

**LEAD AND CADMIUM REMOVAL FROM AQUEOUS SOLUTION USING
GROUNDWATER TREATMENT PLANT SLUDGE**

By

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FINAL PROJECT REPORT

Submitted to the Civil Engineering Programme
in Partial Fulfillment of the Requirements
for the Degree
Bachelor of Engineering (Hons)
(Civil Engineering)

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CERTIFICATION OF APPROVAL

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Approved:



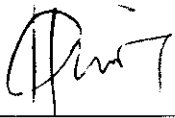
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June 2008

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.



Nurhidayati Mat Daud

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ABSTRACT

The adsorption of Pb (II) and Cd (II) ions onto groundwater treatment plant sludge (GWTS) in aqueous solution was studied in batch system. GWTS was dried and ground before the adsorption experiments. The ground GWTS was characterized by X-ray Fluorescent (XRF). The effects of pH, initial concentration of Pb (II) and Cd (II) ion of the solution, contact time and amount of adsorbent and on adsorption have been investigated. Removal of Pb (II) and Cd (II) ions was found as highly dependent on the pH of the solution. pH 5.5 and 7.5 were found to be the optimum value for maximum uptake of Pb (II) and Cd (II) from the solution respectively. The removal efficiency of Pb (II) and Cd (II) was found to correlate with the initial concentration, adsorbent dosage as well as the contact time between Pb (II) and Cd (II) and the adsorbent. In kinetics studies, both Pb (II) and Cd (II) were described by pseudo first order and pseudo second order kinetic model. The equilibrium data were analyzed using both Langmuir and Freundlich isotherm model. Pb (II) was found to conform to Langmuir Equation ($R^2 = 0.9497$) than Freundlich isotherm ($R^2 = 0.5188$), while Cd (II) better fitted to Freundlich isotherm with $R^2 = 0.8836$ larger than $R^2 = 0.7821$ of Langmuir model.

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Many researches for finding ways and new technologies to remove or minimize the effect of heavy metals released to the environment have been conducted and are still on going around the world.

Two metals of interest are lead (Pb) and cadmium (Cd). They were chosen based on their industrial applications and potential pollution impact on the environment. Pb has the atomic number of 82. Pb has a dull luster and is a dense, ductile, very soft, highly malleable, bluish-white metal that has poor electrical conductivity (Eisler, 2003). Lead exists in both inorganic forms; Pb (II) and less frequently Pb (IV), in organic forms (Patee, 2003). The principal uses of lead are for storage batteries, tetraalkyl lead for gasoline, cable coating, pigments and chemicals, building and construction, and caulking (Benhima *et al.*, 2007).

Cd has the atomic number of 48. Cd is a soft, malleable, ductile, toxic, bluish-white bivalent metal. It is similar in many respects to zinc but reacts to form more complex compounds (Eisler, 2003). It is insoluble in water, although its chloride and sulfate salts are freely soluble (Eisler, 2003). The dominant form of cadmium was free, readily bioavailable, cadmium ion, Cd ²⁺; however rare examples of Cd ¹⁺ can be found (Eisler, 2003). Cadmium is used mainly for the production of nickel–cadmium batteries, in metal plating, and for the manufacture of pigments, plastics and synthetics and alloys (Benhima *et al.*, 2007).

1.2 Problem Statement

There are at least 20 metals that are classified as toxic including lead (Pb) and cadmium (Cd) and half of them are being emitted to the environment especially in the marine, land and industrial in quantities that pose risks to human health (Kazemipour *et al.*, 2007). Even treated industrial wastewaters also contain high concentrations of heavy metals (Kazemipour *et al.*, 2007).

Lead and cadmium polluted water is mainly discharged from industrial processes such as metallurgy, mining, painting, smelting, batteries, and alloy industries (Benhima *et al.*, 2007). Lead ions are also present in automobile fuel and subsequently emitted into the atmosphere in the exhaust gases (Chaari *et al.*, 2007). In Malaysia, major industrial water polluters are food processors (40%), rubber and oil palm industries (35%), industrial chemicals and electronics (12%), and textiles (9%) as affirmed by the American Malaysian Chamber of Commerce (2001). Besides that, wastewater pollution in Malaysia also contributed by small to medium-sized factories like electroplating and metal-works, printing, dyeing and paper factories (Isa *et al.*, 2007).

It is well known that heavy metals can damage nerves, liver and bones and also interfere with the normal functioning of various metallo-enzymes (Garg *et al.*, 2007). Lead poisoning has occurred for at least 2500 years, and the adverse health effects of lead have been widely recognized for centuries (Patee and Pain, 2003). Pb is on top of the list of environmental threats because, even at extremely low concentrations, lead has been shown to cause brain damage in children (Kazemipour *et al.*, 2007). Cd is a non-essential and non-beneficial, highly toxic element to plants and animals (Kazemipour *et al.*, 2007). The adverse effects of cadmium on human beings include high blood pressure, kidney damage, destruction of testicular tissues and red blood cells (Garg *et al.*, 2007).

Due to these scenarios, there are many standards set by authorities around the world including Malaysia. The 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.

The World Health Organization (WHO) has established the maximum admitted concentration values for cadmium and lead are 0.005 mg/L and 0.05 mg/L, respectively (Benhima *et al.*, 2007).

Chemical reduction and precipitation, ion exchange, electro dialysis, reverse osmosis and evaporation are commonly used technologies to remove heavy metals. Most of the treatment methods are high cost and non-environmental friendly. This is where this research comes into picture, where the utilization of groundwater treatment plant sludge, which is a waste material, as adsorbent in the adsorption of toxic lead and cadmium wastewater, will be an alternative economical treatment method.

1.3 Objectives and Scope of Study

The aim of this study is to investigate the potential and capability of groundwater treatment plant sludge in adsorbing the heavy metals from aqueous solution with a view to achieve a feasible solution to the heavy metals contaminated water problem. Detailed objectives of the project are:

1. To study the effect of pH, initial concentration, contact time, and adsorbent dosage required for the maximum uptake of Pb (II) and Cd (II) from aqueous solution.
2. To study the kinetics of Pb (II) and Cd (II) uptake by the adsorbent.
3. To obtain a suitable isotherm model that would describe the adsorption of Pb (II) and Cd (II) onto the adsorbent.

CHAPTER 2

LITERATURE REVIEW

2.1 Heavy Metals Removal Technologies

A variety of technologies have been used for the treatment of heavy metals in water and wastewater, including conventional coagulation/precipitation, membrane filtration, ion exchange and adsorption. Choice of treatment depends on effluent characteristics such as concentration of heavy metals, pH, temperature, flow volume, biological oxygen demand, the economics involved and the social factor standard set by government agencies (Singh *et al.*, 2007).

Coagulation/precipitation is among the most commonly method employed removal technique. In this process chemicals transform dissolved metals into an insoluble solid which is precipitated (Mondal *et al.*, 2006). Dissolved metals may also be adsorbed on the surface and be co-precipitated with other precipitating species or separated by coagulation and flocculation (Mondal *et al.*, 2006). The efficiency of the removal depends on the pH of the process. However, this technique is usually encumbered by problems associated with the treatment and disposal of the resulting waste sludge (Aziz *et al.*, 2007 and Freitas *et al.*, 2007).

In membrane filtration technique heavy metals and separated from water by passing it through a semi permeable barrier or membrane (Mohan *et al.*, 2007). Pressure difference is the driving force for the separation (Mohan *et al.*, 2007). Various types of membrane filtration techniques available includes Microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and hyperfiltration or reverse osmosis (RO) (Choong *et al.*, 2007). Some drawbacks of using membranes include: the systems require higher cost than other treatment methods, the discharge of the concentrate can be a problem, water loss associated with concentrate stream membrane fouling and flux decline (Choong *et al.*, 2007). Ion exchange is not economically appealing because of high operational cost (Kazemipour *et al.*, 2008).

2.1.1 Adsorption

Adsorption is a process that removes substances from liquid solutions by using solids. Nowadays, removal technique by adsorption has become popular among the researchers around the world as it is comparatively more economical than ion exchange, extraction or electro dialysis and technically easier compared to chemical precipitation or reverse osmosis.

In the adsorption process, the transfer of adsorbate from solution to adsorbent continues until the concentration of the adsorbate remaining in the solution is in equilibrium with the concentration of the adsorbate adsorbed by the adsorbent (Isa *et al.*, 2007). Physical adsorption is caused mainly by Van der Waals forces and electrostatic forces between adsorbate molecules and the atoms which compose the adsorbent surface (Choong *et al.*, 2007). Conventionally used adsorbents are activated alumina, activated carbon, greensand (KMnO₄ coated gluconite), granular ferric hydroxide, iron oxide coated sand, copper-zinc granules, etc (Mondal *et al.*, 2006).

Adsorption process can be operated on either batch or continuous-flow basis. In the batch processes, the adsorbate and wastewater are mixed together in a reaction vessel until the desired level of treatment is achieved. Most batch adsorption systems are limited to small volume of wastewaters and operated using fill-and-draw technique. On the other hand, the continuous-flow adsorption systems, which are capable of treating large volume of wastewaters, are operated in columns using upflow or downflow techniques.

Adsorption by commercial activated carbon is an effective purification and separation technique used in industry especially in water and wastewater treatments that can remove heavy metals from wastewater (Benhima *et al.*, 2007). The use of commercial activated carbon is not suitable for developing countries because of its high cost (Choong *et al.*, 2007).

2.1.1.1 Adsorption isotherm

The adsorption capacity of an adsorbent operating in batch system may be determined by the use of experimental isotherms. The equilibrium adsorption isotherm is fundamental in describing the interactive behavior between adsorbate and adsorbent, and is important in the design of adsorption systems (Namasivayam *et al.*, 2008). Several models have been applied in the literature to describe the experimental data of adsorption isotherm. Most frequently employed models are Freundlich and Langmuir. The Freundlich isotherm is expressed as

$$q_e = K_f C_e^{1/n} \quad (2.1)$$

The straight line forms of the Freundlich isotherm is

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (2.1a)$$

Langmuir's isotherm model suggests a monolayer adsorption occurring on homogeneous surface (Oliveira *et al.*, 2007)

$$q_e = \frac{bQ_0C_e}{1 + bC_e} \quad (2.2)$$

Langmuir equation can be written in a variety of linear forms to facilitate fitting of experimental data for parameter evaluations. The employed straight line form of the Langmuir isotherm is

$$\frac{C_e}{q_e} = \frac{1}{Q_0b} + \frac{1}{Q_0} C_e \quad (2.2a)$$

where

q_e = amount of solute adsorbed per unit weight of adsorbent (mg/g)

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

k , n , Q_0 and b are constants

2.1.1.2 Adsorption Kinetics

To investigate the mechanism of heavy metals adsorption, several kinetic modeling can be applied (Singh *et al.*, 2007). Two commonly used kinetics model are pseudo-first-order and pseudo-second-order models. These models are important in water treatment process design. The pseudo-first-order and pseudo-second-order models can be respectively expressed as

$$\frac{dq}{dt} = k_1(q_e - q) \quad (2.3)$$

$$\frac{dq}{dt} = k_2(q_e - q)^2 \quad (2.4)$$

where

q_e = amount of solute adsorbed at equilibrium per weight of adsorbent (mg/g)

q = amount of solute adsorbed at time t per unit weight of adsorbent (mg/g)

k_1 , k_2 are constants

The following linearised time dependence functions can be obtained by integrating and rearranging Equation 2.3 and 2.4 for the boundary conditions $t = 0$ to >0 and $q = 0$ to >0 (Isa *et al.*, 2007).

$$\ln(q_e - q) = \ln q_e - k_1 t \quad (2.3a)$$

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (2.4a)$$

2.2 Utilization of low cost adsorbent

Recently more researchers are looking forward for adsorbents that are naturally available and abundant. The broad low-cost adsorbents can be divided into three categories which are biomass, agricultural and industrial wastes and nano-sized particle (Weng *et al.*, 2007).

Adsorption of Pb (II) onto Tunisian smectite-rice clay in aqueous solution with maximum adsorption capacity around 25 mg/g was reported by (Chaari *et al.*, 2007).

Pb (II) and Cd (II) ion adsorption onto inert organic matter (IOM) obtained from ground dried plants: *Euphorbia echinus*, *Launea arborescens*, *Senecio anthophorbium* growing in semi-arid zones of Morocco and *Carpobrotus edulis* as the Mediterranean plant was reported by (Benhima *et al.*, 2007). The adsorption capacity found were 130 to 175 mg/g for Pb (II) and 11 to 28 mg/g for Cd (II).

Influence of limestone particle as a post-treatment method for removing heavy metals including cadmium (Cd) and lead (Pb) from water or selected wastewater was reported by (Aziz *et al.*, 2007). Limestone has significantly removed more than 90% of most metals followed by 80% and 65% removals using crushed bricks and gravel, respectively.

An investigation of the adsorption lead (Pb) and cadmium (Cd) that exist in industrial wastewater onto the carbon produced from nutshells of walnut, hazelnut, pistachio, almond, and apricot stone was reported (Kazemipour *et al.*, 2008). The maximum removal occurred at pH 6–10, flowrate of 3 mL/min, and 0.1 g of the adsorbent.

The adsorption of Cd ²⁺ and Pb ²⁺ on sugar beet pulp (SBP), a low-cost material, has been studied and it is found that dose of 8 g/L was sufficient for the optimum removal of both the metal ions (Pehlivan *et al.*, 2007).

2.2.1 Groundwater treatment plant sludge (GWTS)

Groundwater treatment plant sludge (GWTS) is a by-product generated during the production of drinking water from groundwater where aluminium or iron based salts are used as coagulants to remove colour, turbidity and humic substances. GWTS for this project was taken from Air Kelantan Sdn Bhd's treatment plant located at Chica, Kota Bharu Kelantan. Treated groundwater is the main source of water for resident in Kelantan. Sludge from this plant is called alum-coagulation sludge as alum is used as the coagulant in the coagulation process. GWTS which is classified as waste is disposed in landfill. The current study tries to see any beneficial use of GWTS before it goes to the landfill. Aluminium or iron hydroxides are the important component of the drinking water treatment plant sludge once it has been dewatered and this opens the possibility of reusing it to control pollutants since aluminium or iron ions can enhance their adsorption and chemical precipitation (Razali *et al.*, 2006).

CHAPTER 3

RESEARCH METHODOLOGY

3.1 Introduction

This chapter details the materials, instruments and methods for the experimental phase. The overall methodology for this research is divided into three major parts. The first part is the preparation of the sludge prior to its characterization using XRF. The second part is the batch test including the preparation of the aqueous solution containing the heavy metals. The third part is analysis of the sample from the resultant batch tests.

3.2 Health, Safety and Environment

While conducting laboratory works, safety steps were always employed. OSHA Guide of Chemical Hazard was referred before entering the laboratory so that all possible hazards can be avoided and prevented. (Refer Appendix 1).

3.3 Materials

3.3.1 Chemicals

All chemicals are of analytical reagent grade and obtained from the Environmental Laboratory, Civil Engineering Department, Universiti Teknologi Petronas including: Plumbum Chloride (PbCl_2), Cadmium Chloride (CdCl_2), hydrochloric acid (HCl) and sodium hydroxide (NaOH). Aqueous solutions are prepared by mixing with distilled water.

3.3.2 Adsorbent

Water treatment plant sludge was used as the adsorbent for heavy metals removal. The sludge was taken from Air Kelantan Sdn Bhd's treatment plant. The sludge is dried and

grinded before the batch tests were conducted. Plate 3.1 showed the GWTS used as adsorbent in the removal of lead and cadmium from aqueous solution.

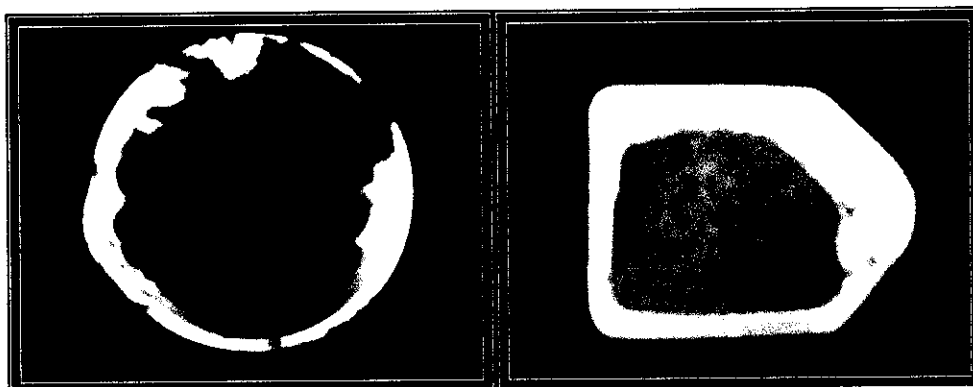


Plate 3.1: GWTS before and after dried and ground.

3.4 Equipments

The chemical composition of the GWTS was analyzed using X-Ray Fluorescent (XRF). Digital pH meter was used for pH measurement (Plate 3.2). pH meter was calibrated with buffers of pH 4.00, 7.00 and 10.00. In the batch adsorption studies, the solutions and adsorbents were agitated with an orbital shaker (Plate 3.3). The solutions were filtered using 0.45 μ m filter paper (Plate 3.4). Finally, the concentrations of Pb (II) and Cd (II) in the solutions were determined using Atomic Absorption Spectrophotometer (AAS) (Plate 3.5).

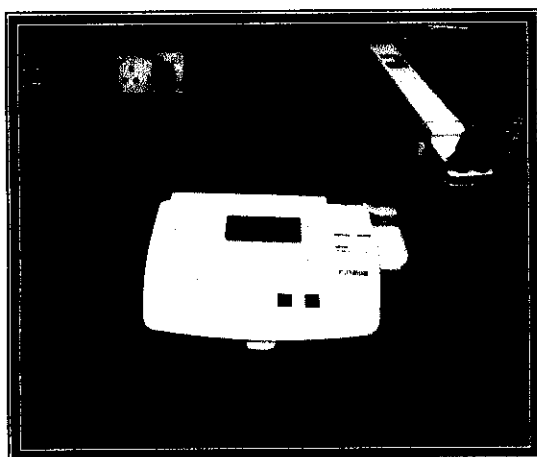


Plate 3.2: pH meter

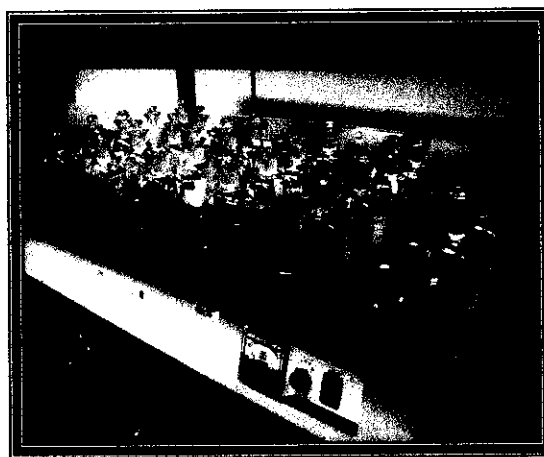


Plate 3.3: Orbital shaker

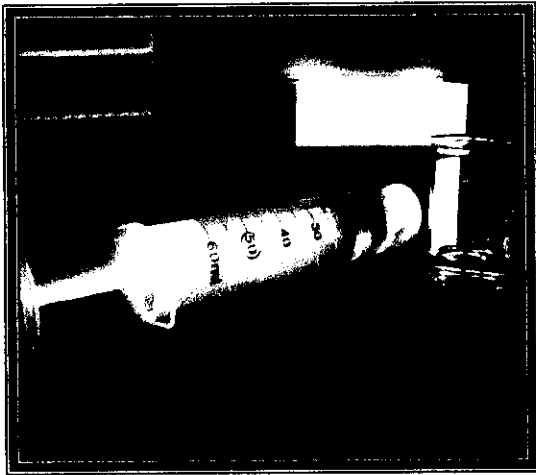


Plate 3.4: Syringe and 0.45um
filter paper

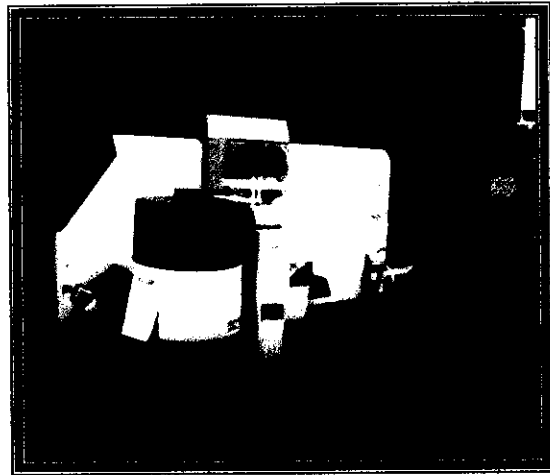


Plate 3.5: Atomic Absorption
Spectrophotometer (AAS)

3.5 Methodology

3.5.1 Preparation of Dry Powdered Sludge

Prior to testing the sludge for the characteristics, it needs to be dried and made free from moisture. 1 kg of sludge sample was put on a tray and left in the drying oven at a temperature of 103 °C for 24 hours to free it from moisture. The dried powdered sludge was submitted to the authorized technicians for the XRD test.

3.5.2 Preparation of lead and cadmium solution

Aqueous solution containing lead was prepared by dissolving 2.6844 g of Plumbum Chloride (PbCl_2) in 20 liter distilled water to produce a solution containing 100 mg/L of Pb (II). Cd solution of the same concentration is prepared by dissolving 3.26155 g Cadmium Chloride (CdCl_2) in 20 liter of distilled water respectively. (Refer to appendix for detailed calculation).

These solutions were used to prepare the desired solutions for batch tests. The following mass balance equation was employed to prepare heavy metals solutions of various concentrations:

$$M_1V_1 = M_2V_2 \quad (3.1)$$

Where,

M_1 = original concentration
 M_2 = desired concentration
 V_1 = original volume
 V_2 = desired volume

3.5.3 Preparation of other working solutions

Standard acid (1N H₂SO₄) and base solutions (1N NaOH) were used for the adjustment of pH.

3.5.4 Batch studies

Batch tests were conducted at room temperature (28 ± 1° C) to determine the optimum pH, optimum contact time, and optimum adsorbent dosage.

3.5.4.1 Test for effect of pH

Seven conical flasks; each were filled with 100 ml of 100 mg/L lead solution. Each conical flask of every set of Pb samples were adjusted to pH 1.0 – 6.0 and from pH 1.0 to 8.0 for Cd since removal of Pb (II) and Cd (II) to be favored at low pH (Benhima *et al.*, 2007; Kim *et al.*, 2007; Chaari *et al.*, 2007; Garg *et al.*, 2007; and Pehlivan *et al.*, 2007). The initial pH adjustment for the samples was made by the addition of (1N H₂SO₄) and (1N NaOH) solutions. 200 mg of adsorbent was measured and added to each flask. The flasks were then agitated at 150 rpm for 60 minutes. After filtering through 0.45µm filter paper, the final pH values and the concentrations of the samples were measured. The same procedures were repeated for 10 mg/L Cd (II) solution

3.5.4.2 Test for effect of initial concentration and agitation time

Five sets of nine conical flasks with 100 ml of Pb solutions were used in the test. The set of flasks were filled with 20, 50, 100, 150 and 200 mg/L of Pb solutions. pH of the solutions were adjusted to the optimum. 200 mg of adsorbent was added to each flask, followed by agitation at 150 rpm using an orbital shaker. The flasks were removed from the shaker one after another at 10, 30, 60, 90, 120, 150, 180, 360 and 1440 minutes. The variation of agitation times employed in this test enabled kinetic study of the heavy metals adsorption onto the sorbent. For Cd solution, the same procedures were repeated but at initial concentrations of 5, 10, 20, 50 and 100 mg/L.

3.5.4.3 Test for effect of adsorbent dosage

A set of six conical flasks were each filled with 100 ml of 100 mg/L Pb (II). pH of the solution were adjusted to their optimum values and the adsorbent amount in each set was varied from 25 mg to 400 mg. The flasks filled with the Pb (II) solutions were then agitated at 150 rpm for 60 minutes. The information on the amount of the adsorbent used and Pb adsorbed was used to determine the adsorption isotherms. Same steps were repeated for 10 mg/L of Cd (II) for optimum contact time of 180 minutes.

CHAPTER 4

RESULT AND DISCUSSIONS

4.1 Introduction

In this chapter, the result of the batch adsorption tests conducted on Pb (II) and Cd (II) are presented and discussed to assess the feasibility of Groundwater Treatment Plant Sludge (GWS) as adsorbent for the removal of lead and cadmium from aqueous solutions. Also, the rate of lead uptake and factors affecting the adsorption process such as pH, contact time, initial concentration of adsorbate and adsorbent dosage are discussed.

4.2 Characterization of the adsorbent

Physiochemical analysis of the adsorbent was carried out and has been given in Table 4.1. Table 4.1 shows that Ferric Oxide (Fe_2O_3) is the major component of the adsorbent. Silica (SiO_2) was 16.4% and oxides of other metals were present in traces.

Table 4.1: Chemical analysis of the adsorbent

Constituents	Percentage (%) by weight
Fe_2O_3	56.4
SiO_2	16.4
CaO	16.3
Al_2O_3	6.15
P_2O_5	2.53
Rayleigh	1.47
Compton	0.74
MnO	0.310
Re	0.211
BaO	0.193
K_2O	0.0555
Tb_4O_7	0.0445
SrO	0.0186

4.3.2 Cadmium

The adsorption of Cd (II), on the other hand, occurred at higher pH range and reached a maximum value approximately pH 7.5 (Figure 4.1b). This behavior of low removal at very low pH is apparently due to the higher concentration of H^+ ions present in the solution that compete with Cd^{2+} for the adsorption sites of GWTS, leaving cadmium ions free in the solution. This means that at higher H^+ ions concentration, the GWTS becomes more positively charged thus reducing the attraction between GWTS surface and cadmium cations. The increase in the removal of cadmium ions at the range of pH from 4 to 8 is due to the concentration of the H^+ ions exist in the solution will be decreased as pH increased and hence will not give the chance to compete with cadmium ions on the adsorption sites of GWTS. The surface of the adsorbent becomes more negatively charged which attracts the positive charge of Cd^+ and $Cd(OH)^+$ ions hook up the free binding sites (Al-Anber *et al.*, 2007).

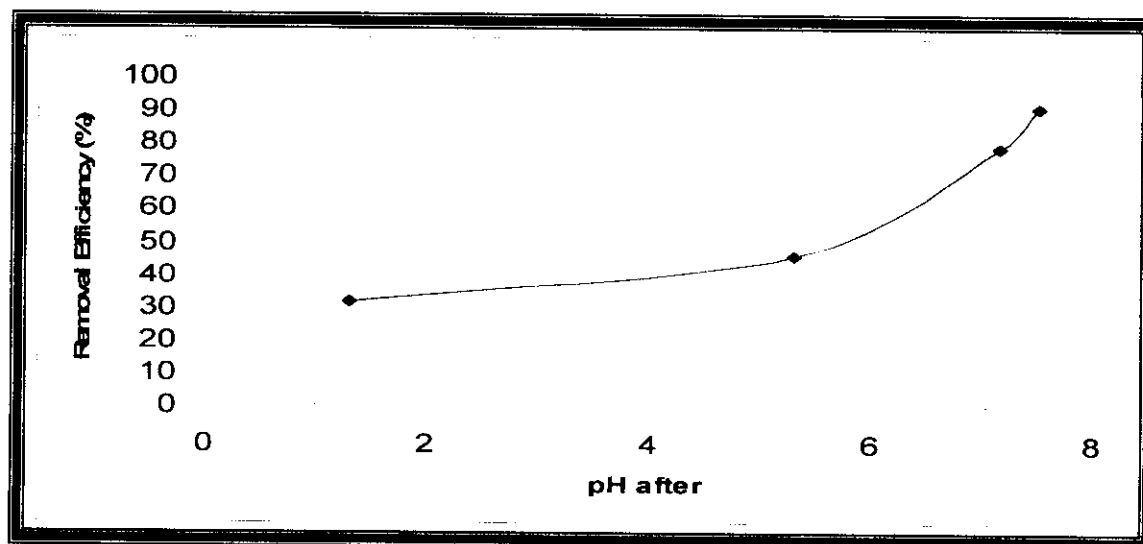


Figure 4.1b: Effect of pH on the removal of Cd (II) by GWTS: [Cd (II)] = 10 mg/L; volume, 100 ml; contact time, 1 h; agitation speed, 150 rpm; adsorbent dosage, 2g/L.

4.4 Effect of Contact Time and Initial Lead Concentration

4.4.1 Lead

Figures 4.2a and 4.2b present the effect of contact time on the removal and uptake of Pb (II) per unit mass of adsorbent at different initial Pb (II) concentrations. Figure 4.2a shows the removal efficiencies for 10-200 mg/L Pb (II) with contact times up to 360 minutes. It is apparent that an increase in the contact time resulted in an increase of the removal efficiency of Pb (II) ions from the solutions. The lead percent adsorption increases with time until the equilibrium is attained between the amounts of lead adsorbed on the GWTS and the remaining in solution.

Figure 4.2a shows that the equilibrium contact times for total treatment of 9.89, 24.76, 48.35, 14.67 and 198.12 mg/L Pb (II) obtained from the study are 60, 60, 60, 90 and 150 minutes respectively. It can be concluded that the rate of lead binding with sludge is more at initial stages. 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.

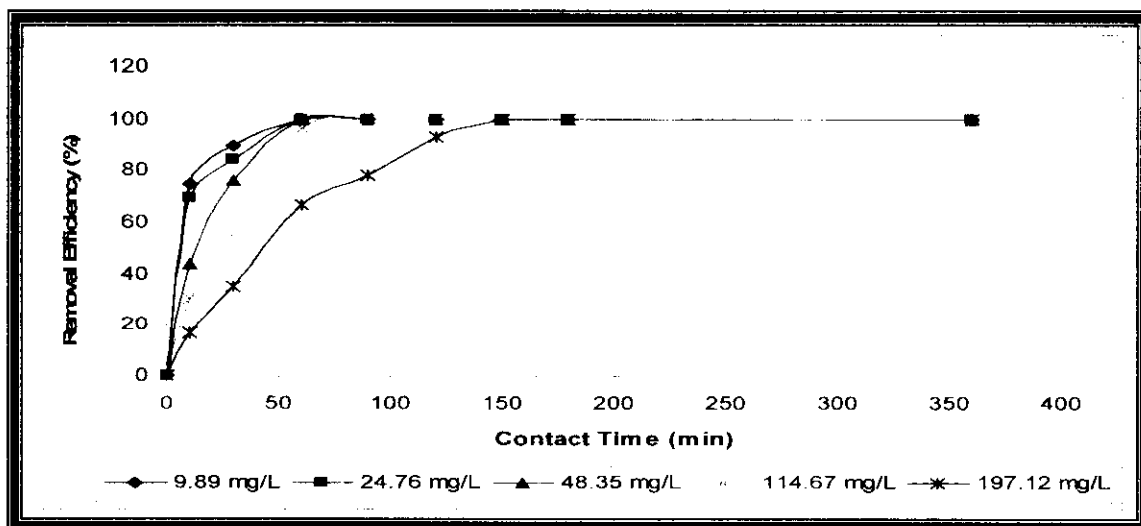


Figure 4.2a: Effect of contact time and initial Pb (II) concentration on the removal efficiency of Pb from aqueous solutions: pH 5.5; volume, 100 ml; agitation speed, 150 rpm; adsorbent dosage, 2g/L

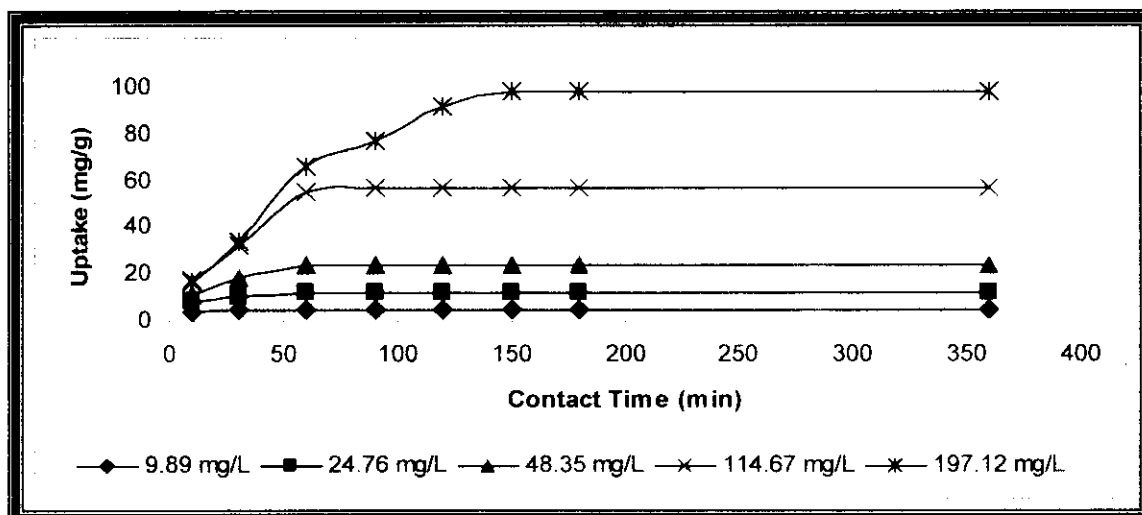


Figure 4.2b: Effect of contact time and initial Pb (II) concentration on the uptake of Pb per weight adsorbent: pH 5.5; volume, 100 ml; agitation speed, 150 rpm; adsorbent dosage, 2g/L.

Figure 4.2b provides a better understanding of Pb (II) adsorbed per unit weight of GWTS. A rapid uptake of 200 mg/L Pb (II) which was the highest concentration tested occurred in the first 90 minutes, followed by a more gradual uptake before the equilibrium was attained. For 100 mg/L of Pb (II), the uptake was rapid at the beginning before the equilibrium was reached at 90 minutes. Less time was required to achieve equilibrium in the treatment of lower concentrations of Pb (II). The actual uptake was higher for higher initial concentrations; i.e. 4.945, 12.38, 24.175, 57.335, and 98.56 mg/g adsorbent for initial Pb (II) concentrations of 9.89, 24.76, 48.35, 14.67 and 198.12 mg/L respectively.

4.4.2 Cadmium

The equilibrium time was longer for Cd (II) than Pb (II) and this was particularly evident at high Cd (II) concentrations. Figure 4.3a shows that for initial concentration of 5 and 10 mg/L, the equilibrium time for nearly 100% removal were 120 minutes and 150 minutes respectively, whereas after 360 minutes 96.4% removal was obtained for initial concentration of 20 mg/L. For initial concentration of 50 and 100 mg/L, after 1440 minutes the removals were only 73.4% and 60.7% respectively. At these stages, the total

Cd (II) uptake was 2.485, 4.97, 9.63, 17.87 and 31.38 mg/g adsorbent for initial Cd (II) concentrations of 4.97, 9.94, 19.78, 48.69 and 98.54 mg/L respectively.

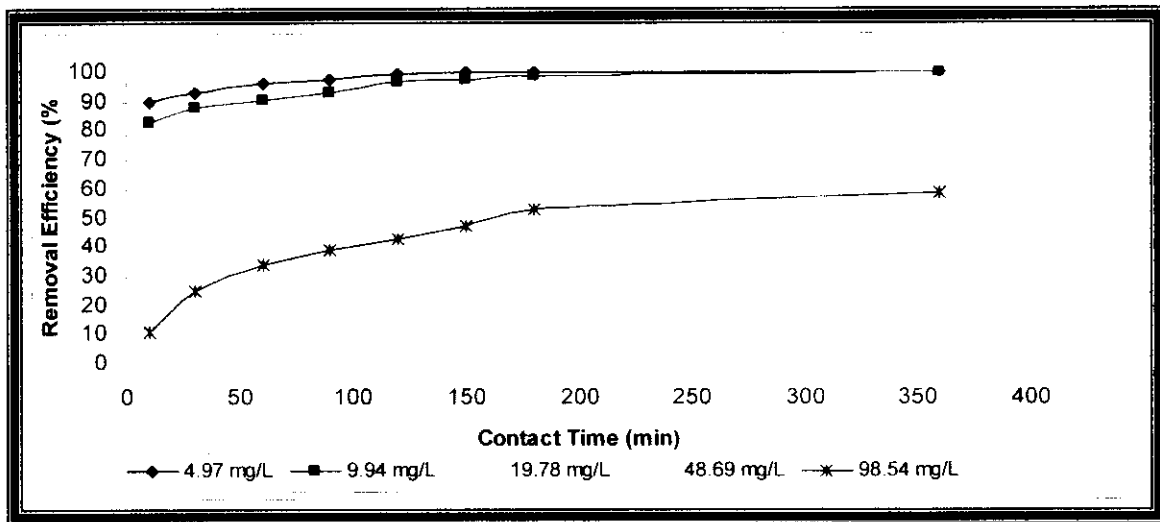


Figure 4.3a: Effect of contact time and initial Cd (II) concentration on the removal efficiency of Cd from aqueous solutions: pH 7.5; volume, 100 ml; agitation speed, 150 rpm; adsorbent dosage, 2g/L.

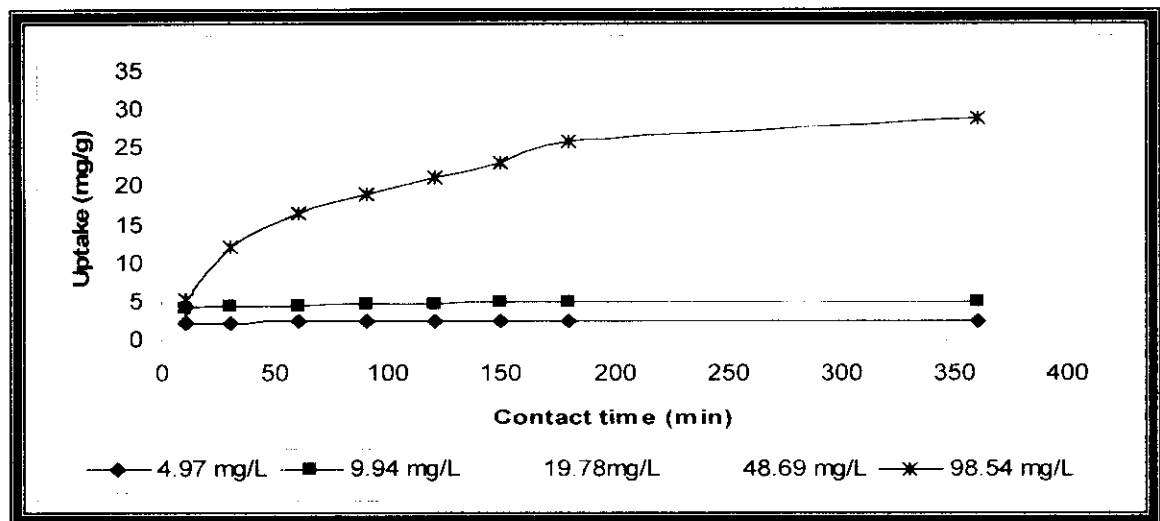


Figure 4.3b: Effect of contact time and initial Cd (II) concentration on the uptake of Cd per weight adsorbent: pH 7.5; volume, 100 ml; agitation speed, 150 rpm; adsorbent dosage, 2g/L.

4.5 Kinetics Studies

4.5.1 Lead

The kinetics of Pb (II) adsorption was analyzed using the pseudo first order and pseudo second order kinetic models. The first and second order reaction rate constants calculated from these linear plots using the first and second order equations (Equation 2.3a and 2.4a) are shown in Tables 4.2 and 4.3 respectively. Figures 4.4 and 4.5 show the plots of $\log(q_e - q)$ versus t (min) and t/q versus t for different initial concentrations respectively. Based on the high R^2 values obtained from the first and second order kinetic plots (i.e. from 0.9309 to 0.9999), it is concluded that adsorption of Pb (II) can be described by both models. Nevertheless, the R^2 values also indicated that the sorption kinetics of Pb (II) is better expressed by the second order reaction rates. Compliance to second order kinetic order model strongly suggest chemical adsorption or chemisorption between the adsorbent and adsorbate.

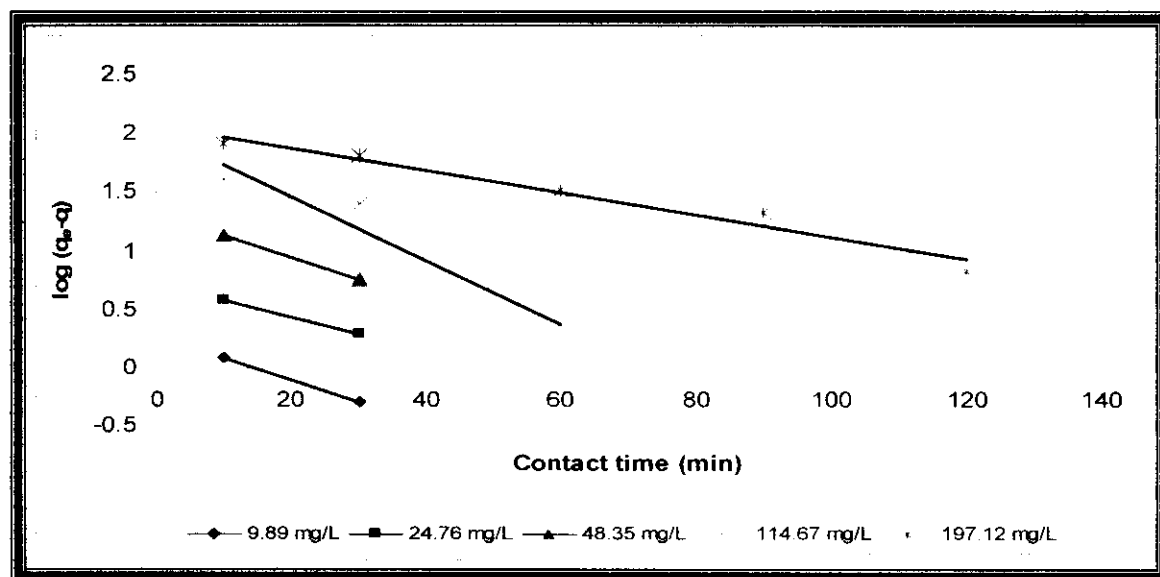


Figure 4.4: Pseudo First order kinetic plot for Pb (II) adsorption at different initial concentrations: pH 5.5; volume, 100 ml; agitation speed, 150 rpm and adsorbent dosage, 2g/L.

Table 4.2: Pseudo-1st-order rate of constants

[Pb(II)] (mg/L)	$K_1(\text{min}^{-1})$	R^2	Equation
9.89	0.0444479	0.9999	$y = -0.0193x + 0.2832$
24.76	0.0338541	0.9999	$y = -0.0147x + 0.7292$
48.35	0.0426055	0.9999	$y = 0.0306x + 0.665$
114.67	0.0626416	0.9309	$y = -0.0272x + 2.0046$
197.12	0.0172725	0.9877	$y = -0.0075x + 2.0004$

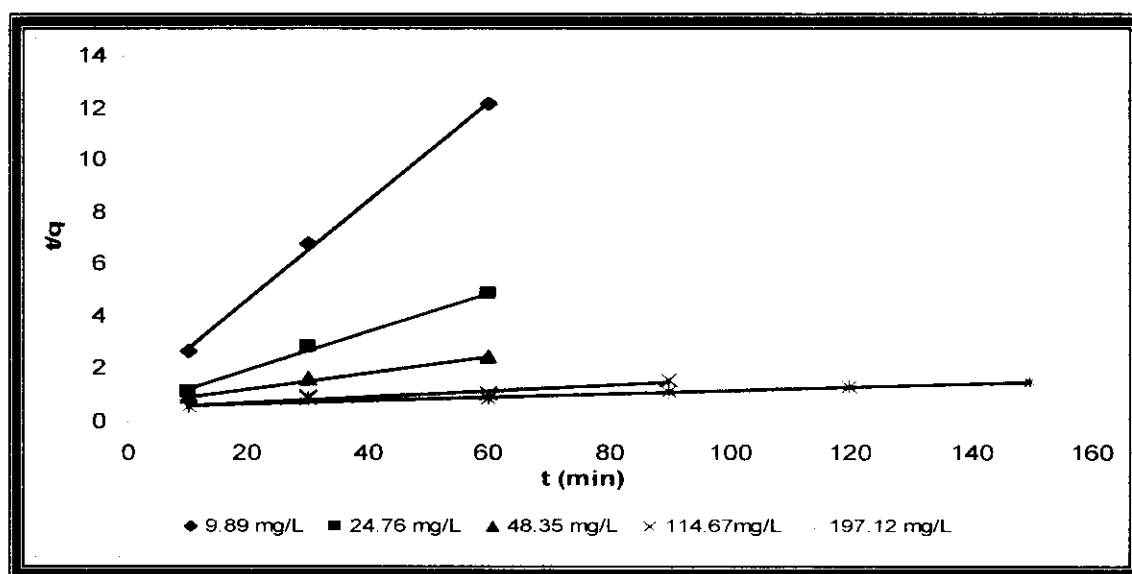


Figure 4.5: Pseudo Second order kinetic plot for Pb (II) adsorption at different initial concentrations: pH 5.5; volume, 100 ml; agitation speed, 150 rpm and adsorbent dosage, 2g/L.

Table 4.3: Pseudo-2nd-order rate of constants

[Pb(II)] (mg/L)	K_2 (g/mg min)	R^2	Equation
9.89	0.038258661	0.9988	$y = 0.1881x + 0.9248$
24.76	0.010033892	0.9947	$y = 0.073x + 0.5311$
48.35	0.00635403	0.997	$y = 0.0403x + 0.2556$
114.67	0.000260337	0.9544	$y = 0.0114x + 0.4992$
197.12	0	0.9693	$y = 0.0062x + 0.5894$

4.5.2 Cadmium

The pseudo first order and second order kinetic plots for adsorption of Cd (II) onto GWTS are depicted in Figure 4.6 and Figure 4.7. The first order and second order reaction rate constants calculated from slopes of the plots using the first and second order equation (Equation 2.3a and 2.4a) were represented in Table 4.4 and Table 4.5.

The lowest value of R^2 observed was only 0.8949 indicated that Cd (II) adsorption onto GWTS can be presented by both kinetic models. With smallest correlation value of only 0.9956 the reaction of Cd (II) fits better to second order kinetic model.

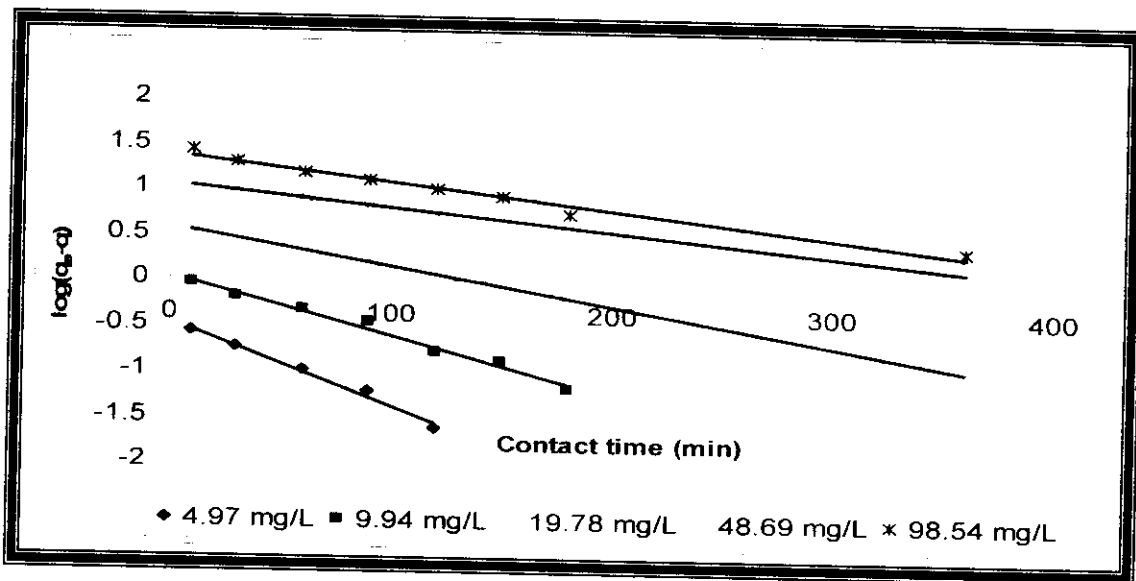


Figure 4.6: Pseudo First order kinetic plot for Cd (II) adsorption at different initial concentrations: pH 7.5; volume, 100 ml; agitation speed, 150 rpm and adsorbent dosage, 2g/L.

Table 4.4: Pseudo-1st-order rate of constants

[Cd(II)] (mg/L)	$K_1(\text{min}^{-1})$	R^2	Equation
4.97	0.0209573	0.9877	$y = -0.0091x - 0.4725$
9.94	0.0147392	0.9817	$y = -0.0064x + 0.0201$
19.78	0.0096726	0.9883	$y = -0.0042x + 0.5616$
48.69	0.0057575	0.8949	$y = -0.0025x + 1.0491$
98.54	0.0066787	0.9682	$y = -0.0029x + 1.3633$

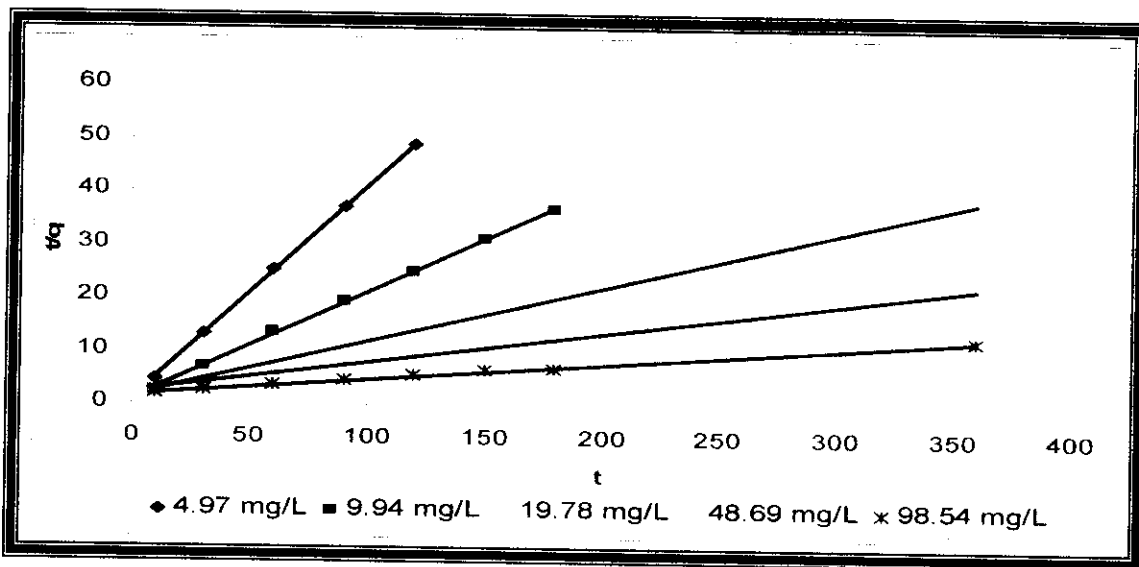


Figure 4.7: Pseudo Second order kinetic plot for Cd (II) adsorption at different initial concentrations: pH 7.5; volume, 100 ml; agitation speed, 150 rpm and adsorbent dosage, 2g/L.

Table 4.5: Pseudo-2nd-order rate of constants

[Cd(II)] (mg/L)	K_2 (g/mg min)	R^2	Equation
4.97	0.195662492	0.9999	$y = 0.3996x + 0.8161$
9.94	0.03796488	0.9998	$y = 0.1988x + 1.041$
19.78	0.007195817	0.9976	$y = 0.1026x + 1.4629$
48.69	0.001221161	0.9972	$y = 0.0552x + 2.4952$
98.54	0.000491553	0.9956	$y = 0.0298x + 1.8066$

4.6 Effect of Adsorbent Dosage

The test to observe the effects of different mass of adsorbent used in the adsorption of Pb (II) from same adsorbate concentrations was carried out. Figure 4.8a and 4.8b illustrate the uptake of Pb (II) ions by different adsorbent dosage. While the amount of Pb and Cd adsorbed (mg/g adsorbent) by GWTS decreased with increasing amount of adsorbent (g/L), the removal efficiencies increased from around 18% to 95% and from 47% to 96% for Pb and Cd respectively.

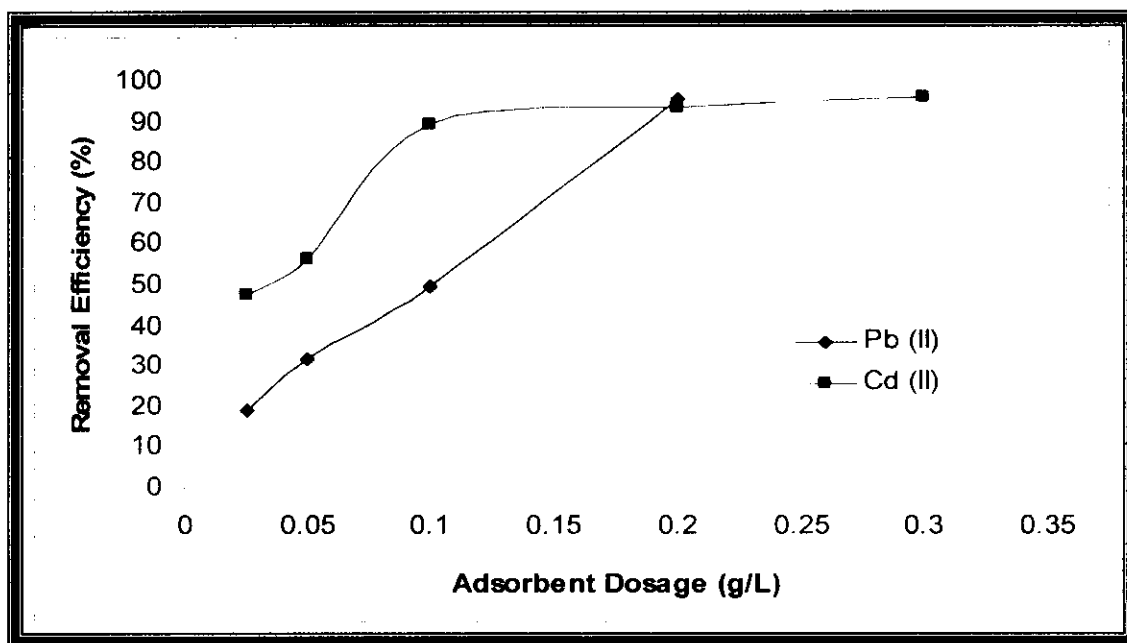


Figure 4.8a: Effect of adsorbent dosage variation on removal efficiency of Pb (II) and Cd (II): pH 5.5 and contact time, 60 minutes for Pb (II); pH 7.5 and contact time, 150 minutes for Cd (II); volume, 100 ml; agitation speed, 150 rpm for both metals.

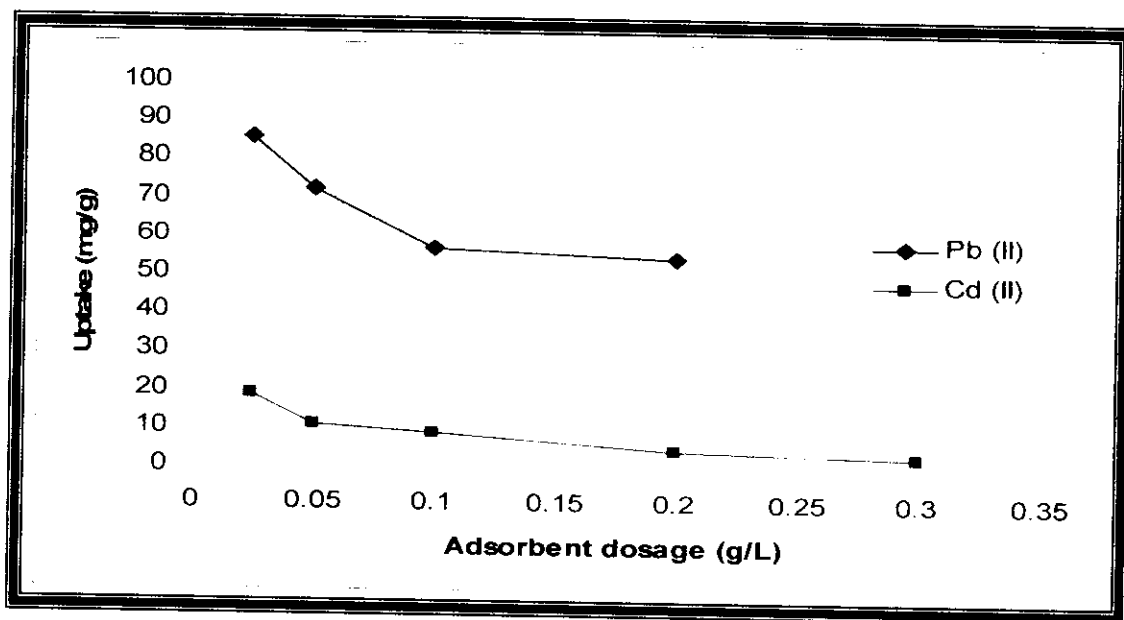


Figure 4.8b: Effect of adsorbent dosage variation on the uptake of Pb (II) and Cd (II): pH5.5 and contact time, 60 minutes for Pb (II); pH 7.5 and contact time, 150 minutes for Cd (II); volume, 100 ml; agitation speed, 150 rpm for both metals.

4.7 Isotherm model

Adsorption isotherm plays a crucial role in the predictive modeling procedures for analysis and design of an adsorption system. In this study, the adsorption data of Pb (II) and Cd (II) were correlated with Langmuir and Freundlich models (Equation 2.1 and 2.2). The plot of linearised Langmuir and Freundlich equations (Equation 2.1a and 2.2a) for Pb (II) are shown in Figure 4.9a and 4.10a respectively. While the plot of linearised Langmuir and Freundlich equations Cd (II) are shown in Figure 4.9b and 4.10b respectively.

The Langmuir model makes several assumptions, such as the adsorption energies are uniform and independent of the surface coverage and complete coverage of the surface by a monolayer of adsorbate indicates maximum adsorption. The plots of C_e/q_e against C_e for Pb (II) and Cd (II) gave straight lines, indicating that Langmuir model was applicable to the present study.

Regression value ($R^2 = 0.9497$) presented in Table 4.6 indicates that the adsorption data for Pb (II) removal fitted better with Langmuir isotherm. The maximum adsorption capacities corresponding to complete coverage of available sites, or the limiting adsorption capacities calculated from the slopes were 62.5 mg/g and 21.413276 mg/g for Pb (II) and Cd (II) respectively.

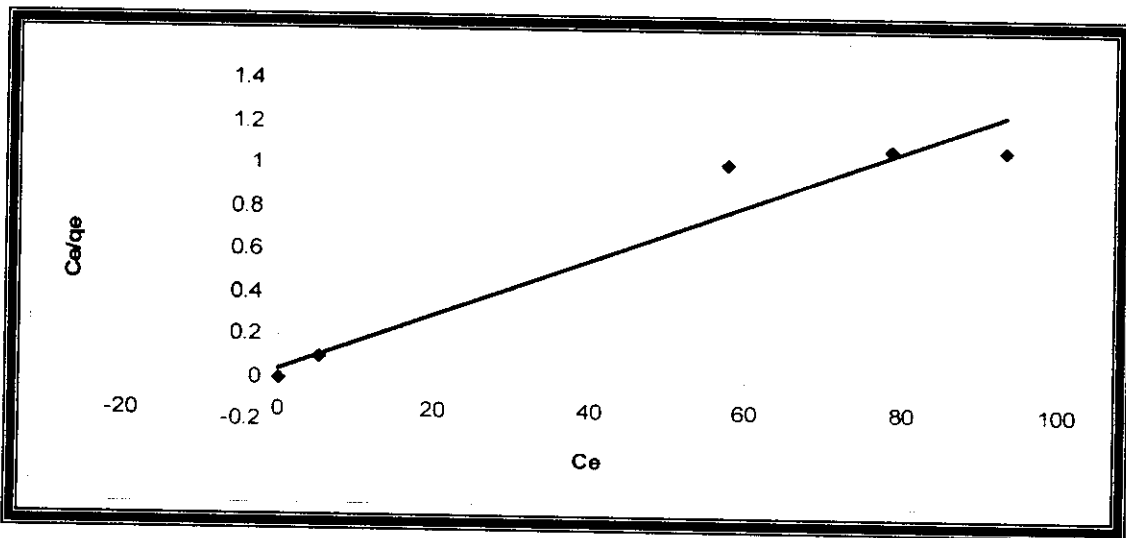


Figure 4.9a: Langmuir isotherm for Pb (II) adsorption: pH 5.5 and contact time, 60 minutes; volume, 100 ml; agitation speed, 150 rpm.

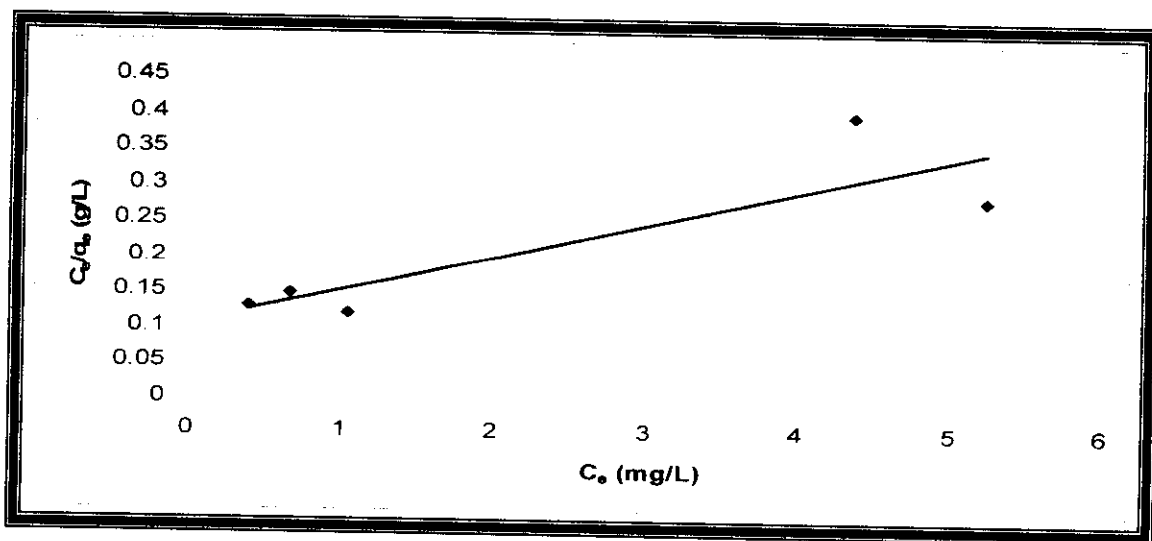


Figure 4.9b: Langmuir isotherm for Cd (II) adsorption: pH 7.5 and contact time, 150 minutes; volume, 100 ml; agitation speed, 150 rpm.

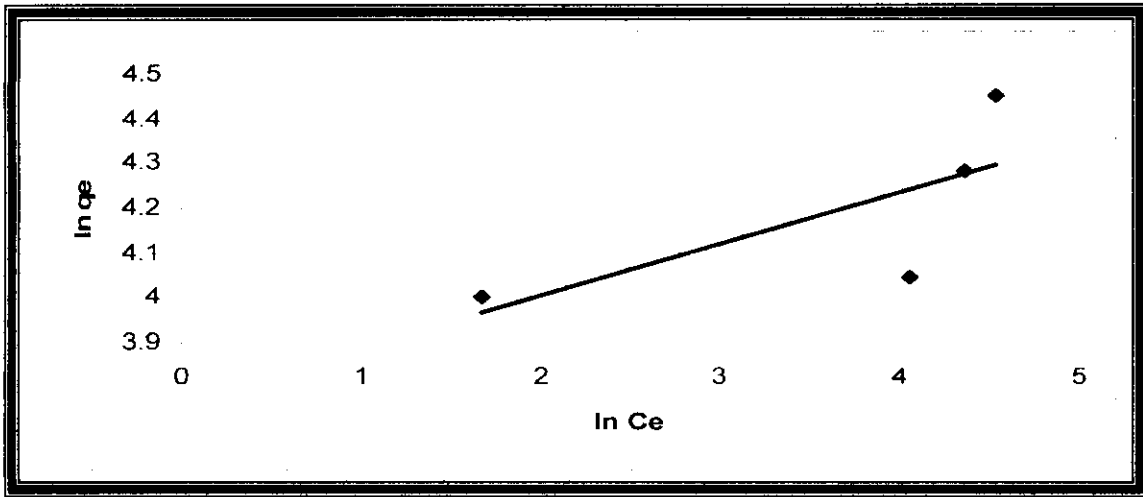


Figure 4.10a: Freundlich isotherm for Pb (II) adsorption: pH 5.5 and contact time, 60 minutes; volume, 100 ml; agitation speed, 150 rpm.

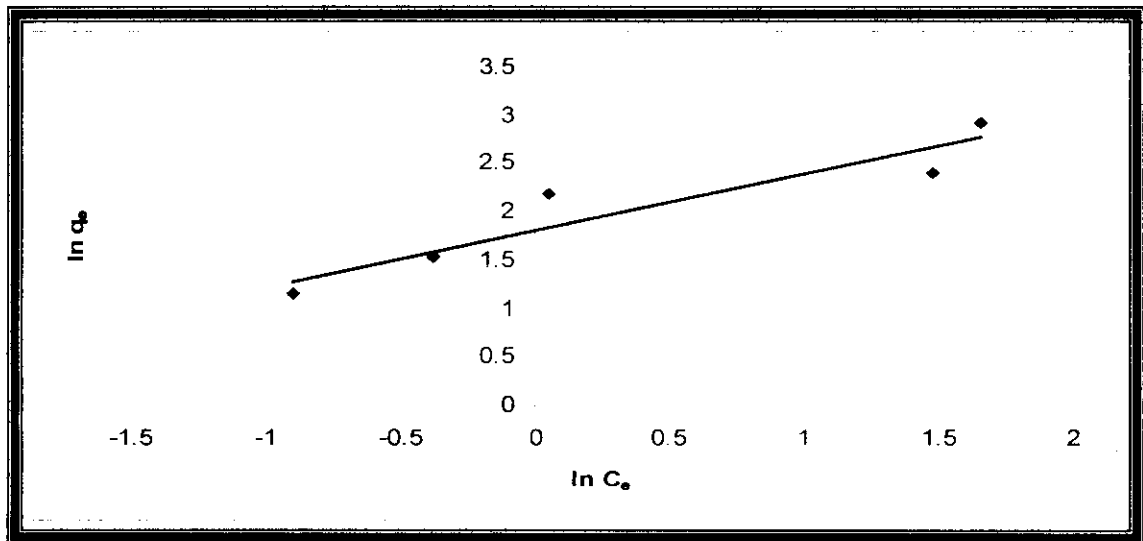


Figure 4.10b: Freundlich isotherm for Cd (II) adsorption: pH 7.5 and contact time, 150 minutes; volume, 100 ml; agitation speed, 150 rpm.

Table 4.6: Langmuir constants for Pb (II) and Cd (II)

Adsorbate	Q_0 (mg/g)	b (L/mg)	R^2	Equation
Pb (II)	62.5	0.4040404	0.9497	$y = 0.016x + 0.0396$
Cd (II)	21.413276	0.4427	0.7821	$y = 0.0467x + 0.1055$

Table 4.7: Freundlich constants for Pb (II) and Cd (II)

Adsorbate	K_f	n	R^2	Equation
Pb (II)	43.8117	8.8028169	0.5188	$y = 0.1136x + 3.7799$
Cd (II)	6.1257427	1.84229919	0.8836	$y = 0.5428x + 1.8125$

However, the R^2 value of Cd (II) for Langmuir plot was lower than that for the Freundlich plot, thereby suggesting that the Freundlich model is more suitable to describe the adsorption of Cd (II) onto the GWTS. The Freundlich model encompasses the heterogeneity of the adsorbent surface, the exponential distribution sites and their energies (Isa *et al.*, 2007).

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Research Conclusions

From this study, it can be concluded that GWTS can be utilized as a low-cost adsorbent in the removal of Pb (II) and Cd (II) from aqueous solutions. The treatment is found to be pH dependent. Thus, pH adjustment is required for maximum Pb (II) and Cd (II) uptake. Adsorption of Pb is favored under acidic conditions with pH 5.5 being the optimum value and pH 7.5 is optimum for Cd (II).

The adsorption by batch process conducted on 10 to 200 mg/L of Pb and 5 to 100 mg/L of Cd was demonstrated by the observed high removal efficiencies. In particular, total (100%) removal of 10, 20 and 50 mg/L of Pb (II) was achieved after only 1 hour contact time, whereas 90 and 150 minutes of contact time between the solute and the adsorbent result in total removal of 100 and 200 mg/L Pb (II). On the other hand, 98.72 % removal of 10 mg/L Cd (II) from aqueous solution can be obtained after 180 minutes of contact time. Although the removal efficiency of higher Pb (II) and Cd (II) concentration required longer contact time than of lower concentrations, higher uptake of Pb (II) and Cd (II) per unit weight of adsorbent was noticed at 200 mg/l Pb (II) and at 100 mg/l Cd (II) concentrations with uptake of 98.56 and 31.38 mg/g respectively. .

Adsorption equilibrium of Pb (II) can be well described by Langmuir isotherm model, while Cd (II) was better to conform to the Freundlich model. Therefore, GWTS is proposed to be a new single-use adsorbent in for the removal of toxic heavy metals from wastewater.

5.2 Recommendations for future studies

Several recommendations for future studies can be derived from the results obtained from this research. Several parameters affecting the adsorption capacity of GWTS in the adsorption of Pb (II) and Cd (II) from aqueous solution have not been studied, such as the effect of temperature, which also, governs the kinetic rates of adsorption and the effect of the particle size. The capacity of the GWTS to adsorb Pb (II) and Cd (II) should also be compared with other of adsorbents; thereby the least expensive method with comparative efficiency should be employed in real wastewater treatment applications. In addition, a real wastewater consisting of various components with different molecular sizes and concentrations, to a certain degree will compete with Pb (II) and Cd (II) for the adsorption sites. Such phenomena may result in lower efficiency of Pb (II) and Cd (II) removal and different adsorption characteristics. Therefore, an adsorption study of a real wastewater should be conducted to prove the adsorption efficiency of the GWTS, which was shown to be good for synthetic wastewater only.

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APPENDICES

Appendix 1

OSHA Guide of Chemical Hazard

1.0 CADMIUM

1.1 Cadmium (II) Compounds

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

1.2 First Aid Procedures

Code	Definition
Eye: Irrigate immediately	If this chemical gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with this chemical.
Skin exposure	If this chemical gets on the skin, wash the contaminated skin using soap or mild detergent and water. Be sure to wash the hands well before eating or smoking and at the close of work.
Breathing	If a person breathes in large amounts of cadmium dust, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.
Swallowing	When cadmium dust or liquids containing cadmium dust have been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.
Rescue	Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

1.3 Toxicity

Short-term	Long-term
<p>Can cause irritation of the nose and throat. If enough has been inhaled, after a delay of several hours, a person may also develop cough, chest pain, sweating, chills, shortness of breath and weakness. Death may occur. Ingestion of cadmium dust may cause nausea, vomiting, diarrhea, and abdominal cramps.</p>	<p>Repeated or prolonged exposure to cadmium may cause loss of sense of smell, ulceration of the nose, shortness of breath (emphysema), kidney damage, and mild anemia. Exposure to cadmium had also been reported to cause an increased incidence of cancer of prostate in man.</p>

2.0 LEAD

2.1 Lead (II) Compounds

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

2.2 First Aid Procedures

Code	Definition
Eye: Irrigate immediately	If this chemical gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with this chemical.
Skin exposure	If this chemical gets on the skin, wash the contaminated skin using soap or mild detergent and water. Be sure to wash the hands well before eating or smoking and at the close of work.
Breathing	If a person breathes in large amounts of cadmium dust, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.
Swallowing	When cadmium dust or liquids containing cadmium dust have been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.
Rescue	Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

2.3 Toxicity – Effects to humans

Inhalation or ingestion of inorganic lead has caused peripheral neuropathy with paralysis of the muscles of the wrists and ankles, encephalopathy, anemia (due to decreased red blood cell life and impaired heme synthesis), proximal kidney tubule damage, decreased kidney function, and chronic kidney disease. Lead can accumulate in the soft tissues and bones, with the highest accumulation in the liver and kidneys, and elimination is low. Lead can penetrate the placental barrier, resulting in neurologic disorders of infants.

2.3.1 Signs and symptoms of exposure

Short-term	Long-term
Cause decreased appetite, insomnia, headache, muscle and joint pain, colic and constipation.	Weakness, weight loss, nausea, vomiting, constipation, blue or blue-black dot-like pigmentation on the gums, severe headache and abdominal cramps, delirium, convulsions and coma.

Appendix 2

2.1 Preparation of lead solution (PbCl₂)

$$\text{Formula weight of PbCl}_2 = 278.106$$

$$\text{Atomic weight of Pb} = 207.2$$

$$\text{PbCl}_2/\text{Pb} = 278.106/207.2$$

$$= 1.34221 \text{ g/mol}$$

For 100 ppm:

$$= 0.134221 \text{ g/L}$$

For 20 liter of 100 ppm:

$$= 2.68442 \text{ g/L of PbCl}_2$$

2.2 Preparation of cadmium solution (CdCl₂)

$$\text{Formula weight of CdCl}_2 = 183.317$$

$$\text{Atomic weight of Cd} = 112.411$$

$$\text{CdCl}_2/\text{Cd} = 183.317/112.411$$

$$= 1.63077 \text{ g/mol}$$

For 100 ppm:

$$= 0.163077 \text{ g/L}$$

For 20 liter of 100 ppm:

$$= 3.26155 \text{ g/L of CdCl}_2$$

Appendix 3

EXPERIMENTAL DATA FOR BATCH STUDIES

1. Test for optimum pH

1a. 100 ml of 114.67 mg/L Pb (II); 200 mg; 1 h agitation time

pH _i	C _i (mg/L)	C _f (mg/L)	pH _f	% Pb (II) removal
1	114.67	100.7611	1	12.1295
1.7	114.67	89.4224	2.76	22.01762
1.8	114.67	58.5899	4.02	48.90564
1.98	114.67	23.8361	4.66	79.21331
2	114.67	5.474	5.49	95.2263
3	114.67	0	7.35	-
4	114.67	0	7.67	-
5	114.67	0	8.21	-
6	114.67	0	8.53	-

1b. 100 ml of 9.94 mg/L Cd (II); 200 mg; 1 h agitation time

pH _i	C _i (mg/L)	C _f (mg/L)	pH _f	% Pb (II) removal
1	9.94	6.8362	1.314	31.22535
2	9.94	5.4378	5.326	45.29376
3	9.94	2.1175	7.16	78.69718
4	9.94	0.9244	7.53	90.7002
5	9.94	0	8.562	-
6	9.94	0	8.908	-
7	9.94	0	9.491	-
8	9.94	0	9.521	-

2. Test for effect of initial concentration & contact time and pseudo first order and second order kinetics.

2a. 100 ml of 9.89 mg/L Pb (II); 200 mg GWS.

contact time,t (min)	Co(mg/L)	Ce(mg/L)	q	qe	t/q	qe-q	log (qe-q)
0	9.89	9.89	0	4.945			
10	9.89	2.46	3.715	4.945	2.69179	1.23	0.08990511
30	9.89	1.01	4.44	4.945	6.756757	0.505	0.29670862
60	9.89	0	4.945	4.945	12.13347	0	
90	9.89	0	4.945	4.945	18.2002	0	
120	9.89	0	4.945	4.945	24.26694	0	
150	9.89	0	4.945	4.945	30.33367	0	
180	9.89	0	4.945	4.945	36.4004	0	
360	9.89	0	4.945	4.945	72.80081	0	
1440	9.89	0	4.945	4.945	291.2032	0	

2b. 100 ml of 24.76 mg/L Pb (II); 200 mg GWS.

contact time,t (min)	Co(mg/L)	Ce(mg/L)	q	qe	t/q	qe-q	log (qe-q)
0	24.76	24.76	0	12.38	0	12.38	1.09272064
10	24.76	7.64	8.56	12.38	1.168224	3.82	0.58206336
30	24.76	3.88	10.44	12.38	2.873563	1.94	0.28780173
60	24.76	0	12.38	12.38	4.846527	0	
90	24.76	0	12.38	12.38	7.26979	0	
120	24.76	0	12.38	12.38	9.693053	0	
150	24.76	0	12.38	12.38	12.11632	0	
180	24.76	0	12.38	12.38	14.53958	0	
360	24.76	0	12.38	12.38	29.07916	0	
1440	24.76	0	12.38	12.38	116.3166	0	

2c. 100 ml of 48.35 mg/L Pb (II); 200 mg GWS.

contact time,t (min)	Co(mg/L)	Ce(mg/L)	q	qe	t/q	qe-q	log (qe-q)
0	48.35	48.35	0	24.175	0	24.175	1.38336648
10	48.35	27.12	10.615	24.175	0.942063	13.56	1.13225969
30	48.35	11.57	18.39	24.175	1.631321	5.785	0.76230336
60	48.35	0	24.175	24.175	2.481903	0	
90	48.35	0	24.175	24.175	3.722854	0	
120	48.35	0	24.175	24.175	4.963806	0	
150	48.35	0	24.175	24.175	6.204757	0	
180	48.35	0	24.175	24.175	7.445708	0	
360	48.35	0	24.175	24.175	14.89142	0	
1440	48.35	0	24.175	24.175	59.56567	0	

2d. 100 ml of 114.67 mg/L Pb (II); 200 mg GWS.

contact time,t (min)	Co(mg/L)	Ce(mg/L)	q	qe	t/q	qe-q	log (qe-q)
0	114.67	114.67	0	57.335	0	57.335	1.75841982
10	114.67	80.132	17.269	57.335	0.579072	40.066	1.60277599
30	114.67	50.876	31.897	57.335	0.940527	25.438	1.40548296
60	114.67	3.87	55.4	57.335	1.083032	1.935	0.28668097
90	114.67	0	57.335	57.335	1.569722	0	
120	114.67	0	57.335	57.335	2.092962	0	
150	114.67	0	57.335	57.335	2.616203	0	
180	114.67	0	57.335	57.335	3.139444	0	
360	114.67	0	57.335	57.335	6.278887	0	
1440	114.67	0	57.335	57.335	25.11555	0	

2e. 100 ml of 197.12 mg/l Pb (II); 200 mg GWS.

contact time,t (min)	Co(mg/L)	Ce(mg/L)	q	qe	t/q	qe-q	log (qe-q)
0	197.12	197.12	0	98.56	0	98.56	1.99370069
10	197.12	163.28	16.92	98.56	0.591017	81.64	1.911903
30	197.12	128.56	34.28	98.56	0.875146	64.28	1.80807587
60	197.12	65.32	65.9	98.56	0.91047	32.66	1.51401618
90	197.12	43.1	77.01	98.56	1.168679	21.55	1.33344727
120	197.12	13.56	91.78	98.56	1.307474	6.78	0.83122969
150	197.12	0	98.56	98.56	1.521916	0	
180	197.12	0	98.56	98.56	1.826299	0	
360	197.12	0	98.56	98.56	3.652597	0	
1440	197.12	0	98.56	98.56	14.61039	0	

2f. 100 ml of 4.97 mg/L Cd (II); 200 mg GWS

contact time,t (min)	Co(mg/L)	Ce(mg/L)	q	qe	t/q	qe-q	log (qe-q)
10	4.97	0.51329166	2.22835417	2.485	4.48761698	0.2566458	-0.59066579
30	4.97	0.35419699	2.307901505	2.485	12.9988216	0.1770985	-0.75178513
60	4.97	0.20236846	2.38381577	2.485	25.1697303	0.1011842	-0.99488717
90	4.97	0.1165465	2.42672675	2.485	37.0869938	0.0582733	-1.23453076
120	4.97	0.04743368	2.46128316	2.485	48.7550567	0.0237168	-1.62494318
150	4.97	0	2.485	2.485	60.362173	0	
180	4.97	0	2.485	2.485	72.4346076	0	
360	4.97	0	2.485	2.485	144.869215	0	
1440	4.97	0	2.485	2.485	579.476861	0	

2g. 100 ml of 9.94 mg/L Cd (II); 200 mg GWS

contact time, t (min)	Co(mg/L)	Ce(mg/L)	q	qe	t/q	qe-q	log (qe-q)
10	9.94	1.7241924	4.1079038	4.97	2.43433159	0.8620962	-0.06444427
30	9.94	1.2273912	4.3563044	4.97	6.8865711	0.6136956	-0.21204699
60	9.94	0.9188536	4.5105732	4.97	13.3020788	0.4594268	-0.33778367
90	9.94	0.6635944	4.6382028	4.97	19.4040675	0.3317972	-0.47912728
120	9.94	0.317086	4.811457	4.97	24.9404702	0.158543	-0.79985293
150	9.94	0.2601298	4.8399351	4.97	30.9921511	0.1300649	-0.88583989
180	9.94	0.127729	4.9061355	4.97	36.6887543	0.0638645	-1.19474048
360	9.94	0	4.97	4.97	72.4346076	0	
1440	9.94	0	4.97	4.97	289.738431	0	

2h. 100 ml of 19.78 mg/L Cd (II); 200 mg GWS

contact time, t (min)	Co(mg/L)	Ce(mg/L)	q	qe	t/q	qe-q	log (qe-q)
10	19.78	6.6392559	6.57037205	9.6283895	1.52198383	3.0580175	0.485439955
30	19.78	5.8545833	6.96270835	9.6283895	4.30866819	2.6656812	0.425808201
60	19.78	4.01597296	7.88201352	9.6283895	7.61226809	1.746376	0.242137745
90	19.78	3.71324006	8.03337997	9.6283895	11.2032545	1.5950095	0.202763282
120	19.78	2.9893514	8.3953243	9.6283895	14.2936706	1.2330652	0.090986041
150	19.78	2.3876438	8.6961781	9.6283895	17.2489568	0.9322114	-0.03048559
180	19.78	2.0498014	8.8650993	9.6283895	20.3043411	0.7632902	-0.11731031
360	19.78	0.71905245	9.530473775	9.6283895	37.7735681	0.0979157	-1.00914756
1440	19.78	0.523221	9.6283895	9.6283895	149.557722	0	

2i. 100 ml of 48.69 mg/L Cd (II); 200 mg GWS

contact time,t (min)	Co(mg/L)	Ce(mg/L)	q	qe	t/q	qe-q	log (qe-q)
10	48.69	41.8868	3.4016	17.87481	2.939793	14.47321	1.1605649
30	48.69	32.8761	7.90695	17.87481	3.7941305	9.96786	0.9986019
60	48.69	28.975	9.8575	17.87481	6.086736	8.01731	0.9040287
90	48.69	25.6553	11.51735	17.87481	7.8142976	6.35746	0.8032836
120	48.69	23.47724682	12.60637659	17.87481	9.5189922	5.26843341	0.7216815
150	48.69	20.33606016	14.17696992	17.87481	10.58054	3.69784008	0.5679481
180	48.69	18.66127023	15.01436489	17.87481	11.988519	2.860445115	0.4564336
360	48.69	16.58907252	16.05046374	17.87481	22.429258	1.82434626	0.2611073
1440	48.69	12.94038999	17.87480501	17.87481	80.560319	0	

2j. 100 ml of 98.54 mg/L Cd (II); 200 mg GWS

contact time,t (min)	Co(mg/L)	Ce(mg/L)	q	qe	t/q	qe-q	log (qe-q)
10	98.54	88.1381176	5.201	31.375	1.9227072	26.174	1.4178701
30	98.54	74.230182	12.15491	31.375	2.4681384	19.22009	1.2837554
60	98.54	65.376363	16.58	31.375	3.6188179	14.795	1.170115
90	98.54	60.449363	19.045	31.375	4.7256498	12.33	1.0909631
120	98.54	56.621084	21.27	31.375	5.6417489	10.105	1.0045363
150	98.54	52.39450632	23.075	31.375	6.5005417	8.3	0.9190781
180	98.54	46.47412458	26.035	31.375	6.9137699	5.34	0.7275413
360	98.54	40.56970632	28.985	31.375	12.420217	2.39	0.3783979
1440	98.54	38.65911426	31.375	31.375	45.896414	0	

3. Test for effect of adsorbent dosage and adsorption isotherms.

3a. 100 ml of 114.67 mg/L Pb (II), 1 hour agitation time

m (g)	Co (mg/L)	Ce (mg/L)	Removal (%)	x (mg)	qe @ x/m (mg/g)	ln Ce	ln qe	Ce/qe (g/L)
0.025	114.67	93.22	18.70585	2.145	85.8	4.534962	4.452019	1.08648
0.05	114.67	78.45	31.58629	3.622	72.44	4.362461	4.282759	1.082965
0.1	114.67	57.64	49.73402	5.703	57.03	4.054217	4.043577	1.010696
0.2	114.67	5.29	95.38676	10.938	54.69	1.665818	4.001681	0.096727
0.3	114.67	0						
0.4	114.67	0						

3b. 100 ml of 9.89 mg/L Cd (II), 2.5 hour agitation time

m (g)	Co (mg/L)	Ce (mg/L)	Removal (%)	x (mg)	qe @ x/m (mg/g)	ln Ce	ln qe	Ce/qe (g/L)
0.025	9.89	5.24815	46.9348	0.4642	18.5674	1.6579	2.9214	0.282654
0.05	9.89	4.38255	55.6871	0.5507	11.0149	1.4776	2.3992	0.3978747
0.1	9.89	1.0568	89.3145	0.8833	8.8332	0.0552	2.1785	0.1196395
0.2	9.89	0.6843	93.0809	0.9206	4.60285	-0.3794	1.5267	0.1486688
0.3	9.89	0.4071	95.8837	0.9483	3.160967	-0.8987	1.1509	0.1287897
0.4	9.89	0						