorption using *Alisma plantago aquatica*' 4th International Conference on Environmental Engineering and Applications ICEEA 2013, August 24-25, Hotel Royal, Singapore.

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Curriculum Vitae



Ushakumary.E.R received the Bachelor's degree in Chemical Engineering from Government Engineering College, Thrissur, Kerala, India in 1992, and the Master's degree in Chemical Engineering with Environmental Engineering specialization from the Indian Institute of Technology (IIT) Madras, Chennai in 2004. She has about 13 years of experience in teaching. She started her career as Lecturer in Chemical Engineering, Government Engineering College, Thrissur, Kerala, India. She is currently the Associate Professor in the department of Chemical Engineering, Government Engineering College Kozhikode, Kerala , India. The author joined the Division of Safety and Fire Engineering, School of Engineering , Cochin University of Science and Technology, in September 2008, as a doctoral student. Her areas of interest include Environmental Engineering, Food and preservatives, Optimization of chemical processes.

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