LEAD AND CADMIUM REMOVAL FROM AQUEOUS SOLUTION USING WASTE MATERIAL
(MICROWAVE INCINERATED RICE HUSK ASH)

by

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FINAL PROJECT REPORT

Submitted to the Civil Engineering Programme
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for the Degree
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CERTIFICATION OF APPROVAL

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Approved:

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TRONOH, PERAK

June 2008

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

Sri Rahayu bt Mohd Hussin

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ABSTRACT

Presence of heavy metals in aquatic systems has become a serious problem. Heavy metals such Cadmium (Cd) and Lead (Pb) are mostly resulted from industrial activities and adverse effects on environment as well as human health. As a result, there has been a great deal of attention given to new technologies for removal of heavy metal ions from contaminated waters. Commonly used treatment technologies were mostly effective, except for their high operational cost. Thus, this study proposed Microwave Incinerated Rice Husk Ash (MIRHA), locally available agricultural waste for the removal of Pb (II) and Cd (II) from synthetic wastewater by batch adsorption process. Adsorption involves separation of a substance from one phase accompanied by its accumulation or concentration at the surface of another. Influences of pH, initial metal concentration, contact time and absorbent dosage on the removal efficiency of those metals from aqueous solution were studied. pH 3.0 and 4.0 were found to be optimum condition for maximum adsorption of Pb (II) and Cd (II) ions from aqueous solution. The removal efficiency of both metals correlated with the contact time between adsorbent and adsorbate, initial metal concentration as well as adsorbent dosage. Adsorption of Pb (II) and Cd (II) were reached equilibrium after 60 and 120 minutes respectively; with both found to be better fitted with pseudo second order kinetic model. The maximum removal percentage of Pb (II) and Cd (II) were achieved at an adsorbent loading weight of 400 mg and 200 mg correspondingly. The equilibrium adsorption capacity of adsorbent used for Pb (II) and Cd (II) was calculated to be Langmuir and Freundlich respectively. The experimental data were found to fit the Langmuir isotherm for Pb (II) ($R^2 = 0.9991$) and Freundlich isotherm for Cd (II) ($R^2 = 0.7951$).

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CHAPTER 1

1.0 INTRODUCTION

1.1 Background Study

Environmental contamination with heavy metals arises mainly as a result of industrial activities, especially in industries using electrolytic treatments, in engineering processes and in the manufacture of plastics and pigments, although other sources, such as agriculture and waste disposal also contribute to this kind of contamination. Cadmium and lead are examples of heavy metals from industrial activities which are extremely toxic even in very small quantities. These heavy metals are discharged into the atmosphere, water and land-based environments and may reach high concentrations, especially near the discharge site.

Various treatment techniques have been employed to eliminate or reduce heavy metals in water including precipitation, adsorption, ion exchange and reverse osmosis. Studies on the treatment of heavy metals bearing effluents have revealed adsorption to be a highly effective technique (Chand *et al.*, 1994). Biosorption is an alternative technique for removing heavy metals from aqueous solutions, based on the property of a certain class of biomass to accumulate this kind of pollutant through physical or chemical adsorption. The most commonly used natural biosorbents are totally renewable, their cost is low and their use and handling involve no additional risks; they may also be specifically selective for different pollutants and are generally disposed of by incineration (Khan, *et al.*, 2004).

Research in recent years has focused on some natural biomaterials including agricultural products and by-products. The use of agricultural products and by-products has been widely investigated as a replacement for current costly methods of removing heavy metals from water and wastewater. Some agricultural materials can be effectively used as a low-cost adsorbent and can accumulate high concentration of heavy metals.

Modification of agricultural by-product could enhance their natural capacity and add value to them. Adsorbent generated from these biomass are cost effective and efficient (Kumar, 2006). Some previous investigations on the removal of heavy metal ions with many agricultural byproducts have been reported (Isa *et al.*, 2008; Chuah, *et al.*, 2005, Ghani, *et al.*, 2007).

Therefore, this study is to explore the possibility of using microwave incinerated rice husk ash, one of the low-cost agricultural waste products, to be used as adsorbent for removing heavy metals; Cadmium (Cd) and Lead (Pb) from aqueous solution. The influences of various factors such as pH, contact time, initial heavy metals concentration and absorbent dosage on adsorption efficiency will be studied.

1.2 Problem Statement

Trace quantities of many metals, such cadmium, chromium, copper, iron, lead, manganese, mercury, nickel and zinc are important constituent of most water. Most of these metals are necessary for growth of biological life and absence of sufficient quantities of them could limit growth of algae.

However, excessive release of heavy metals into the environment due to industrialization and urbanization has posed a great problem worldwide. Many of these metals are classified as priority pollutants. Unlike organic pollutants, the majority of which are susceptible to biological degradation, heavy metal ions do not degrade into harmless end products. The presence of heavy metal ions is a major concern due to their toxicity to many life forms. Heavy metal contamination exists in aqueous wastes of many industries, such as metal plating, mining operations, tanneries, radiator manufacturing, smelting, alloy industries and storage batteries industries, etc. (Khan *et al.*, 2004).

Several episodes due to heavy metal contamination in aquatic environment increased the awareness about heavy metal toxicity. Lead (Pb) can affect harmfully the nervous system, the hemo group syntheses and the vascular system, especially of children. Cadmium (Cd) is a possible carcinogen and its chronic exposition to high concentrations can result in respiratory illness (Mugica *et al.*, 2002). "Itai-Itai" is a disease that occurred in Japan due to cadmium toxicity. It affected the bones and joint of old women and resulted in a number of deaths.

Metals can be distinguished from other toxic pollutants, since they are non-biodegradable and can accumulate in living tissues, thus becoming concentrated along the food chain (Kumar, 2006).

Since contamination of water due to heavy metal compounds is a severe problem with regards to health hazards, a lot of research has been undertaken in this field to remove them from contaminated water using different techniques. There are several treatment methods capable of this level of performance — membranes, coagulation, ion exchange, disposable iron media, softening etc (Thomas *et al.*, 2007). But most of them were found to be less effective and had many drawbacks when applied in the field. It is very difficult to select an efficient method for heavy metals removal. Some are effective but economically not feasible, some are economically feasible but are not effective. Some are not user friendly, technologically not sound, energy dependent, post treatment requiring, skill manpower requiring, quality of treated water in respect to other parameters in water not maintaining with standard.

1.3 Objectives and Scope Study

The objectives of this study are:

- To investigate microwave incinerated rice husk ash (MIRHA) capability in removing heavy metals, cadmium (Cd) and lead (Pb) from aqueous solution.
- To determine effects of operating parameters (pH, contact time, initial concentration and adsorbent dosage) on Cd and Pb removal.
- To study kinetics of Cd and Pb removal.

- To determine the most suitable isotherm that describes Cd and Pb removal.

The scope of this project concerned on the adsorption studies of two types of heavy metals; cadmium and lead using MIRHA through batch studies. The batch test included equilibrium and kinetic studies. In equilibrium studies, the optimum pH and reaction time for efficient adsorption were investigated. Using the optimum contact time and pH, the effect of two parameters; initial heavy metals concentration and adsorbent dosage were evaluated.

In order to achieve the objective, a few tasks of research were carried out for the first stage of project (FYP 1) to collect all technical details from previous studies regarding the materials and methodology involved. For the second stage (FYP 2), laboratory process, batch test was conducted and all the outcome results gathered were analyzed. The Freundlich and Langmuir isotherm models are used to analyze the adsorption equilibrium while the pseudo-first order and pseudo-second order kinetic equations were used to study the kinetics of Cd (II) and Pb (II) removal using MIRHA.

CHAPTER 2

2.0 LITERATURE REVIEW

2.1 Introduction

Toxic pollutants either organic or inorganic in nature enter the environment through various ways. Most of the organic compounds eventually degrade, regardless of the rate and the level of decomposition. Biodegradation process depends on the ability of microorganism to develop enzymatic mechanism for attacking complex organic structures, while inorganic materials such metal elements present harder challenge (Isa *et al.*, 2008). Cadmium and Lead are examples of elements that cannot be degraded to a substance lesser than the elemental form itself. Since all of them are widely used in industries, hence large amount of heavy metals get into waste streams. Therefore, it is very crucial to provide methods for protecting the environment from heavy metals contamination.

2.2 Heavy metals in the environment

Cadmium (Cd)

Cadmium is flammable in powder form and is toxic by inhalation of dust and fume. Soluble compound of cadmium are highly toxic. It is a metal found in natural deposits as ores containing other elements. The greatest use of cadmium is primarily for metal plating and coating operations, including transportation equipment, machinery and baking enamels, photography, television phosphors. It is also used in nickel-cadmium and solar batteries and in pigments. Metallic constituent in effluent discharges are being regulated.

Lead (Pb)

Pb has been established as a toxic heavy metal. It can be harmful by ingestion or inhalation of dust or fumes. The problem of Pb pollution due to use in Pb service pipes, particularly with soft water was the first recognized metal pollution. Other sources of Pb pollution are battery industry, auto-exhaust, paints, etc. This metal is also widely used for alloys, vibration damping in heavy construction and cable covering (George, *et al.*, 2004).

2.3 Health Effect

Heavy metals have a harmful effect on human physiology and other biological systems when they exceed the allowable limits. Major health effects due to Pb(II) poisoning are nervous and renal breakdown, weakness, headache, brain damage, convulsions behavioral disorders, constipation and ultimately death (Ayyapan *et al.*, 2005). Cadmium (Cd) is a possible carcinogen and its chronic exposition to high concentrations can result in respiratory illness (Mugica *et al.*, 2002). Besides chronic exposure, these contaminants present even at low concentrations in the environment can prove to be harmful to human health. Therefore Department of Environmental (DOE) regulates the legislation concerning the quality of water sources. The government had enlisted 23 parameters limits of Standard A and B effluents, including Pb (II) and Cd (II) in the Malaysian-Environmental Quality Act 1974 (Sewage and Industrial Effluents). The quality of wastewater discharged downstream of water supply sources shall only need to conform to the less stringent standard B parameter limits.

The standard B discharge limit of Pb and Cd under the Malaysian-Environmental Quality Act 1974 (Sewage and Industrial Effluents) are kept below 1.0 mg/L, where the maximum limit under the standard is 0.02 mg/L for Cd and 0.50 mg/L for Pb. Environmental Protection Agency (EPA) also has regulated the limit of metals inside the drinking water. The primary drinking water standard for cadmium is 0.005 mg/L while lead concentration is limited to 0.015 mg/L (Safe Drinking Act 1974)

2.4 Heavy Metal Removal

The greater environmental awareness in recent years has required greater treatment of industrial effluent. As such there has been a great deal of research into finding cost-effective methods for the removal of contaminants from wastewater. In recent years considerable attention has been devoted to the study of removal of heavy metal ions from solution by adsorption using agricultural materials. Natural materials that are available in large quantities or certain waste from agricultural operations may have potential to be used as low cost adsorbents, as they represent unused resources, widely available and are environmentally friendly.

Conventionally, there are several methods for heavy metal removal. Thomas *et al.* (2007) have done some studies on the methods of heavy metals removal including coagulation and flocculation, precipitation, adsorption and ion exchange, membrane filtration, alternative methods like ozone oxidation, bioremediation and electrochemical treatments. Coagulation is the destabilization of colloids by neutralizing the forces that keep them apart. Cationic coagulants provide positive electric charges to reduce the negative charge (zeta potential) of the colloids. As a result, the particles collide to form larger particles. Rapid mixing is required to disperse the coagulant throughout the liquid. Flocculation is the action of polymers to form bridges between the larger mass particles or flocs and bind the particles into large agglomerates or clumps. Bridging occurs when segments of the polymer chain adsorb on different particles and help particles aggregate. An anionic flocculant will react against a positively charged suspension, adsorbing on the particles and causing destabilization either by bridging or charge neutralization.

Membrane separation is a pressure driven process. Pressure driven processes are commonly divided into four overlapping categories of increasing selectivity:

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Membrane separation is a pressure driven process. Pressure driven processes are commonly divided into four overlapping categories of increasing selectivity:

Adsorption phenomena are operative in most natural physical, biological, and chemical systems. Adsorption operations employing solids such as activated carbon, metal hydrides and synthetic resins are widely used in industrial applications for purification of waters and wastewaters. The process of adsorption involves separation of a substance from one phase accompanied by its accumulation or concentration at the surface of another. Physical adsorption is caused mainly by van der Waals forces and electrostatic forces between adsorbate molecules and the atoms which compose the adsorbent surface (Thomas *et al.*, 2007). The adsorbate is the substance that is being removed from the liquid phase at the interface. The adsorbent is the solid, liquid or gas phase onto which the adsorbates accumulate (George *et al.*, 2004). Thus adsorbents are characterized by surface properties such as surface area and polarity.

Generally, batch and column adsorption studies were conducted to study the feasibility of using materials for purification of heavy metals (Arrayapan *et al.*, 2005; Ajmal *et al.*, 2003; Wong *et al.*, 2003) They determined that the efficiency of the adsorption is based on certain parameters such pH, contact time, initial concentration, adsorbent particle size, adsorbent dosage, flow rate, bed depth etc. Wong *et al.* (2003), used tartaric acid modified rice husk as adsorbent and have carried out batch studies for the removal of lead and copper. The effect of various parameters such as pH, initial concentration of adsorbate, particle size, temperature etc has been reported. Arrayapan *et al.*, (2005) also investigated on the effects of initial metal concentration, contact time, pH and adsorbent dose on the removal of Pb(II).

Therefore in this study, most of the parameters investigated and application used were similar with the previous projects, but the author used rice husk ash as the adsorbent.

2.6 Adsorption Isotherm

The quantity of adsorbate that can be taken up by an adsorbent is a function of both the characteristics and concentration of adsorbate and the temperature. Generally, the amount of material adsorbed is determined as the function of the concentration at a constant temperature, and the resulting function is called an adsorption isotherm. Adsorption isotherms are developed by exposing a given amount of adsorbate in a fix volume of liquid to varying amounts of adsorbent (George *et al.*, 2004). The isotherms that most commonly used to describe adsorption characteristics are the empirical relationship Freundlich and the theoretically derived Langmuir relationship.

Freundlich isotherm is expressed as

$$\frac{x}{m} = K_f C_e^{1/n} \tag{2.1}$$

The Langmuir equation, derived based on equilibrium between condensation and evaporation of adsorbed molecules, considering a monomolecular adsorption layer (Isa, et al., 2007) is

$$\frac{x}{m} = \frac{abC_e}{1 + bC_e} \tag{2.2}$$

Where

x/m = amount of adsorbate adsorbed per unit mass of adsorbent (mg adsorbate/g adsorbent)

C_e = equilibrium concentration of adsorbate in solution after adsorption (mg/L)

K_f, n, a and b are constants

The straight-line form of the Freundlich isotherm is

$$\log\left(\frac{x}{m}\right) = \log K_f + \frac{1}{n}\log C_e \tag{2.1a}$$

Langmuir equation adsorption isotherm was developed by assuming: (1) a fixed number of accessible sites are available on the adsorbent surface, all of which have the same energy, (2) adsorption are reversible (George, *et al.*, 2004).

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2.8 Utilization of low-cost adsorbent in adsorption

In recent years researches have focused on the development of cost effective adsorbents using various natural sources and industrial wastes. Industrial and agricultural wastes are potential low-cost adsorbents for metal removal since some of them have displayed high ion exchange capability. In general, a sorbent can be assumed as "low cost" if it requires little processing, is abundant in nature, or is a by product or waste material from another industry (Bailey *et al.*, 1999).

Several researchers have made significant contributions in this area, utilizing a number of agricultural waste by-products such as sugarcane bagasse, rice husk, oil palm shell, coconut shell, coconut husk etc. for the elimination of heavy metals from wastewater (Khan *et al.*, 2004). Low cost materials including maize (*Zea mays*) leaf as adsorbent for Pb (Babarinde *et a*l., 2006), solid sorbent such olive stone (Blazquez *et al.*, 2005), biomaterials such as baggase, charred rice husk, activated charcoal and eucalyptus bark (EB) were tested for removal of chromium (Sarin *et al.*, 2006), Rice husks, maize cobs and sawdust for removing Pb (Ghani *et al.*, 2007), *platanus orientalis* leaves (POL) and their ash (Mahvi *et al.*, 2007) and biomass prepared from ficus religiosa leaves (Qaiser *et al.*, 2007).

Some research conducted also utilized carbon derived from agriculture wastes such pith, bagasse and saw dust (Ayyappan *et al.*, 2005), coir pith carbon which is generated in the separation process of the fiber from coconut husk (Namasivayam and Sangeetha, 2006). Pretreatment of adsorbent is also commonly used to increase the adsorption capacity of these materials such as tartaric acid modified rice husk (TARH) (Wong *et al.*, 2003) and treated oil palm fiber (Isa *et al.*, 2008) in removing Cr (IV). Ajmal *et al.* (2003) showed that the treated materials give higher rate of adsorption compared with untreated materials.

2.9 Rice husk

Rice husk is an agricultural waste material generated in rice producing countries, especially in Asia. The annual world rice production is approximately 500 million metric tons, of which 10 – 20% is rice husk. Dry rice husk contains 70 – 85% of organic matter (lignin, cellulose, sugars, etc) and the remainder consists of silica, which is present in the cellular membrane (Khan *et al.*, 2003). In recent years, attention has been focused on the utilization of unmodified (Ajmal *et al.* 2003; Khan *et al.*, 2004; Kermain *et al.*, 2006; Bhattacharya *et al.*, 2006; Saravanane *et al.*, 2001) or modified rice husk as an adsorbent for the removal of pollutant. Ayyapan *et al.*, (2003) utilized rice husk ash produced from incinerated rice husk as adsorbent and found that it was a good adsorbent for mercury (Hg II) in aqueous solution and Wong *et al.* (2003) performed studies on tartaric acid modified rice husk and found it effective in removing Pb(II), Zn(II), Ni(II) and Cr(VI).

CHAPTER 3

3.0 MATERIALS AND METHODOLOGY

3.1 Health, Safety and Environment

Project involving laboratory works must emphasis on the safety. Safety precautions must be employed so that all possible hazard could be avoided (Refer Appendix 1).

3.2 Materials

3.2.1 Adsorbent (Microwave Incinerated Rice Husk Ash)

Rice husk for this study was obtained from the BERNAS factory of Kg. Gajah. It was incinerated in a furnace for 2 hours at 800°C without any pre-treatment. Plates 3.1 and 3.2 shows rice husk and incinerated rice husks ash (800°C) respectively.

Plate 3:1 Rice Husk

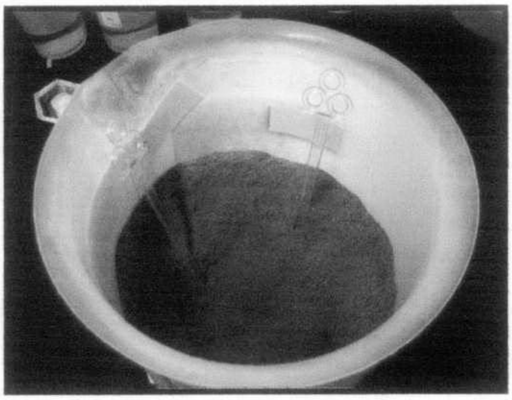

Plate 3:2 Rice Husk Ash (800°C)

3.2.2 Chemicals

Lead Chloride (PbCl2), Cadmium Chloride (CaCl2), Sodium Hydroxide (NaOH) and Hydrochloric Acid (HCl) were used.

3.2.3 Equipment

pH measurements were made with a pH meter. For the batch test, the heavy metals solutions and adsorbent mixture were shaken with an orbital shaker. The final heavy metals concentrations were tested by using an Atomic Adsorption Spectrophotometer (AAS). Plate 3.3 – 3.5 shows the primary equipments used for this study.

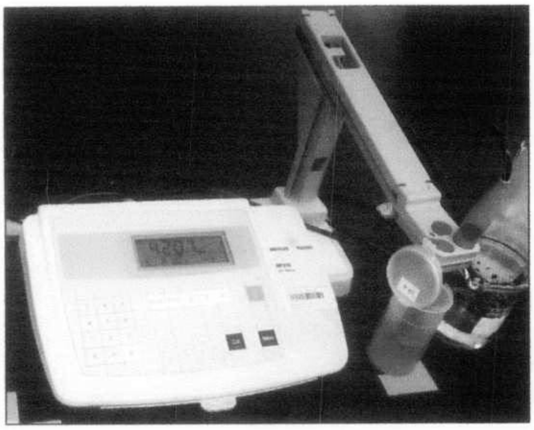

Plate 3:3 pH meter

Plate 3:4 AAS

Plate 3:5 Orbital Shaker

3.3 Methodology

Figure 3.1 shows the flow chart of the methodology involved in this study.

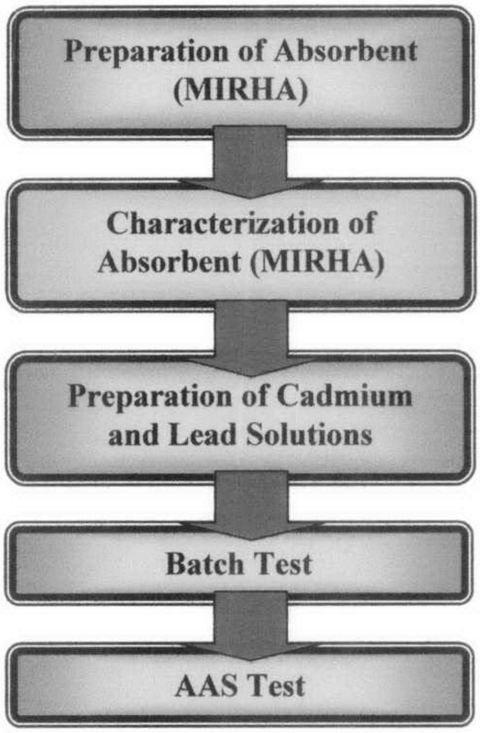

Figure 3:1 Flow Chart of Methodology

3.3.1 Preparation of Adsorbent (RHA)

Rice husk was thoroughly washed with distilled water to remove all dirt and was dried at 105°C for 2 hour till constant weight. Then the rice husk was incinerated at 800°C for 2 hour in a microwave furnace. Finally, the rice husk ash was powdered and stored in desiccators before use. Figure 3.2 shows the process in preparing microwave rice husk ash (MIRHA).

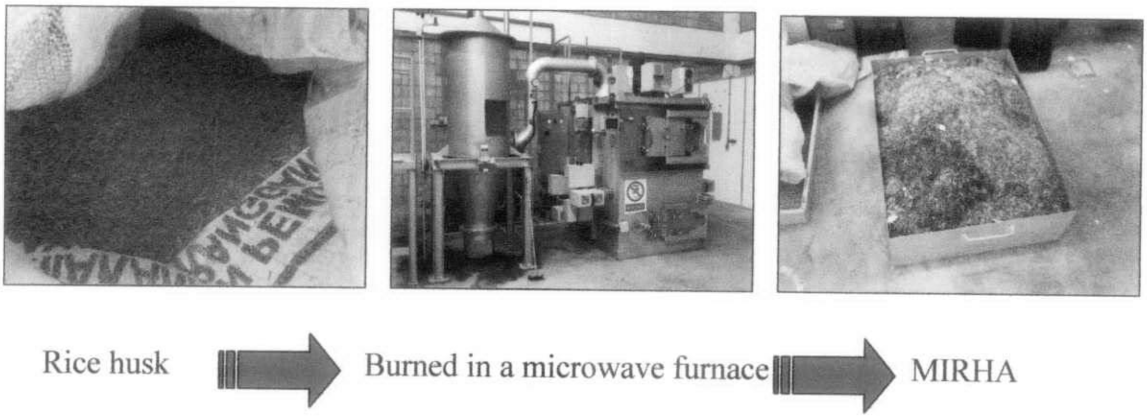

Figure 3:2 Processes in preparing of rice husk ash

3.3.2 Characterization of Absorbent (MIRHA)

X-Ray Fluoroscence (XRF)

The purpose of using XRF is to identify the elemental composition of samples. An electron can be expelled from its orbit by the absorption of a light wave, which is called photon, with sufficient energy. As a consequence from this ejection, an electron from a higher energy level orbital is transferred into a lower energy level orbital and during this process, a photon (fluorescent light which is a characteristic X-ray of the element) is emitted from this photon is equal to the difference in the energy between the two orbital during the transition by the electron. By determining the energy of the X-ray light emitted, the element can be identified.

3.3.3 Preparation of Pb (II) and Cd (II) Solutions

Stock solution of 1000 mg/L was prepared. The stock solution will be diluted with distilled water for desired concentration of Pb (II) and Cd (II) (Refer Appendix 2).

3.3.4 Batch Test

Batch tests were conducted at room temperature; 27 ± 2 °C for studying the effect of contact time, pH, initial concentration of heavy metals and adsorbent dosage. 250 ml of shaker bottles containing 100 ml of Pb (II) and Cd (II) solutions were used in all batch experiments.

Test for effect of pH

28 conical flasks containing 100 ml Pb (II) solution with 100 mg/L concentration were prepared with different initial pH; 1, 2, 3, 4, 5, 6, 7 each. The initial pH was adjusted using 1.54N NaOH or 1N HCl. 200 mg MIRHA was added into all flasks and then agitated with 150 rpm for 1 hour. After filtering the content, the final pH of the solution was measured and the amount of Pb (II) remaining in solution was obtained by measuring using an AAS. Similar procedure was applied for Cd metal.

Test for effect of contact time and initial concentration

Amount of 200 g of MIRHA were placed in 5 set of 12 conical flasks contained 100 ml Pb (II) solution. The sets were filled with 10, 20, 50, 100 and 200 mg/L of Pb (II) solution. The pH of solution is according to the optimum pH obtained before. All the flasks were shaken at 150 rpm using orbital shaker. The time required for reaching the equilibrium condition would be estimated by drawing samples at regular intervals of time; 20, 40, 60, 90, 120, 150, 180, 240 and 360 minutes. The contents of the flask were filtered through 0.45 μm cellulose acetate membrane filters (Whatman filter) and the filtrate was analyzed for Pb (II) concentration using AAS. The optimum contact time obtained is used for batch kinetic. The procedure was repeated for Cd metal but different initial concentrations were used; 5, 10, 20, 30 and 50 mg/L.

Test for effect of adsorbent dosage

15 conical flasks were filled with 100 ml Pb (II) solution of 100 mg/L concentration. The initial pH of solution was adjusted to the optimum value obtained. The adsorbent

(MIRHA) mass is varied between 50 mg to 400 mg. All the flasks are agitated at 150 rpm for the equilibrium contact time. The contents of the flask were filtered through Whatman filter and the filtrate was analyzed for metal concentration using AAS. The same procedure was repeated for Cd (II).

CHAPTER 4

4.0 RESULTS & DISCUSSION

4.1 Characteristics of MIRHA

To identify the characteristics of MIRHA, the sample was sent for XRF testing at mechanical engineering laboratory. The results obtained are shown in Table 4.1. From the XRF test, it was identified that the MIRHA consisted of high composition of silicon oxide (SiO_2) content which are 75.8 percent.

Table 4:1 Results of XRF test for MIRHA

	At 800°C(%)		At 800°C(%)
O	45.6		
Si	35.4	SiO_2	75.8
P	0.849	P_2O_5	1.94
K	7.98	K_2O	9.62
Ca	1.66	CaO	2.33
Fe	1.22	Fe_2O_3	1.75
Re	3.71	Re	3.71
Mg	-	MgO	-
Al	-	Al_2O_3	-
S	-	SO_3	-
Cl	-	Cl	-
Mn	-	MnO	-
Compton	0.61	Compton	0.61
Rayleigh	1.07	Rayleigh	1.07
Norm.	100	Norm.	100

* SiO_2 = Silicon Dioxide, P_2O_5 = Phosphorus Pentoxide, K_2O = Potassium Oxide, CaO = Calsium Oxide, Fe_2O_3 = Ferric Oxide, Re = rhenium, MgO = Magnesium oxide, Al_2O_3 = Aluminum Oxide, SO_3 = Sulfur trioxide, Cl = Chlorine.

4.2 Effect of pH

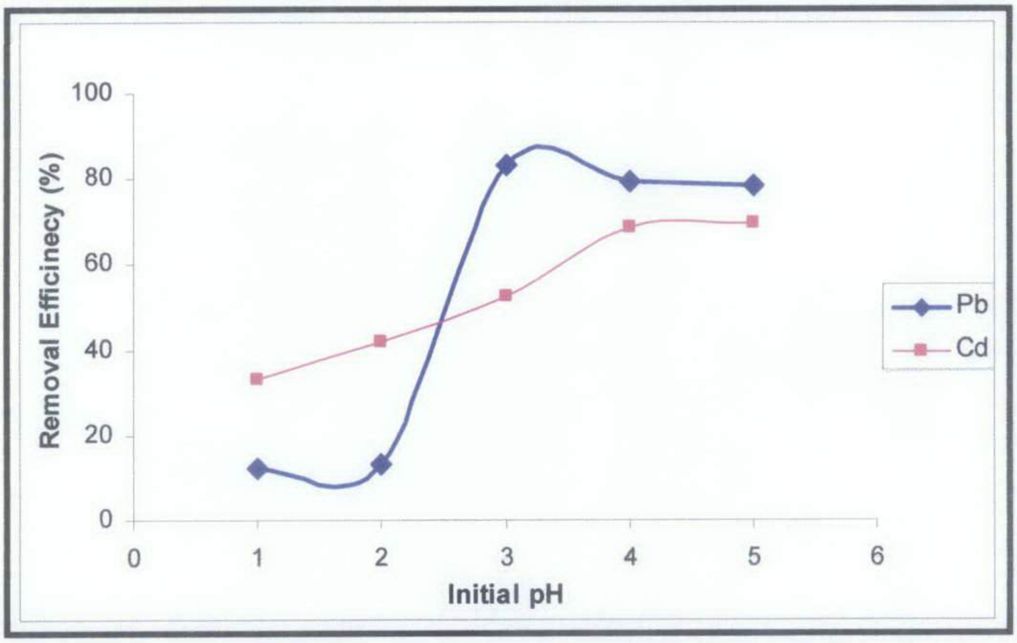

Figure 4:1 Effect of pH on the removal efficiency of Pb (II) and Cd (II) by MIRHA: [Pb (II)] = 100 mg/L; Cd (II) = 10 mg/L; volume, 100 ml; contact time, 1hr; agitated speed, 150 rpm; temperature 27±1 °C; adsorbent dosage, 2g/L

pH is an important parameter for adsorption of metal ions from aqueous solution because it affects the solubility of the metal ions, concentration of the counter ions on the functional groups of the adsorbent and the degree of ionization of the of the adsorbate during reaction (Nomanbhay and Palanisamy, 2005). Therefore, in the beginning of the experiment, the pH of Pb (II) solution was varied from 1 to 7 using 1N Hydrochloric Acid (HCl) or 5N Sodium Hydroxide (NaoH) in order to study the effect of pH. The weight of MIRHA was fixed at 200 mg. The critical pH values were 5.9 for Pb (II). The selection of the optimum pH must take into account the fact that, if too high a pH value is chosen, precipitation of lead would occur. This would defeat the purpose of employing adsorption.

Test showed that the precipitation occurred at pH 6. Figure 4.2 shows the graph of removal efficiency against pH of Pb (II) solution. From the result obtained, the maximum Pb (II) removal for initial concentration of 115 mg/L was achieved at 82% at low pH which is from 3.0 to 4.0 (Figure 4.2). Similar observations were found by maiz leaf, rice husk and saw dust (Babarinde *et al.*, 2006 and Ghani *et al.*, 2007). It also can be seem that the adsorption was not so efficient at lower pH, (i.e. pH 1 and pH 2) which is less than 20 percent.

At pH values below 8, cadmium is in its free ionic form (Cd^{2+}) (George, *et al.*, 2004) and, as such, above pH 8, the removal of the Cd ions will be considered not totally through the adsorption process. As can be seen, as pH rises, the percentage of cadmium removed increases considerably from 30% at pH 1, to up to over 60% at initial pH 4. According to Low (1995), at low pH values the surface of the adsorbent would be closely associated with hydronium ions (H_2O^+) which hinder the access of metal ions, by repulsive forces, to the surface functional groups, consequently decreasing the percentage of metal removal. However, from the final pH measured after the adsorption shows that precipitation was already occurred at initial pH 5. Therefore it can be obtained that initial optimum pH was pH 4 with removal 68.58% and the final pH measured after adsorption was 6.89. This shows that the removal of Cd (II) achieved is governed by adsorption process and not precipitation.

Similar finding were obtained by other researchers. Blazquez *et al.* (2004), reported that the optimum pH obtained in their study ranged from 6 to 8 in removing cadmium ions using olive stone while Mahvi *et al.* (2007), was also reported similar pattern of Cd (II) removal by *platanus orientalis* leaves at neutral pH (i.e. pH 7).

4.3 Effect of Contact Time and Initial Concentration

Adsorption experiments were conducted for different contact time with fix amount of adsorbent. The initial pH solution was adjusted to the optimum pH obtained. This experiment examined two aspects of the sorption process, the effect of time and the impact of varying the metal concentration.

4.3.1 Lead

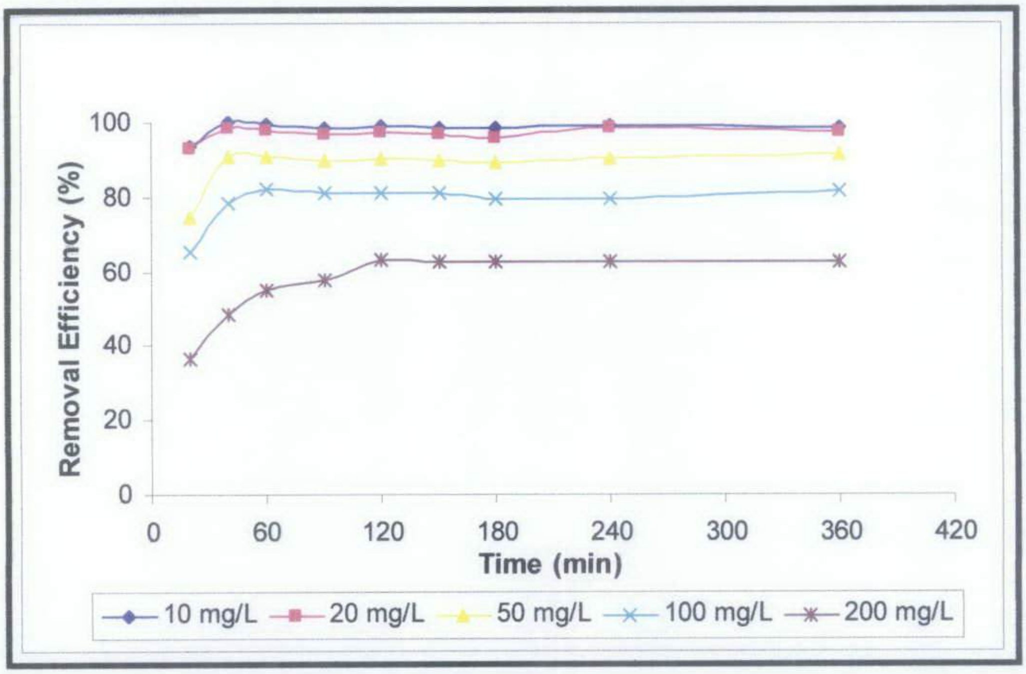

Figure 4.2a: Effect of initial concentration Pb (II) and contact time on the removal efficiency of Pb (II) from aqueous solution: pH 3; volume, 100 ml; agitated speed, 150 rpm; temperature 27±1 °C; adsorbent dosage, 2g/LFigure

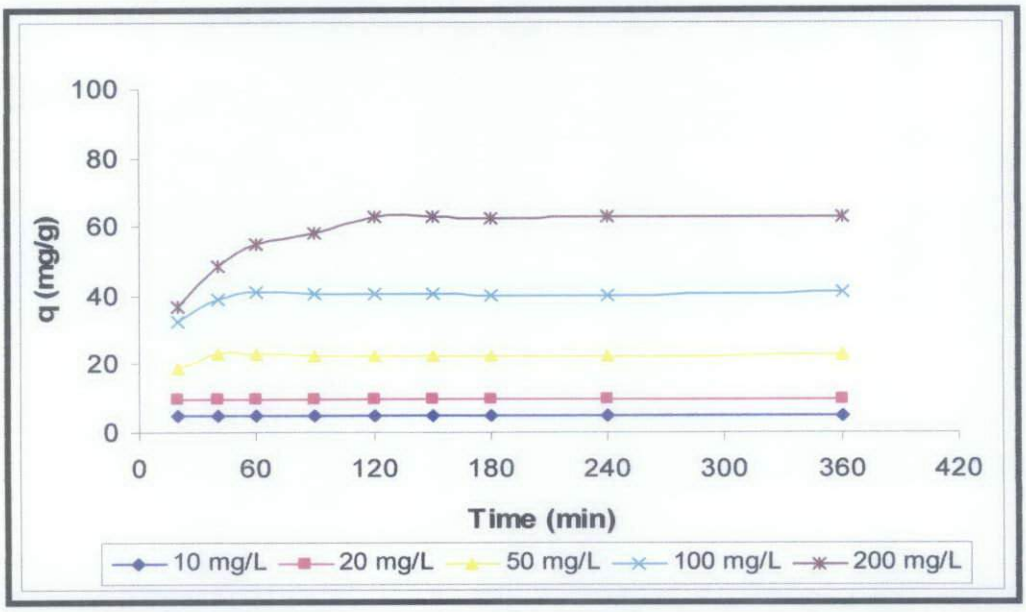

Figure 4.2b: Effect of initial concentration Pb (II) and contact time on the uptake of Pb (II) per unit weight adsorbent: pH 3; volume, 100 ml; agitated speed, 150 rpm; temperature 27±1 °C; adsorbent dosage, 2g/L

Figure 4.2 shows the effect of contact time on the removal and the uptake of Pb (II) per unit mass of adsorbent for different initial Pb (II) concentration. Different Pb (II) concentrations ranging from 10 to 200 mg/l were agitated at different contact time (20, 40, 60, 90, 120, 150, 180, 240 and 360 minutes). Figure 4.2a shows the removal efficiency Figure 4.2a show that the sorption process was rapid and mostly being complete within short duration; 40, 60 and 120 min. In the beginning, the ions adsorbed, occupied selectively the active sites on the adsorbents. As the contact time increased the active sites on the adsorbents were filled. The rate of adsorption became slower gradually and reached a plateau. Babarinde *et al.* (2006) has reported that removal of Pb (II) ions using maize leaf rapidly increase and become plateau after 30 min. It shows that the sorption has been achieved equilibrium within the first 30 min. Similar adsorption were observed by Ayyappan *et al* (2005), Babarinde *et al* (2006) and Abdel-Halim *et al.*, (2003).

Figure 4.2b provides understanding of Pb (II) adsorbed per unit weight of MIRHA. A rapid intake of highest concentration; 200 mg/L was performed in the early 60 minutes and then more gradual uptake until the equilibrium was achieved. However the rapid uptake occurred distinctly in lesser time for most of lower concentration.

Different concentrations of heavy metal solution resulted in different percentage of removal. The results show that the rate of adsorption also varied considerably with increasing initial concentrations. As the concentration increased from 10 to 200 mg/L the percentage removal decreased. This indicates that the metal uptake is highly dependent on the initial concentration of Pb (II) in solution. At lower metal concentration, most of the Pb (II) ions in the solution were occupied in the sorbents surface area, therefore the adsorption in higher. However, at higher concentration the available sites for adsorption is less and hence the percentage metal removal is less. The similar adsorption pattern was also obtained by Ghani *et al.* (2007) and Ayyappan *et a.*, (2005).

4.3.2 Cadmium

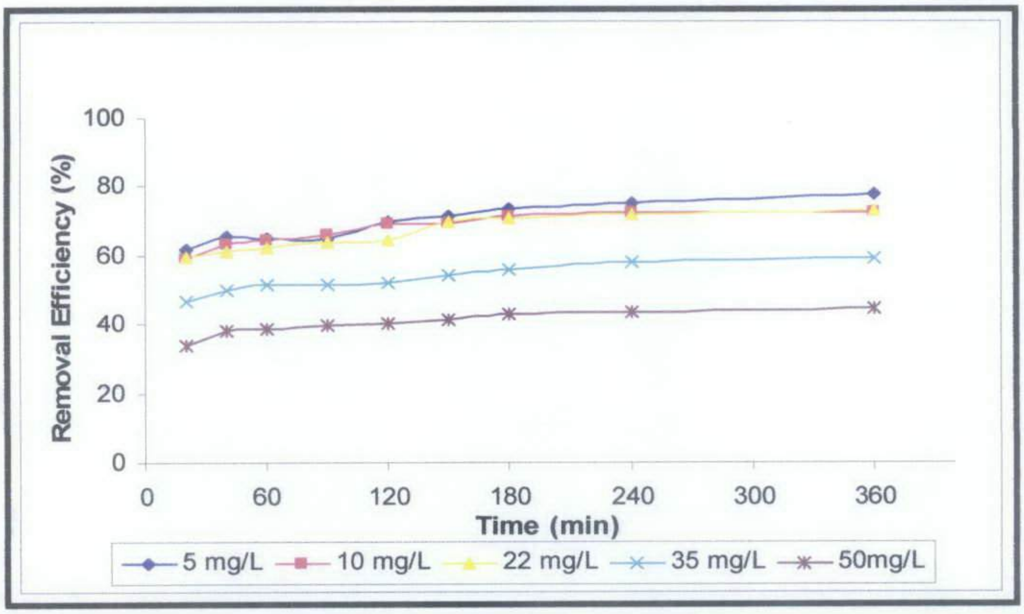

Figure 4.3a Effect of initial concentration Cd (II) and contact time on the removal efficiency of Cd (II) from aqueous solution: pH 4; volume, 100 ml; agitated speed, 150 rpm; temperature 27±1 °C; adsorbent dosage, 2g/L

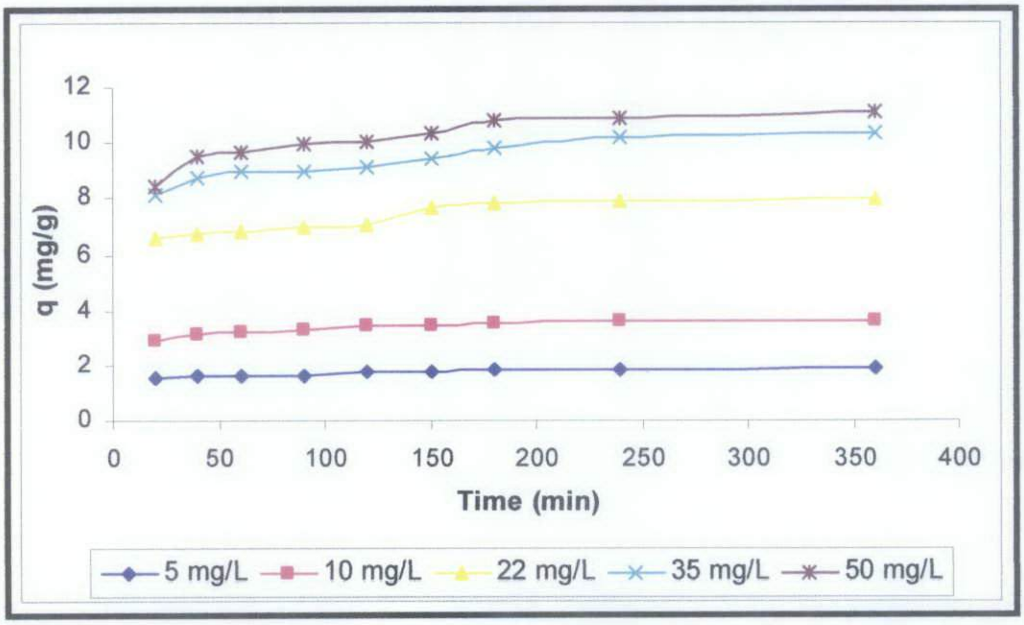

Figure 4.3b Effect of initial concentration Cd (II) and contact time on the removal uptake of Cd (II) per unit weight adsorbent: pH 4; volume, 100 ml; agitated speed, 150 rpm; temperature 27±1 °C; adsorbent dosage, 2g/L

Figure 4.3 present the effect of contact time on the removal at different initial Cd (II) concentration. Experiments were conducted for this purpose, varying contact time from 0 to 360 minutes, using the natural pH in the solution and maintaining all other experimental conditions as used previously. It shows the removal efficiency for 5 to 50 mg/L Cd (II) with contact time up to 360 minutes. It is apparent that an increase in the contact time resulted in increase in removal efficiency of Cd (II) ions from the solutions. However, the percentage removal was found decreased as the initial concentration increases. The necessary time to reach the equilibrium is about 2 to 4 hours.

Higher concentration (> 50mg/L) of Cd (II) has least removal efficiency compared with lower concentration; 5 mg/L which was up to 80%. The times for the adsorption reaching equilibrium were different for different initial concentrations. It can be observed from figure 4.3a the equilibrium contact times of 5 and 10 mg/L of Cd (II) concentration were 120 minutes. Similar contact time was recorded for 22 and 35 mg/L concentration which is 150 minutes. While the highest concentration; 50 mg/L took longer time which is 240 minutes to achieve their adsorption equilibrium.

From Figure 4.3b, it was notified that pattern of uptake performed by all type of concentration quite similar. There was no obviously rapid uptake of MIRHA occurred on all concentrations. It is evident from the figure that the uptake of Cd (II) increase slowly as the time increase until the equilibrium achieved.

4.4 Kinetic Studies

Kinetic modeling of the data was studies using pseudo first and pseudo second order. The two kinetic models are to identify the mechanism responsible for Pb (II) and Cd (II) adsorption.

4.4.1 Lead

Figure 4.4a and 4.4b present the pseudo first and second order kinetics plots for Pb (II) adsorption onto MIRHA. The first and second order reaction constant rates obtained by calculation from the slope and y-intercept of the plots using first and second order equations (Equation 2.3b and 2.4b) are shown in Tables 4.2 and 4.3.

According to the R^2 obtained from the kinetic plots, adsorption of Pb (II) onto MIRHA can be best described by pseudo second order kinetic model rather than pseudo first order since the R^2 values recorded by all concentrations of Pb (II) are closed to 1 (i.e. from 0.9988 to 0.9999), compared with values recorded by pseudo first order plot (0.07999 to 0.8239). Therefore the Pb (II) adsorption classified as chemical adsorption or chemisorption between the adsorbent and the adsorbate.

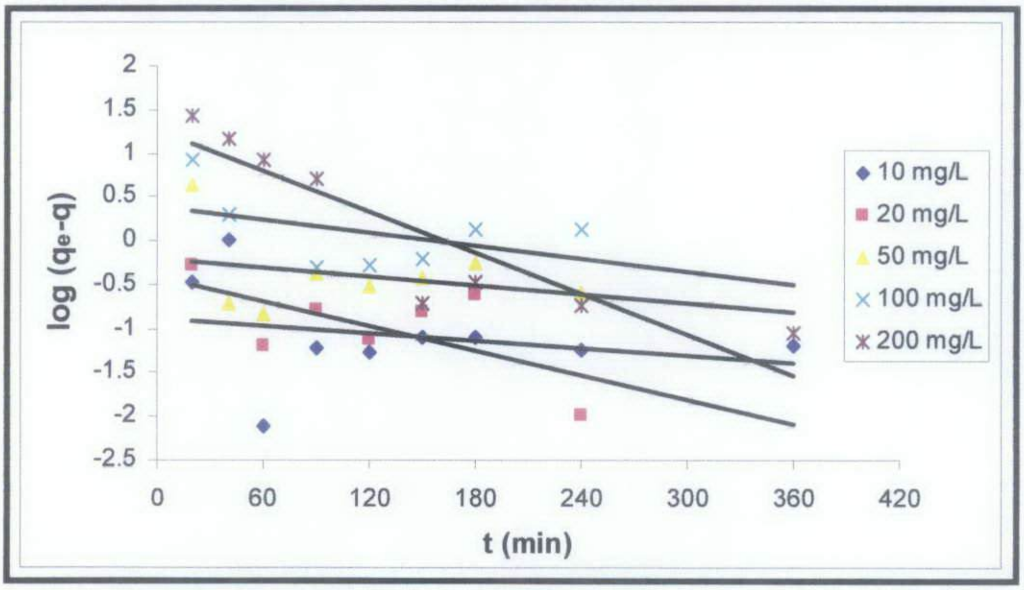

Figure 4.4a: Pseudo first order kinetic plot for Pb (II) adsorption at different initial concentrations: pH 3; volume, 100 ml; agitated speed, 150 rpm; temperature 27±1 °C; adsorbent dosage, 2g/L

Table 4:2 Pseudo first order reaction rate constant for Pb (II) adsorption

Concentration(mg/L)	K'_1 (min^{-1})	R^2	Equation
10	0.0673	0.1194	y = -0.0014x - 0.89
20	0.0108	0.4168	y = -0.0047x - 0.4008
50	0.0039	0.0799	y = -0.0017x - 0.2039
100	0.0058	0.1996	y = -0.0025x + 0.398
200	0.0180	0.8239	y = -0.0078x + 1.2614

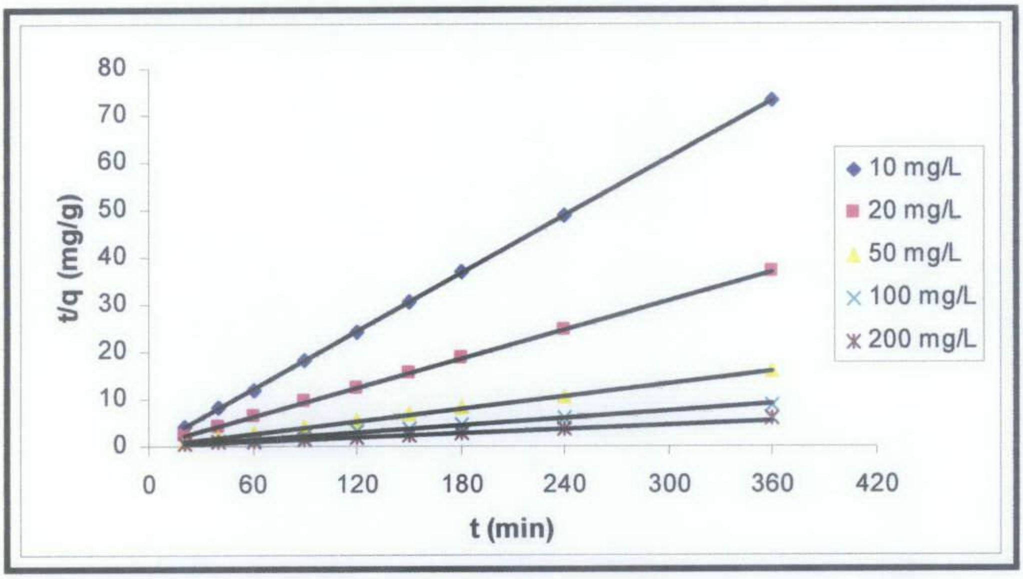

Figure 4.4b: Pseudo second order kinetic plot for Pb (II) adsorption at different initial concentrations: pH 3; volume, 100 ml; agitated speed, 150 rpm; temperature 27±1 °C; adsorbent dosage, 2g/LFig 4.4b:

Table 4:3 Pseudo second order reaction rate constant for Pb (II) adsorption

Concentration (mg/L)	K'_2 (g/mg min)	R^2	Equation
10	0.8688	0.9999	y = 0.2028x + 0.0179
20	0.1731	0.9999	y = 0.1026x + 0.0485
50	0.0313	0.9998	y = 0.0437x + 0.1041
100	0.0014	0.9995	y = 0.0245x + 0.0502
200	0.0014	0.9988	y = 0.0153x + 0.1708

4.4.2 Cadmium

The pseudo first and second order kinetic plots for adsorption of Cd (II) onto MIRHA are demonstrated in Figure 4.5a and 4.5b. While the reaction rate constant calculated are presented in table 4.4 and 4.5.

Best fits, R^2 more than 0.99 were observed for all concentration of Cd (II) indicating that adsorption of Cd (II) was also followed pseudo second order kinetic model.

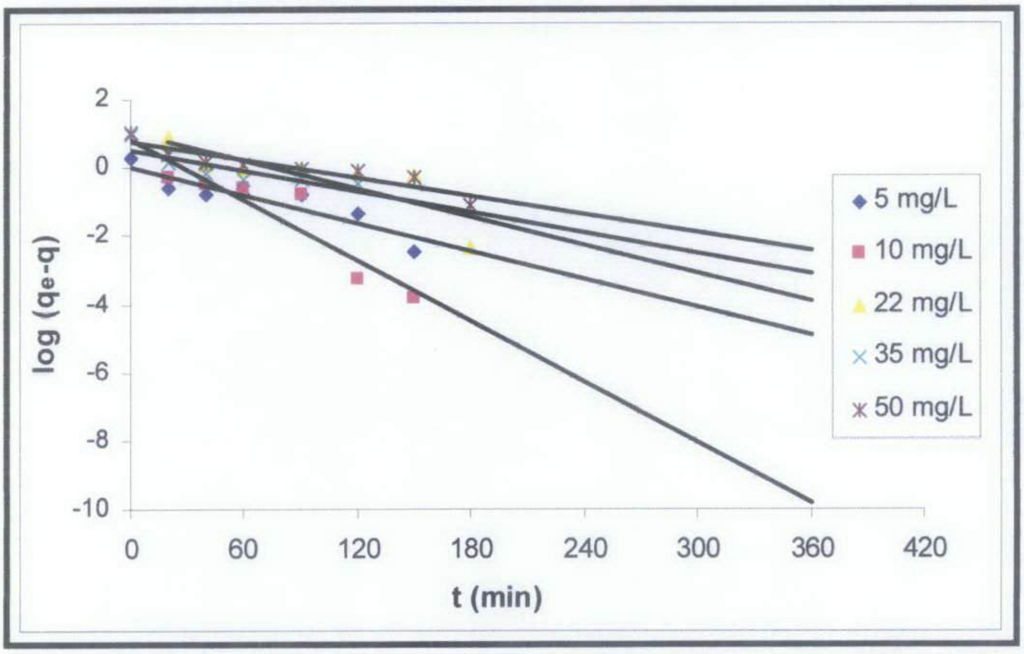

Figure 4.5a: Pseudo first order kinetic plot for Cd (II) adsorption at different initial concentrations: pH 4; volume, 100 ml; agitated speed, 150 rpm; temperature 27±1 °C; adsorbent dosage, 2g/L

Table 4:4 Pseudo first order reaction rate constant for Cd (II) adsorption

Concentration (mg/L)	K'_1 (min^{-1})	R^2	Equation
5	0.0316	0.8242	y = -0.0137x + 0.0008
10	0.0656	0.88	y = -0.0285x + 0.7032
22	0.0318	0.6663	y = -0.0138x + 1.0255
35	0.0230	0.6925	y = -0.01x + 0.5107
50	0.0200	0.8356	y = -0.0087x + 0.7281

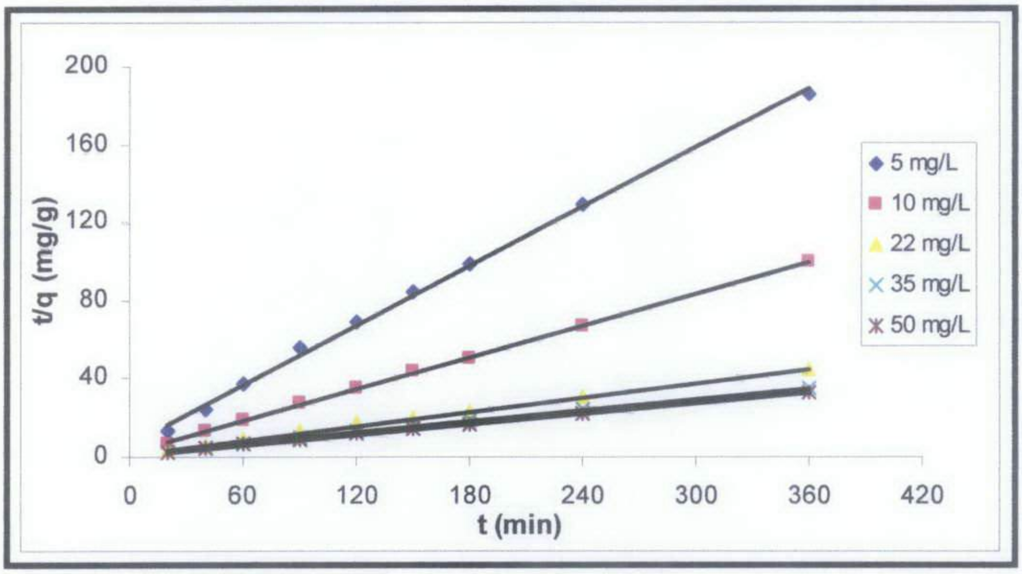

Figure 4.5b: Pseudo first order kinetic plot for Cd (II) adsorption at different initial concentrations: pH 4; volume, 100 ml; agitated speed, 150 rpm; temperature 27±1 °C; adsorbent dosage, 2g/L

Table 4:5 Pseudo second order reaction rate constant for Cd (II) adsorption

Concentration (mg/L)	K'_2 (min^{-1})	R^2	Equation
5	0.0389	0.9981	y = 0.5063x + 6.5858
10	0.0334	0.9997	y = 0.2704x + 2.1862
22	0.0109	0.9985	y = 0.122x + 1.3708
35	0.0075	0.9979	y = 0.0946x + 1.1969
50	0.0028	0.9958	y = 0.0896x + 2.9193

4.5 Effect of Adsorbent Dosage

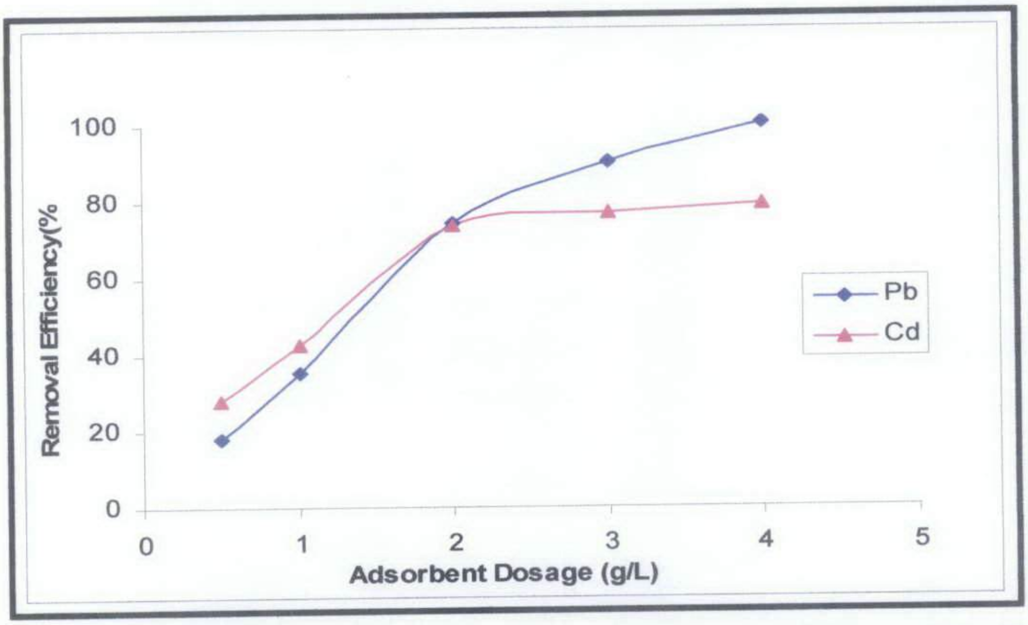

Figure 4.6a: Effect of adsorbent dosage variation on removal efficiency of Pb (II) and Cd (II): pH 3 and pH 4; Pb (II) = 100 mg/L and Cd (II) = 10 mg/L; volume, 100 ml; contact time, 1 hr and 2 hr; agitated speed, 150 rpm; temperature 27±1 °C

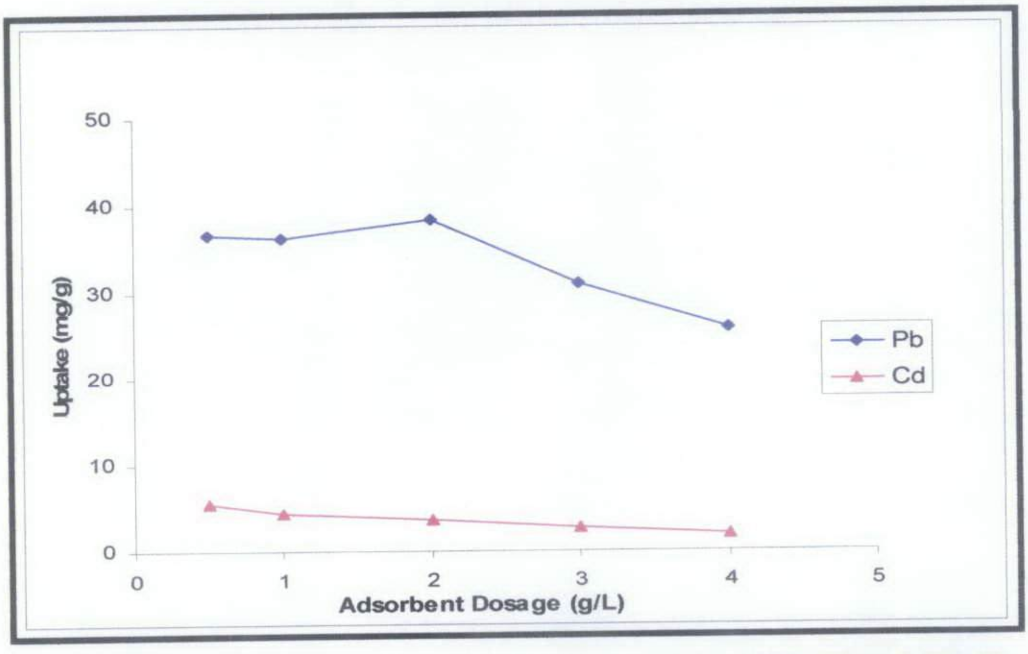

Figure 4.6b: Effect of adsorbent dosage variation on uptake of Pb (II) and Cd (II): pH 3 and pH 4; [Pb] = 100 mg/L and [Cd] = 10 mg/L; volume, 100 ml; contact time, 1 hr and 2 hr; agitated speed, 150 rpm; temperature 27±1 °C

The effect of different mass of adsorbent on removal efficiency of Pb (II) and Cd (II) is presented in Fig.4.6a while the uptake for both metals is illustrated in Figure 4.6b. The dependence of Pb (II) sorption on adsorbent dose was studied by varying the mass of adsorbents from 0.05 to 0.4 g, while keeping other parameters (pH, concentration, and contact time) constant. It can be observed that increasing the adsorbent concentration, up to 4 g/L dosage, resulted in a rapid increase in the percentage of lead uptake (17 - 99% Pb (II) uptake). The increase in Pb (II) removal percentage with increase in adsorbent dose is due to the greater availability of the exchangeable sites or surface area at higher concentration of the adsorbent (Perez-Marın *et al.,* 2007).

The test to observe the effects of different mass of adsorbent onto Cd (II) adsorption from a fixed adsorbate (10 mg/L) concentration at equilibrium contact time (120 min) was conducted through similar procedure as before and the result obtained are presented in Figure 4.6. The figure shows that the capacity of Cd (II) adsorption at equilibrium by MIRHA increases with the quantity of MIRHA introduced (0.5- 4 g/L). This can be explained by the fact that more the mass increases, more the contact surface offered for the ions of Cd (II) to bond with. Beyond 2 g/L of MIRHA, equilibrium was reached and the maximum removal was about 73%. Even though higher dosage resulted in more removal of Cd (II), however the removal was not totally dominated by adsorption process. Above concentration 2 g/L, it was observed that the final pH measured was more than 8. Therefore it can be notify that the Cd (II) removal also due to precipitation at those dosages (George *et al.*, 2004).

4.6 Adsorption Isotherm

Relatively simple isotherm model such as Langmuir and Freundlich models often provide description or characteristic of metal adsorption equilibrium on sorbent materials. Adsorption isotherms are important in the modeling procedure for analysis and design of an adsorption system. Therefore, to correlate the isotherm with the adsorption of Pb and Cd metals, the sorption data were tested against the standard isotherm models, the Langmuir and Freundlich equations (Equations 2.1 and 2.2). Then the plot of Langmuir and

Freundlich equations (Equations 2.1a and 2.2a) for Pb and Cd are presented in Figures 4.7a, 4.7b, 4.8a and 4.8b respectively.

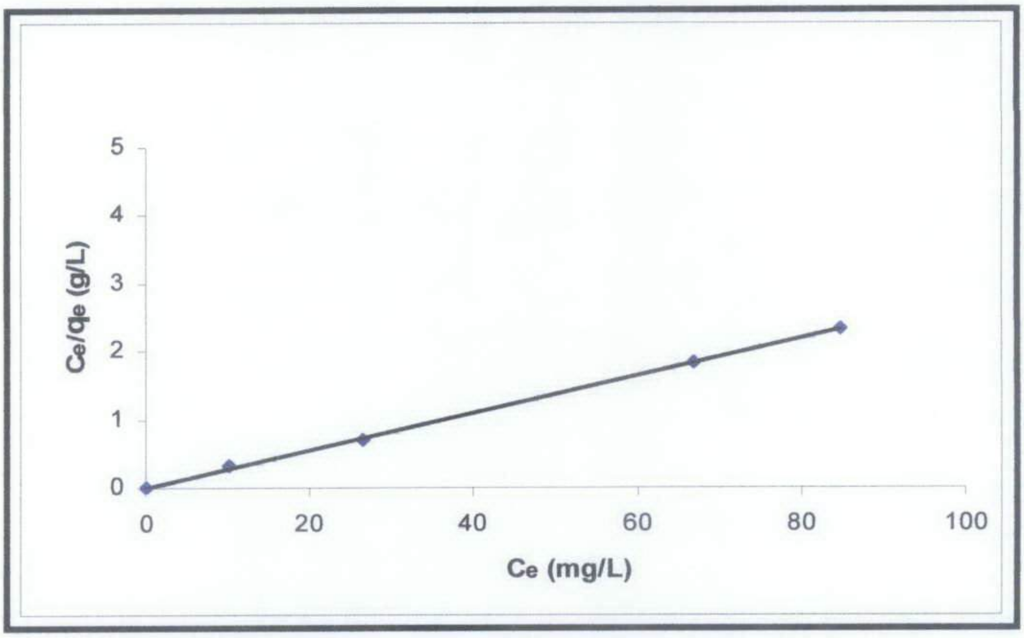

Figure 4.7a: Langmuir isotherm for Pb (II) adsorption: pH 3; [Pb] = 100 mg/L; volume, 100 ml; agitation speed, 150 rpm; temperature 27±1 °C

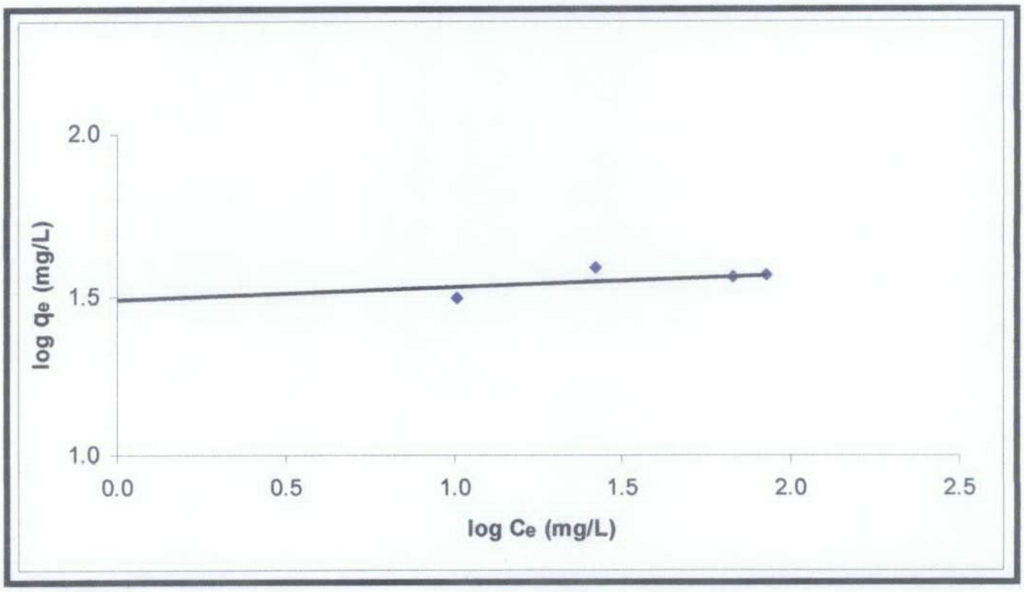

Figure 4.7b: 3Freundlich isotherm for Pb (II) adsorption: pH 3; [Pb] = 100 mg/L; volume, 100 ml; agitation speed, 150 rpm; temperature 27±1 °C.

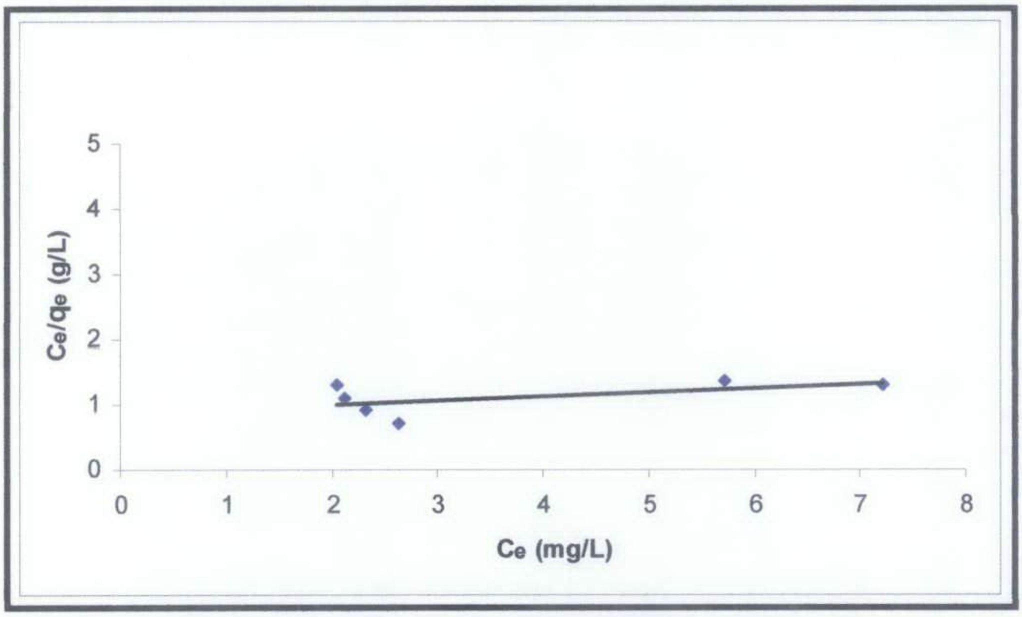

Figure 4.8a: Langmuir isotherm for Cd (II) adsorption: pH 4; [Cd] = 10 mg/L; volume, 100 ml; agitation speed, 150 rpm; temperature 27±1 °C

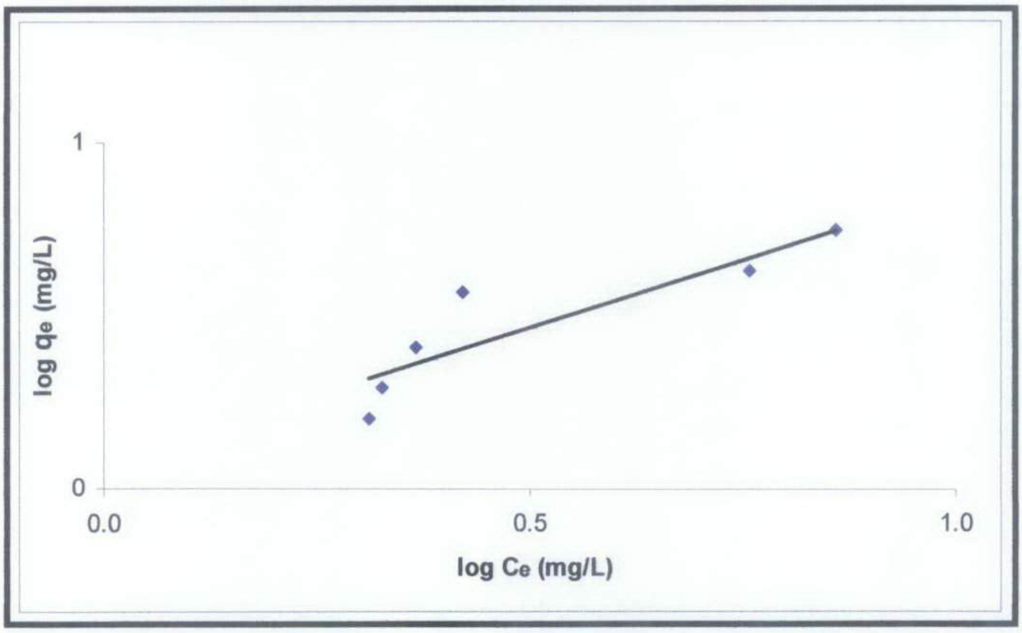

Figure 4.8b: Freundlich isotherm for Cd (II) adsorption: pH 4; [Cd] = 10 mg/L; volume, 100 ml; agitation speed, 150 rpm; temperature 27±1 °C.

Table 4:6 Langmuir constant for Pb (II) and Cd (II) adsorption

Adsorbate	a (mg/L)	b (mg/L)	R^2	Equation
Pb (II)	29.67	2.54	0.9991	y = 0.0337x + 0.0107
Cd (II)	15.48	2.94	0.3267	y = 0.0646x + 0.8651

Table 4:7 Freundlich constant for Pb (II) and Cd (II) adsorption

Adsorbate	K_f	n	R^2	Equation
Pb (II)	4.43	25.00	0.8556	y = 0.04x + 1.4883
Cd (II)	1.08	1.29	0.7951	y = 0.7774x + 0.0809

Langmuir isotherm makes several assumptions, such as the adsorption energy are uniform, through the entire accessible site on adsorbent surface and complete coating of the available sites provide maximum adsorption. Straight line plots of C_e/q_e against C_e for both metals indicated the applicability of the model to the present system (Isa et al., 2008).

Value of R^2 established from plotting the isotherm data are shown in Table 4.6 and 4.7 for both Pb (II) and Cd (II). From the Table, it is demonstrated that Pb (II) was better fitted with the Langmuir while Cd (II) adsorption followed the Freundlich models. Lower regression value ($R^2 = 0.8556$) of Pb (II) plotted using Freundlich indicated that Langmuir model is more suitable to describe the nature of Pb (II) adsorption. However, higher R^2 value of Cd (II) through Freundlich isotherm signified that adsorption of Cd (II) is more fitted with Freundlich rather than Langmuir model. The models plotted provide information on the feature of the adsorbent and the adsorbate. The maximum capacity of adsorption to complete fulfill the available sites calculated from the slopes were 29.67 mg/g and 15.48 mg/g for Pb (II) and Cd (II) correspondingly.

CHAPTER 5

5.0 CONCLUSION AND RECOMMENDATION

5.1 Research Conclusion

Rice husk is an abundant waste material in Malaysia. Microwave incinerated rice husk ash (MIRHA) produced from incineration of rice husk can be utilized as low-cost adsorbent in heavy metals removal from aqueous solution. Effect of pH, contact time, initial concentration and adsorbent dosage was analyzed to determine the adsorption efficiency. The results obtained in this study clearly demonstrate the potential of waste products (MIRHA) for the removal of Pb (II) and Cd (II) from aqueous solutions.

Adsorption of Pb and Cd is served to be pH dependent. Therefore to establish the optimum pH of metal solution is important to get maximum adsorption efficiency. From the experiment, it was found that the adsorption is preferred under acidic condition where optimum pH for Pb (II) and Cd (II) were 4 and 6.89 respectively.

To determine the effect of various concentrations, tests conducted on 10 - 100 mg/L of Pb concentration demonstrated very high removal efficiency which is close to 100%. However, removal recorded Cd (II); 5 - 50 mg/L solutions seem a little bit lower which was only capable to reach up to 80%. Adsorption process reached equilibrium within 40 to 60 minutes contact time for most lower concentration of Pb(II) and the highest concentration took longer time to achieve the equilibrium, which was 120 minutes. Meanwhile, Cd (II) solution requires longer time to reach equilibrium. The equilibrium time varies from 120 to 240 minutes as the initial concentration of Cd (II) increased, where the concentration of Cd (II) (i.e. 10 mg/L) recorded 120 minutes to achieve equilibrium with percentage removal of 69.19%. Although the removal efficiency of higher Pb (II) and Cd (II) concentration are lower and required longer time to achieved equlibrium, higher uptake of adsorbate per unit weight of adsorbent was noticed; for 100mg/L Pb (II) (62.82 mg/g) and 10 mg/L Cd (II) (10.82 mg/g) concentrations.

From the study of the effect of adsorbent dosage onto removal efficiency, it is clear that as the mass of adsorbent increase, the removal efficiency increases as well. This can be described by the higher availability of the free sites on the adsorbent surface which allowed more adsorption to take place and resulted in higher removal efficiency of metals.

High and uniform regression values (R^2) obtained from kinetic models plotted for both heavy metals are found to follow the pseudo second order kinetic model which is chemical adsorption reaction. The adsorption equilibrium of Pb (II) can be well described by Langmuir isotherm model, while Cd (II) was better conformed to the Freundlich model. MIRHA have high capacity in removing Pb (29.67 mg/g) and Cd ions (15.48 mg/g).

5.2 Recommendation for Future Study

Several recommendations can be proposed based on the results obtained from this study. The present study only focused on certain parameters that affect metals removal in aqueous solution such pH, agitation time, initial metal concentrations and adsorbent dosage. Therefore, it is proposed to further study other parameters including the effect of temperature, which also affects the kinetic rates of adsorption and the effect of particles size. MIRHA incinerated at different temperature might have different adsorption capacities.

The capacity of the MIRHA should also be compared with other methods of adsorbent treatments; thereby the least expensive method with comparative efficiency should be employed in real wastewater treatment application. Besides, a real wastewater consisting various components and particles with different characteristics which may result in different adsorption behaviors, therefore and adsorption study of real industrial wastewater should be conducted to prove the adsorption capacity of MIRHA, which was shown to be good for synthetic wastewater.

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Appendix 1

OSHA Guide of Chemical Hazard

1.0 CADMIUM

1.1 Cadmium (II) Compounds

Personal Protection & Sanitation	First Aid
Skin: Prevent skin contact Eyes: Prevent eye contact Wash skin: When contaminated Remove: When wet or contaminated	Eye: Irrigate immediately Skin: Water flush promptly Breathing: Respiratory support Swallow: Medical attention immediately

2.0 LEAD

2.1 Lead (II) Compounds

Personal Protection & Sanitation	First Aid
Skin: Prevent skin contact Eyes: Prevent eye contact Wash skin: When contaminated Remove: When wet or contaminated	Eye: Irrigate immediately Skin: Water flush promptly Breathing: Respiratory support Swallow: Medical attention immediately

3.0 HAZARD ANALYSIS

ACTIVITY	POTENTIAL HAZARD	PRECAUTION STEP
Laboratory works	Heat, gases, light, pressure from equipment Repetitive movement, sustained posture, burns, physical injury	• Space required around equipment to operate. • Appropriate placement of equipment, height, layout

Working with small volumes of corrosive liquids (< 1 liter).	Eye or skin damage	• Safety glasses or goggles • Light chemical-resistant gloves • Lab coat
Working with large volumes of corrosive liquids (> 1 liter), small to large volumes of acutely toxic corrosives, or work which creates a splash hazard	Large surface area skin or eye damage, poisoning, or great potential for eye and skin damage	• Safety goggles and face shield • Heavy chemical-resistant gloves • Lab coat and chemical-resistant apron
Working with small volumes of organic solvents (< 1 liter).	Skin or eye damage Slight poisoning potential through skin contact	• Safety glasses or goggles • Light chemical-resistant gloves. • Lab coat
Working with large volumes of organic solvents (> 1 liter), small to large volumes of very dangerous solvents, or work which creates a splash hazard	Major skin or eye damage; potential poisoning through skin contact	• Safety goggles and face shield • Heavy chemical-resistant gloves • Lab coat and chemical resistant apron
Working with toxic or hazardous chemicals (solid or liquid).	Eye or skin damage; potential poisoning through skin contact.	• Safety glasses (goggles for large quantities) • Light chemical-resistant gloves • Lab coat
Working with acutely toxic or hazardous chemicals (solid or liquid).	Increased potential for eye or skin damage; increased potential poisoning through skin contact.	• Safety goggles • Appropriate heavy chemical-resistant gloves for liquids, appropriate chemical-resistant glove for solids • Lab coat. • Gown and shoe covers if necessary.
Working with solid radioactive materials or waste.	Cell damage, potential spread of radioactive materials.	• Safety glasses • Impermeable gloves • Lab coat.
Minor chemical spill cleanup.	Skin or eye damage, respiratory damage.	• Safety glasses or goggles • Appropriate chemical-resistant gloves • Lab coat (consider chemical-resistant apron and boots or shoe covers). • Consider keeping Silver Shield or 4H gloves in the lab spill kit.

Working with radioactive chemicals (corrosives, flammables, liquids, powders, etc.).	Cell damage or spread of contamination plus hazards for the specific chemical.	• Safety glasses (or goggles for splash hazard) • Light chemical-resistant gloves, lab coat. Note: Select glove for the applicable chemical hazards above.
Working with cryogenic liquids.	Major skin, tissue, or eye damage.	• Safety glasses or goggles for large volumes • Heavy impermeable insulated gloves, lab coat.
Glassware washing.	Lacerations.	• Heavy rubber gloves • Lab coat.
Dangerous Goods (e.g. LPG, flammable liquids)	Fire, explosion, asphyxia, toxicity	• Secure hazardous materials storage. • Ventilation and isolation requirements. • Piping to eliminate transport of gases or liquids
Handling chemicals and blood products	Toxicity Fumes Bacteria, viruses and other pathogens	• Secure hazardous materials storage • Ventilation and isolation requirements
Cleaning	Hazardous substances, infectious diseases	• Supervisions and procedure
Waste disposals	Exposure to hazardous substances, disease	• Isolation of disposal systems

Appendix 2

2.1 Preparation of Lead Solutions

Lead Chloride ($PbCl_2$)

Atomic Weight (Pb) = 207.2

Molecular Weight ($PbCl_2$) = 207.2 + (35.5x2)

= 278.2

For 1000mg/L concentration; = 278.2/207.2x 1000

= 1342.21 mg of $PbCl_2$

Amount of **1342.21 mg** of $PbCl_2$ used to prepare 1000 mg/L of lead stock solution

2.2 Preparation of Cadmium Solution

Cadmium Chloride ($CdCl_2$)

Atomic Weight (Cd) = 112.41

Molecular Weight ($CdCl_2$) = 112.41 + (35.5x2)

= 183.41

For 1000mg/L concentration; = 183.41/112.41 x 1000

= 1631.62 mg of $CdCl_2$

Amount of **1631.62 mg** of $CdCl_2$ used to prepare 1000 mg/L of lead stock solution

The following basic mass balance calculation was employed to prepare lead and cadmium solutions of various concentrations:

$$M_1V_1 = M_2V_2$$

where, M_1 – original concentration

M_2 – desired concentration

V_1 – original volume

V_2 – desired volume

Eg: For 100 mg/L:

$$(100\ \text{mg/L})(1\text{L}) = (1000\ \text{mg/L})\ (V_2)$$

$$V_2 = 100\ \text{ml}$$

To prepare for concentration of 100 mg/L lead, amount of 100 mL from stock solution is transferred to the 1000 mL volumetric flask. The flask is then filled with distilled water until to the dilution mark and shaken vigorously. Similar procedure used to prepare for other lead concentration from stock solution.

3.2 Test for Effect of Initial Concentration & Contact Time and Pseudo First Order & Pseudo Second Order Kinetics

3.2a. 100 ml of 10 mg/L Pb (II); 200 mg MIRHA

t (min)	C_o (mg/L)	C_e (mg/L)	$C_{e\ average}$ (mg/L)	% Pb (II) Removal	q	q_e	t/q	$q_e - q$	$\log(q_e - q)$
20	10	0.0103 1.9997 0	0.67	93.30	4.67	5	4.29	0.34	-0.4750
40	10	0 0 0.018	0.01	99.94	5.00	5	8.00	0.00	-2.5229
60	10	0 0.0678 0.0312	0.03	99.67	4.98	5	12.04	0.02	-1.7825
90	10	0.1821 0.0741 0.1548	0.14	98.63	4.93	5	18.25	0.07	-1.1643
120	10	0.1353 0.2457 0	0.13	98.73	4.94	5	24.31	0.06	-1.1972
150	10	0 0.3922 0.1178	0.17	98.30	4.92	5	30.52	0.09	-1.0706
180	10	0.1957 0.2053 0.136	0.18	98.21	4.91	5	36.66	0.09	-1.0482
240	10	0 0.1835 0.1375	0.11	98.93	4.95	5	48.52	0.05	-1.2716
360	10	0.1015 0.1844 0.1431	0.14	98.57	4.93	5	73.04	0.07	-1.1457

3.2b. 100 ml of 20 mg/L Pb (II); 200 mg MIRHA

t (min)	C_o (mg/L)	C_e (mg/L)	$C_{e\ average}$ (mg/L)	% Pb (II) Removal	q	q_e	t/q	$q_e - q$	$\log(q_e - q)$
20	20	0.973 2.6914 0.4456	1.37	93.15	9.32	9.82	2.15	0.51	-0.2967
40	20	0.2412 0.6842 0.1366	0.35	98.23	9.82	9.82	4.07	0.00	-

“ Table 3.2b continued”

60	20	0.5198	0.48	97.61	9.76	9.82	6.15	0.06	-1.2291
		0.9142							
		0							
90	20	0	0.68	96.58	9.66	9.82	9.32	0.16	-0.7905
		2.052							
		0							
120	20	0	0.50	97.49	9.75	9.82	12.31	0.07	-1.1487
		0.8632							
		0.6428							
150	20	0.9322	0.66	96.71	9.67	9.82	15.51	0.15	-0.8268
		0.2371							
		0.8047							
180	20	1.0392	0.83	95.86	9.59	9.82	18.78	0.23	-0.6308
		0.8395							
		0.6053							
240	20	0	0.37	98.13	9.81	9.82	24.46	0.01	-2.1549
		0.8793							
		0.2427							
360	20	0.5194	0.55	97.25	9.73	9.82	37.02	0.10	-1.0223
		0.1112							
		1.0194							

3.2c. 100 ml of 50 mg/L Pb (II); 200 mg MIRHA

t (min)	C_o (mg/L)	C_e (mg/L)	$C_{e\ average}$ (mg/L)	% Pb (II) Removal	q	q_e	t/q	$q_e - q$	log ($q_e - q$)
20	50	10.3275	12.80	74.41	18.60	22.66	1.08	4.06	0.6083
		15.2664							
		12.7911							
40	50	3.1184	4.69	90.63	22.66	22.66	1.77	0.00	-2.6021
		6.6545							
		4.2821							
60	50	0	4.60	90.81	22.70	22.66	2.64	-0.04	-
		7.8828							
		5.9025							
90	50	4.8639	5.13	89.75	22.44	22.66	4.01	0.22	-0.6527
		3.7836							
		6.7275							
120	50	4.3821	4.91	90.18	22.55	22.66	5.32	0.11	-0.9393
		5.3498							
		4.9981							
150	50	6.0039	5.04	89.92	22.48	22.66	6.67	0.18	-0.7447
		3.9194							
		5.1967							

" Table 3.2c continued"

180	50	5.0251 5.6542 5.4517	5.38	89.25	22.31	22.66	8.07	0.35	-0.4578
240	50	5.7471 5.4852 3.2127	4.82	90.37	22.59	22.66	10.62	0.07	-1.1707
360	50	4.7471 4.1358 4.0471	4.31	91.38	22.85	22.66	15.76	-0.18	-

3.2d. 100 ml of 100 mg/L Pb (II); 200 mg MIRHA

t (min)	C_o (mg/L)	C_e (mg/L)	$C_{e\ average}$ (mg/L)	% Pb (II) Removal	q	q_e	t/q	$q_e - q$	log ($q_e - q$)
20	100	35.009 35.8706 33.4304	34.77	65.23	32.62	41.08	0.61	8.47	0.9276
40	100	20.7915 22.9424 21.8461	21.86	78.14	39.07	41.08	1.02	2.01	0.3032
60	100	17.0676 16.1728 20.2796	17.84	82.16	41.08	41.08	1.46	0.00	-
90	100	18.9574 18.9239 18.5787	18.82	81.18	40.59	41.08	2.22	0.49	-0.3098
120	100	19.1359 19.4417 18.0324	18.87	81.13	40.57	41.08	2.96	0.52	-0.2882
150	100	18.0271 19.4237 19.7821	19.08	80.92	40.46	41.08	3.71	0.62	-0.2084
180	100	22.8855 18.4988 20.0857	20.49	79.51	39.76	41.08	4.53	1.33	0.1222
240	100	19.0754 19.8895 22.6851	20.55	79.45	39.73	41.08	6.04	1.36	0.1319
360	100	19.7154 17.0975 18.6271	18.48	81.52	40.76	41.08	8.83	0.32	-0.4949

3.2e. 100 ml of 200 mg/L Pb (II); 200 mg MIRHA

t (min)	C_o (mg/L)	C_e (mg/L)	$C_{e\ average}$ (mg/L)	% Pb (II) Removal	q	q_e	t/q	$q_e - q$	log ($q_e - q$)
20	200	127.0348 131.0905 122.9347	127.02	36.49	36.49	62.82	0.55	26.33	1.4205
40	200	102.8622 105.9285 100.3893	103.06	48.47	48.47	62.82	0.83	14.35	1.1569
60	200	95.6275 86.3594 89.7531	90.58	54.71	54.71	62.82	1.10	8.11	0.9090
90	200	81.8349 87.3993 84.0258	84.42	57.79	57.79	62.82	1.56	5.03	0.7016
120	200	64.8855 82.4297 75.7648	74.36	62.82	62.82	62.82	1.91	0.00	-
150	200	77.8658 76.5341 69.8201	74.74	62.63	62.63	62.82	2.40	0.19	-0.7212
180	200	78.1611 69.4241 77.5348	75.04	62.48	62.48	62.82	2.88	0.34	-0.4685
240	200	74.8044 77.5353 71.8203	74.72	62.64	62.64	62.82	3.83	0.18	-0.7447
360	200	75.2793 78.5204 69.8203	74.54	62.73	62.73	62.82	5.74	0.09	-1.0458

3.2f. 100 ml of 5 mg/L Cd (II); 200 mg MIRHA

t (min)	C_o (mg/L)	C_e (mg/L)	C_e average (mg/L)	% Pb (II) Removal	q	q_e	t/q	$q_e - q$	log ($q_e - q$)
20	5	2.0235 2.1631 1.5865	1.92	61.51	1.54	1.78	13.01	0.24	-0.62
40	5	1.2451 1.8383 2.1413	1.74	65.17	1.63	1.78	24.55	0.15	-0.82
60	5	1.0248 1.7532 2.4841	1.75	64.92	1.62	1.78	36.97	0.16	-0.80

" Table 3.2f continued"

90	5	1.3415 2.1617 1.8066	1.77	64.60	1.62	1.78	55.73	0.16	-0.78
120	5	1.5963 1.7263 1.2722	1.53	69.37	1.73	1.78	69.20	0.05	-1.34
150	5	1.5437 1.1217 1.6759	1.45	71.06	1.78	1.78	84.44	0.00	-2.45
180	5	1.1544 1.7527 1.1121	1.34	73.21	1.83	1.78	98.35	-0.05	-
240	5	1.6188 1.1236 1.0621	1.27	74.64	1.87	1.78	128.62	-0.09	-
360	5	1.3753 0.9972 1.0351	1.14	77.28	1.93	1.78	186.33	-0.15	-

3.2g. 100 ml of 10 mg/L Cd (II); 200 mg MIRHA

t (min)	C_o (mg/L)	C_e (mg/L)	C_e average (mg/L)	% Pb (II) Removal	q	q_e	t/q	q_e . q	log (q_e . q)
20	10	4.2936 4.1118 3.9677	4.12	58.76	2.94	3.46	6.81	0.52	-0.28
40	10	3.8319 3.2013 4.0731	3.70	62.98	3.15	3.46	12.70	0.31	-0.51
60	10	3.9098 3.8015 3.0781	3.60	64.04	3.20	3.46	18.74	0.26	-0.59
90	10	2.9239 3.7753 3.5459	3.42	65.85	3.29	3.46	27.33	0.17	-0.78
120	10	3.2844 2.8443 3.1145	3.08	69.19	3.46	3.46	34.69	0.00	-3.27
150	10	3.2711 2.8683 3.1014	3.08	69.20	3.46	3.46	43.35	0.00	-3.88
180	10	3.2168 2.5605 2.9229	2.90	71.00	3.55	3.46	50.70	-0.09	-
240	10	2.5058 3.1948 2.6567	2.79	72.14	3.61	3.46	66.54	-0.15	-

" Table 3.2g continued"

360	10	2.9465 2.7791 2.5721	2.77	72.34	3.62	3.46	99.53	-0.16	-

3.2h. 100 ml of 22 mg/L Cd (II); 200 mg MIRHA

t (min)	C_o (mg/L)	C_e (mg/L)	C_e average (mg/L)	% Pb (II) Removal	q	q_e	t/q	q_e - q	log (q_e - q)
20	22	8.9375 8.5123 9.3257	8.93	59.43	6.54	7.66	3.06	1.12	0.05
40	22	9.0907 8.3395 8.3138	8.58	60.99	6.71	7.66	5.96	0.95	-0.02
60	22	8.0071 9.1427 7.8872	8.35	62.07	6.83	7.66	8.79	0.83	-0.08
90	22	8.7444 7.9267 7.4201	8.03	63.50	6.98	7.66	12.89	0.68	-0.17
120	22	7.9209 6.9481 8.8071	7.89	64.13	7.05	7.66	17.01	0.61	-0.22
150	22	7.2892 6.6723 6.1046	6.69	69.60	7.66	7.66	19.59	0.00	-2.36
180	22	6.2727 6.0596 6.9925	6.44	70.72	7.78	7.66	23.14	-0.12	
240	22	5.6389 6.9684 6.2258	6.28	71.47	7.86	7.66	30.53	-0.20	
360	22	5.5707 6.5448 5.9824	6.03	72.58	7.98	7.66	45.09	-0.32	

3.2i. 100 ml of 35 mg/L Cd (II); 200 mg MIRHA

t (min)	C_o (mg/L)	C_e (mg/L)	C_e average (mg/L)	% Pb (II) Removal	q	q_e	t/q	q_e - q	log (q_e - q)
20	35	20.0438 19.0901 17.1867	18.77	46.36	8.11	9.41	2.47	1.30	0.11

" Table 3.2i continued"

40	35	15.114 18.2804 19.3051	17.57	49.81	8.72	9.41	4.59	0.69	-0.16
60	35	17.1422 18.9276 15.1732	17.08	51.20	8.96	9.41	6.70	0.45	-0.35
90	35	15.1049 18.6101 17.5047	17.07	51.22	8.96	9.41	10.04	0.45	-0.35
120	35	17.2448 17.1613 16.1726	16.86	51.83	9.07	9.41	13.23	0.34	-0.47
150	35	15.6661 16.9066 15.9462	16.17	53.79	9.41	9.41	15.93	0.00	-
180	35	15.9061 16.0919 14.5174	15.51	55.70	9.75	9.41	18.47	-0.34	-
240	35	13.8751 15.4519 14.8961	14.74	57.88	10.13	9.41	23.69	-0.72	-
360	35	13.4357 14.5263 15.0104	14.32	59.07	10.34	9.41	34.82	-0.93	-

3.2j. 100 ml of 50 mg/L Cd (II); 200 mg MIRHA

t (min)	C_o (mg/L)	C_e (mg/L)	C_e average (mg/L)	% Pb (II) Removal	q	q_e	t/q	q_e - q	log (q_e - q)
20	50	32.9666 31.9726 34.5711	33.17	33.66	8.41	10.82	2.38	2.41	0.38
40	50	30.5164 32.9496 29.7021	31.06	37.89	9.47	10.82	4.22	1.35	0.13
60	50	30.5921 31.4754 29.9359	30.67	38.66	9.67	10.82	6.21	1.15	0.06
90	50	30.9726 30.6431 28.9765	30.20	39.61	9.90	10.82	9.09	0.92	-0.04
120	50	31.6039 27.9131 30.4712	30.00	40.01	10.00	10.82	12.00	0.82	-0.09

" Table 3.2j continued"

150	50	26.9344	29.39	41.22	10.30	10.82	14.56	0.52	-0.29
		29.146							
		32.0912							
180	50	29.7832	28.51	42.98	10.75	10.82	16.75	0.07	-1.13
		27.8316							
		27.9114							
240	50	25.5859	28.36	43.29	10.82	10.82	22.18	0.00	-
		30.8958							
		28.5905							
360	50	28.799	27.83	44.34	11.09	10.82	32.47	-0.27	-
		25.2291							
		29.4571							
1440	50	28.7319	27.69	44.63	11.16	10.82	129.07	-0.34	-
		26.911							
		27.4176							

3.3 Test for Effect of Adsorbent Dosage and Adsorption Isotherm

3.3a. 100 ml of 100 mg/L Pb (II); 1 hr agitation time

Sample	m (g)	C_o (mg/L)	C_e (mg/L)	C_e average (mg/L)	% Pb (II) Removal	x (mg)	x/m @ qe (mg/g)	log Ce (mg/L)	log qe (mg/L)	Ce/qe (g/L)
1	0.05	103	85.9871	84.70	17.76	1.83	36.59	1.93	1.56	2.31
2			80.9179							
3			87.2026							
4	0.1	103	62.0464	66.79	35.15	3.62	36.21	1.82	1.56	1.84
5			67.3738							
6			70.9602							
7	0.2	103	28.7676	26.37	74.40	7.66	38.32	1.42	1.58	0.69
8			26.8886							
9			23.4401							
10	0.3	103	10.1038	10.13	90.16	9.29	30.96	1.01	1.49	0.33
11			10.0336							
12			10.2578							
13	0.4	103	0.0276	0.01	99.99	10.30	25.75	-2.04	1.41	0.00
14			0.0000							
15			0.0000							

3.3b. 100 ml of 10 mg/L Cd (II); 2 hr agitation time

Sample	m (g)	C_o (mg/L)	C_e (mg/L)	C_e average (mg/L)	% Cd (II) Removal	x (mg)	x/m @ qe (mg/g)	log Ce (mg/L)	log qe (mg/L)	Ce/qe (g/L)
1	0.05	10	7.2369	7.22	27.80	0.28	5.56	0.86	0.75	1.30
2			6.8426							
3			7.5795							
4	0.1	10	5.8989	5.73	42.74	0.43	4.27	0.76	0.63	1.34
5			5.2947							
6			5.9844							
7	0.2	10	2.3467	2.63	73.68	0.74	3.68	0.42	0.57	0.71
8			3.1617							
9			2.3879							
10	0.3	10	2.6042	2.32	76.79	0.77	2.56	0.37	0.41	0.91
11			2.2999							
12			2.0578							
13	0.4	10	2.3547	2.12	78.83	0.79	1.97	0.33	0.29	1.07
14			2.1863							
15			1.8107							

Appendix 3

EXPERIMENTAL DATA FOR BATCH STUDIES

3.1 Test for Optimum pH

3.1a. 100 ml of 100 mg/L Pb (II); 200 mg MIRHA; 1 hr agitation time

Sample	pH_i	pH_f	C_i (mg/L)	C_f (mg/L)	$C_{f\ average}$ (mg/L)	% Pb (II) Removal
1	1.02	1.84	115	100.88	100.94	12.23
2				101.34		
3				100.60		
4	2.18	3.14	115	100.14	99.75	13.26
5				101.06		
6				98.05		
7	3.03	4.16	115	7.09	19.62	82.94
8				17.04		
9				34.72		
10	4.05	5.27	115	19.19	23.82	79.29
11				22.51		
12				29.76		
13	5.01	6.58	115	14.27	24.86	78.39
14				32.26		
15				28.04		
16	6.01	7.72	115	6.18	4.94	95.71
17				7.09		
18				1.54		

3.1b. 100 ml of 10 mg/L Cd (II); 200 mg MIRHA; 1 hr agitation time

Sample	pH_i	pH_f	C_i (mg/L)	C_f (mg/L)	$C_{f\ average}$ (mg/L)	% Cd (II) Removal
1	1.00	2.58	10	6.26	6.72	32.78
2				7.03		
3				6.88		
4	2.02	3.99	10	5.72	5.84	41.61
5				5.86		
6				5.94		
7	3.03	6.20	10	4.49	4.74	52.58
8				5.23		
9				4.51		
10	4.01	6.89	10	3.19	3.14	68.58
11				2.93		
12				3.31		
13	5.02	8.07	10	3.02	3.07	69.27
14				3.14		
15				3.05		
16	6.03	8.49	10	2.88	2.82	71.82
17				2.14		
18				3.43		