

**Adsorption of Lead and Cadmium in Aqueous Solution onto Oil-Palm Solid
Wastes, Bentonite and Amberlite Polymeric Adsorbents**

by

Suhairi Bin Amaludin

Dissertation submitted in partial fulfilment of
the requirements for the
Bachelor of Engineering (Hons)
(Chemical Engineering)

JULY 2009

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CERTIFICATION OF APPROVAL

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Approved by,

(AP. Dr. M. Azmuddin Bin Abdullah)

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

July 2009

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.

Suhairi Bin Amaludin

ABSTRACT

The adsorption of heavy metals ion (Pb^{2+} and Cd^{2+}) onto three types of adsorbents; bentonite, oil-palm solid waste and Amberlite XAD polymeric adsorbents is described in this report. The studies were done in batch, as the samples were mixed with a dosage of 2.5g/l of each adsorbent and shake at 150rpm until it reaches equilibrium. Kinetics studies show that bentonite is the best adsorbent, while oil-palm solid waste and Amberlite XAD polymeric adsorbents are comparable. The adsorption isotherm parameters were calculated and fitted into Langmuir isotherm and Freundlich isotherm. All adsorption can be described by Freundlich isotherm with the highest degree of fit of lead on OPEFB (0.954) and cadmium on XAD16 (0.99). The effect of pH is examined over the range of 1-5.5. The adsorption of Pb^{2+} and Cd^{2+} increase with increasing pH and bentonite was highly affected by the increment. Finally, the adsorbents were analyzed by using FTIR to get the infrared spectra, and the functional groups were determined while, the infrared spectra for Amberlite XAD polymeric adsorbents were acquired from product data sheets.

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CHAPTER 1

INTRODUCTION

Nowadays, we were facing a huge environmental impact on our planet. As the manufacturing industries keep rising, so is the increment of toxic waste generation. Industries such as metals and electroplating, release a huge amount of toxic compound especially heavy metals. Even in small doses, these trace materials can give huge impact on the health of human and the environment.

However, major industrial companies have taken corrective measure in order to make sure that their discharge would be at the acceptable level stated in a countries law. Some technique can be applied to remove metals and one of it is adsorption. Studies have been done in identifying a lot of adsorbents that can be used for this purpose, either from nature or commercially synthesis.

1.1 Problem Statement

A lot of studies have been done in order to find alternative and the best adsorbent for the purpose of removing heavy metals from waste stream. Company such as Rohm and Haas has produced synthetic and commercially-available adsorbent such as Amberlite XAD™ that they believe can do the job effectively, but we still need to determine its suitability in adsorbing heavy metal. However, researches were still being pursued in order to find an alternative adsorbent from the nature.

Waste such as oil-palm empty fruit bunch (EFB) and kernel are one of those alternatives. They are abundant and cheap as it is considered as non-valuable by-product from palm-oil producer (especially Malaysia). Bentonite, a type of clay was also another natural, mined adsorbent. Therefore, a research has to be layout to identify the adsorption capability of these adsorbents (both natural and commercial adsorbents) and do the comparison between natural and synthetic adsorbents.

2.1 Objective

The objectives of this project are to study the Lead (II) and Cadmium (II) sorption into three types of adsorbents, bentonite, oil-palm solid waste and the commercial adsorbents and to compare between them. The sorption would be in batch experiment, with initial metal concentration and pH as the function. To study the sorption behavior, both, kinetic and equilibrium models would be tested.

2.2 Scope of Work

The project works are comprised of:

- Adsorbent preparation and pre-treatment.
- Characterization of adsorbent.
- Kinetic studies to identify the adsorbent metal uptake capacity.
- Adsorption isotherm test by varying the initial metal concentration.
- Study the effect of pH on adsorption.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

After the Industrial Revolution Era occurs in Europe, human have been erecting manufacturing facilities and factories in order to mass produce goods and products. As time goes on, small-scale factory have become larger and more advance and sophisticated equipment have been used.

Nowadays, factories have shroomed rapidly in most modern and developing countries, and Malaysia was not excluded. Each factory, besides producing beneficial and high quality products, also produces bad by-products. The effluents that contains a lot of toxic material, has nowhere to go as to be discharge into the main water stream, which will finally reach us as tap water. Realizing this, governments and factories management involves has taken best endeavor to reduce the impact of the effluent to a safer level, through enforcements (law and act) and remediation (waste treatment).

Different industries discharge different effluent. But major industries would discharge effluents that contain heavy metal. These constituents are so toxic even at trace level. Such metals are lead (Pb), copper (Cu), Iron (Fe), Mangan (Mn), Cobalt (Co), Nickel (Ni), Zinc (Zn), Cadmium (Cd), Mercury (Hg), Aluminium (Al) and Chromium (Cr).

Beside from being discharge into the water stream, these metals may exist in the air and soil. All the metals will end up to us, human. The heavy metals in soil will be absorbed by plants. Herbivores (cattle, cow, goat etc) will eat the plant and now receiving the metals. Lastly, human eats these animals.

In order to control and stop these metals from reaching us, it is important to come up with effective remediation techniques and also alternatives to the current practices.

2.2 Impact of Lead and Cadmium on Health and Environment

2.2.1 Lead



Figure 2.1 - Lead metals

Atomic Number	82
Atomic Mass	207.2 g/mol
Electronegativity according to Pauling	1.8
Density	11.34 g/cm ³ at 20 °C
Melting Point	327 °C
Boiling Point	1755 °C
Vanderwaals radius	1.54 Å
Ionic radius	1.32 Å (+2); 0.84 Å (+4)
Isotopes	13

Table 2.1 - Lead Characteristics

Lead is a bluish-white lustrous metal. It is very soft, highly malleable, ductile, and a relatively poor conductor of electricity. It is very resistant to corrosion but tarnishes upon exposure to air. Lead isotopes are the end products of each of the three series of naturally occurring radioactive elements.

2.2.1.1 Production and Application

Lead from mining usually exists as a by-product when ore of zinc, silver and copper are processed. The main lead mineral is in Galena (PbS) and there are also deposits in Cerrussite and Anglessite which are mined.

In 1989, 155 mines in 35 countries produce 2.21 million tons of lead in concentrate. It is mined in Australia, which produces 19 % of the world's new lead, follows by the USA, China, Peru and Canada. Some are also mined in West Germany. World production of

new lead is 6 million tons per year and workable reserves total are estimated 85 million tones, which is less than 15 years supply (*Lead Properties, lenntech.com*).

Since 1970, the world demand for lead's unique chemical, physical and electrical properties has increased by 25 % to a record level of 5627 millions tones in 1990.

Lead is a major constituent of the lead acid battery used extensively in car batteries. It is used as a coloring element in ceramic glazes, as projectiles, in some candles to threat the wick. It is the traditional base metal for organ pipe and it is used as electrodes in the process of electrolysis. One of its major uses is in the glass of computer and television screens, where it shields the viewer from radiation. Other uses are in sheeting, cables, solders, lead crystals glassware, ammunitions, and bearings and as weight in sport equipment. Tetraethyl lead (PbEt₄) was once use in petrol, but later removed as to environmental concern.

2.2.1.2 Sources of Contamination.

For lead contamination, we may see it as nature release (through volcanic emission and geological weathering) but the majorities are caused by human activity. Soil and water contamination was due to effluent discharge by industries (refining, manufacturing etc) that uses lead such as car batteries and electroplating. Lead contamination in water may also being by corrosion of leaded pipeline in water transporting system and through corrosion of leaded paints.

Leaded fuel burning also contributes to lead particulates in air. Other human activities such as industrial processes and solid waste combustion also contribute.

2.2.1.3 Health and Environmental Impact of Lead

Lead is one out of four metals that have the most damaging effects on human health. It can enter human body as food (65%), water (20%) and air (15%). It will be absorbed through lung and gastrointestinal tract and deposited in cell and bones. Unabsorbed lead will excrete through urine and faeces.

Lead can cause several unwanted effects such as:

- Disruption of the biosynthesis of hemoglobin and anemia.
- A rise in blood pressure.
- Kidney damage
- Miscarriage and subtle abortion
- Disruption of nervous systems.
- Brain damages.
- Declined in fertility of men through sperm damage
- Diminishing learning abilities of children
- Behavioral disruptions of children, such as regression, impulsive behavior and hyperactivity.

Lead in the water can affect sea life-cycle. Phytoplankton's body function can be disturbed when lead intervene and phytoplankton is an important sources of oxygen production in seas and many larger sea animals eat it. Therefore lead can disrupt marine ecology. Lead in soils can affect soil organism and adsorbing plant.

2.2.2 Cadmium



Figure 2.2 - Cadmium metals

Atomic Number	48
Atomic Mass	112.4 g/mol
Electronegativity according to Pauling	1.7
Density	8.7 g/cm ³ at 20 °C
Melting Point	321 °C
Boiling Point	767 °C
Vanderwaals radius	1.54 Å

Ionic radius	0.97 Å (+2)
Isotopes	15

Table 2.2 - Cadmium Characteristics

Cadmium is a lustrous, silver-white, ductile, very malleable metal. Its surface has a bluish tinge and the metal is soft enough to be cut with a knife, but tarnishes in air. It is soluble in acids but not in alkalis. It is similar in many respects to zinc but it forms more complex compounds.

2.2.2.1 Production and Application

Cadmium can exist as by-product when ore of zinc, lead and copper were extracted. From smelting the ore, Sphalerite (ZnS), in which CdS is its impurities, the cadmium content varies from mine to mine ranging from 0.07% to 0.83% with average of 0.23%. Approximately 3 kg of cadmium will be produced for every ton of refined zinc. (*M. Ursinyova et. al., 2000*). The main mining countries are Canada, USA, Australia, Mexico, Japan and Peru.

The principal applications of cadmium fall into five categories:

- Protective plating on steel (only 0.05mm thick will provide complete protection against the sea)
- Stabilizer for polyvinyl chloride.
- Pigments in plastics and glasses.
- Electrode material in Nickel-Cadmium batteries.
- Component of various alloys.

(*M. Ursinyova et. al. 2000*)

2.2.2.2 Source of Contamination

About 10-15% of natural cadmium emissions arise from volcanic activity. The rest are mainly from human activity. Waste effluent from metal and steel industries is the major contributor for water and soil contamination, while for air contamination, smoking release 2 – 4 µg of cadmium.

2.2.2.3 Health and Environmental Impact of Cadmium

Human uptakes of cadmium are mainly from food and inhalation (factory emission and smoking). Examples of rich-cadmium foodstuff are liver, mushrooms, shellfish, mussels, cocoa powder and dried seaweed.

Tobacco smoker, when inhaling the smoke, absorbed about 25-30% of cadmium release which is 1 – 2 µg.

Cadmium absorbed will be stored in liver and kidney where more than half of the cadmium body burden is deposited. This will then be excreted from the body via urine and faeces but very slow, comprise only about 0.01 – 0.02% of total body burden of cadmium in human beings.

In clinical evaluation, adverse effects of excessive cadmium exposure may include the following:

- Acute exposure: gastroenteritis (ingestion only), bronchitis (inhalation only), interstitial pneumonitis (inhalation only), pulmonary edema (inhalation only).
- Chronic exposure: proteinuria, osteomalacia (itai-itai disease), pulmonary fibrosis (inhalation only), liver damage, hypertension, lung cancer, prostatic cancer, wild anemia, yellow discoloration of front teeth, anosmia.

(Agency for Toxic Substances and Disease Registry, 1990)

2.3 Effluents Limits

DOE (Department of Environment) is a regulatory body established in Malaysia in concern of environmental issues. Their main role is to enforce and make sure that all of the effluent discharge of every industry shall not exceed the limits stated in the Act.

There are a few regulations in Environmental Quality Act (EQA) 1974, which have relation with lead and cadmium release into air, water and soils. The regulations are:

- Environmental Quality (Sewage And Industrial Effluents) Regulations 1979 - P.U. (A) 12/79, (Third Schedule)

Parameter	Unit	Standards	
		A	B
Cadmium	mg/l	0.01	0.02
Lead	mg/l	0.10	0.50

Table 2.3 - Parameter Limits of Effluents of Standards A and B

(Standards A consist of areas upstream of surface or above subsurface water supply intakes, for the purpose of human consumption including drinking. Such area is stated in Fourth Schedule in the regulation. Other area is considered Standard B).

- Environmental Quality (Clean Air) Regulations 1978 - P.U.(A) 280/78, (Regulations 26)

Substance	Cadmium	Lead
Standard A	0.025	0.04
Standard B	0.015	0.025
Standard C	0.015	0.025

Table 2.4 - Air Impurities Emission Limit

2.4 Heavy Metal Treatment Techniques

Different treatments for wastewater laden with heavy metals have been produced in recent years to decrease the amount of wastewater produced and to improve the quality of the treated effluent. Some physico-chemical treatment techniques are chemical precipitation, coagulation-flocculation, flotation, ion-exchange and membrane filtration. (T.A. Kurniawan *et. al.*, 2006). These techniques have their advantages and limitations in its applications, therefore it is advisable to choose the best techniques upon treatment requirement and strict effluent discharge limits.

Table 2.5 show the summary of all techniques in practice. The techniques which been used in this project works (ion-exchange) are chosen because of capability of removal 100% of heavy metals in waste stream, and ensure that the strict regulatory limits are abide. High operational cost are due to cost to built column (usually ion-exchange resin would be packed inside a column) and the cost of commercial adsorbent. However, if natural adsorbent can be proved to be comparable to the commercial adsorbent, the cost can be reduced.

Type of treatment	Target of removal	Advantages	Disadvantages
Chemical precipitation	Heavy metals, divalent metals	Low capital cost, simple operation	Sludge generation, extra operational cost for sludge disposal
Coagulation–flocculation	Heavy metals and suspended solids	Shorter time to settle out suspended solids, improved sludge settling	Sludge production, extra operational cost for sludge disposal
Dissolved air flotation	Heavy metals and suspended solids	Low cost, shorter hydraulic retention time	Subsequent treatments are required to improve the removal efficiency of heavy metal
Ion exchange	Dissolved compounds, cations/anions	No sludge generation, less time consuming	Not all ion exchange resin is suitable for metal removal, high capital cost
Ultrafiltration	High molecular weight compounds (1000–10000 Da)	Smaller space requirement	High operational cost, prone to membrane fouling
Nanofiltration	Sulphate salts and hardness ions such as Ca(II) and Mg(II)	Lower pressure than RO (7–30 bar)	Costly, prone to membrane fouling
Reverse osmosis	Organic and inorganic compounds	High rejection rate, able to withstand high temperature	High energy consumption due to high pressure required (20–100 bar), susceptible to membrane fouling

Table 2.5 - Summary of the treatability of physico-chemical treatments for inorganic effluents

2.5 Adsorption, Ion Exchange and Isotherm

2.5.1 Adsorption

Adsorption is the accumulation of atoms or molecules on the surface of a material. This process creates a film of the adsorbate on the adsorbent's surface. It is different from absorption, in which a substance diffuses into a liquid or solid to form a solution. The

term desorption is the reverse process while sorption encompasses both processes. (*Adsorption, Wikipedia*)

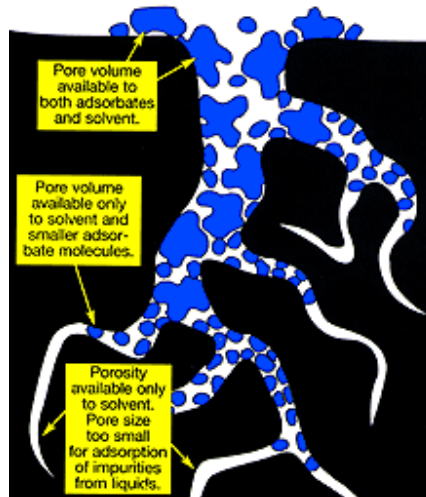


Figure 2.3 - Adsorption inside adsorbent pores. (www.norit-americas.com)

Figure 2.3 shows how adsorption happens on the surface of adsorbent. First, the particle will travel inside the pores until it reach to the point where it cannot go further, when the pore is smaller than the particle. From this point, the particle will accumulate until it fills up the whole pore volume. As adsorption happens, the adsorbate may tend to free itself from the adsorbent by desorption.

The sorption ability of different sorbents is strongly dependent on the available surface area, polarity, contact time, pH, pore size and the degree of hydrophobic nature of the adsorbent and adsorbate. Equilibrium condition is attained when the concentration of solute remains constant, as a result of zero net transfer of solute adsorbed from adsorbent surface. (*M.A. Abdullah et. al, 2008*)

2.5.2 Ion Exchange

Ion exchange is an exchange of ions between two electrolytes or between an electrolyte solution and a complex. In most cases the term is used to denote the processes of

purification, separation, and decontamination of aqueous and other ion-containing solutions with solid polymeric or mineralic 'ion exchangers'.

Typical ion exchangers are ion exchange resins (functionalized porous or gel polymer), zeolites, montmorillonite, clay, and soil humus. Ion exchangers are either cation exchangers that exchange positively charged ions (cations) or anion exchangers that exchange negatively charged ions (anions). There are also amphoteric exchangers that are able to exchange both cations and anions simultaneously. However, the simultaneous exchange of cations and anions can be more efficiently performed in *mixed beds* that contain a mixture of anion and cation exchange resins, or passing the treated solution through several different ion exchange materials.

Ion exchangers can be unselective or have binding preferences for certain ions or classes of ions, depending on their chemical structure. This can be dependent on the size of the ions, their charge, or their structure. Typical examples of ions that can bind to ion exchangers are:

- H^+ (proton) and OH^- (hydroxide)
- Single charged monoatomic ions like Na^+ , K^+ , or Cl^-
- Double charged monoatomic ions like Ca^{2+} or Mg^{2+}
- Polyatomic inorganic ions like SO_4^{2-} or PO_4^{3-}
- Organic bases, usually molecules containing the amino functional group $-\text{NR}_2\text{H}^+$
- Organic acids, often molecules containing $-\text{COO}^-$ (carboxylic acid) functional groups
- Biomolecules which can be ionized: amino acids, peptides, proteins, etc.

Ion exchange is a reversible process and the ion exchanger can be regenerated or loaded with desirable ions by washing with an excess of these ions. (*F. Helfferich, 1962*).

2.5.3 Langmuir Isotherm



In 1916, Irving Langmuir published a new model isotherm for gases adsorbed on solids, which retained his name. It is a semi-empirical isotherm derived from a proposed kinetic mechanism. It is based on four assumptions:

- The surface of the adsorbent is uniform, that is, all the adsorption sites are equivalent.
- Adsorbed molecules do not interact
- All adsorption occurs through the same mechanism.
- At the maximum adsorption, only a monolayer is formed; molecules of adsorbate do not deposit on other, already adsorbed, molecules of adsorbate, only on the free surface of the adsorbent. (*Adsorption, Wikipedia*)

Langmuir model is the simplest theoretical model for monolayer adsorption onto a surface with finite number of identical sites. It is originally developed to represent chemisorptions on a set of distinct, localized adsorption sites. Langmuir has developed a theoretical equilibrium isotherm relating the amount of gas adsorbed on a surface due to the pressure of gas.

The general Langmuir equation is as follows (*M.A. Abdullah et. al, 2008*):

$$Q_e = \frac{K_L C_e}{1 + \alpha_L C_e} \quad (1)$$

When, the equation was linearized it becomes:

$$\frac{C_e}{Q_e} = \frac{\alpha_L C_e}{K_L} + \frac{1}{K_L} \quad (2)$$

In linear form, we can determine the isotherm parameters; α_L , K_L , and also R^2 that describe the degree of fit of the isotherm, by plotting C_e against C_e/Q_e . The isotherm parameters are used in equation 1 and thus obtained the Langmuir isotherm model. The higher the degree of fit, R^2 , the better the model would be.

2.5.4 Freundlich Isotherm

Freundlich expression is an empirical equation applicable to non-ideal sorption on heterogeneous surface as well as multilayer sorption. The model is given as

$$Q_e = K_F C_e^{1/n} \quad (3)$$

If the concentration of solute in the solution at equilibrium, C_e , is raised to the power of $1/n$, with the amount of solute adsorbed being Q_e , then $C_e^{1/n}/Q_e$ is constant at a given temperature. K_F indicates relative indicator of adsorption capacity, while the dimensionless, $1/n$, is indicative of the energy or intensity of the reaction and suggests the favorability and capacity of the adsorbent/adsorbate system. According to the theory, $n > 1$ represents favorable adsorption conditions. Eq. (3) is linearized into logarithmic form for data fitting and parameter evaluation as follows:

$$\log Q_e = \log K_F + (1/n)\log C_e \quad (4)$$

By plotting $\log Q_e$ versus $\log C_e$, constant K_F and exponent $1/n$ can be calculated. (*M.A. Abdullah et. al. 2008*)

2.6 Adsorbents

In order to remove metal from waste stream through adsorption / ion-exchange, scientists and researchers are continually finding more and more adsorbent, derived from natural sources. *S.K.R Yandanaparthi et. al.* has listed a wide range of adsorbent that can remove lead and cadmium, which is in interest with this project. Following are some of the adsorbent in interest (natural and commercial).

2.6.1 Bentonite (Sodium Bentonite)



Figure 2.4 - Bentonite Clay

Sodium bentonite is a natural soft clay substance that belongs to the mineral group composed of essentially of the montmorillonite and is formed from the weathering and aging of volcanic materials (ashes), most often in the present of water. It is a free-flowing powder containing sodium and has strong swelling properties, high thermo stability, high plasticity and tensile strength. A good quality bentonite should be grey/cream in color. It has a very fine velveteen feel and is odorless and non-staining.

Bentonite is quite cheap as it is price at USD7.50 per 100 pound (USD0.17/kg). (malibuwater.com)

Table 2.6 shows the technical data for bentonite (Bentonite PDS, bentonite.co.uk)

Properties	Value
Moisture content	6 – 10 %
Montmorillonite content	75 - 85 %
Consumption	72 – 96 mg/l
Alkalinity	pH 9.2 – 10.2
Compression	0.7 – 0.9 kg/cm ²
Wet tensile	0.24 – 0.35 N/cm ²
Mineral Content	
Silica	61.4 %
Aluminium	18.1 %
Iron	3.5 %
Sodium	2.3 %
Magnesium	1.7 %

Calcium	0.04 %
Titanium	0.02 %
Potassium	0.01 %

Table 2.6 - Technical Data for Bentonite

2.6.1.1 Source of Bentonite

In 2005, U.S. was the top producer of bentonite with almost one-third world share followed by China and Greece, reports the British Geological Survey.

The absorbent clay was given the name bentonite by Wilbur C. Knight in 1898 - after the Cretaceous Benton Shale near Rock River, Wyoming. Other modern discoveries include montmorillonite discovered in 1847 in Montmorillon in the Vienne prefecture of France, in Poitou-Charentes, South of the Loire Valley.

Most high-grade natural sodium bentonite is produced from the western United States in an area between the Black Hills of South Dakota and the Big Horn Basin of Wyoming. Mixed sodium/calcium bentonite is mined in Greece, Australia, India, Russia and the Ukraine. In the United States, calcium bentonite is primarily mined in Mississippi and Alabama. Other major locations producing calcium bentonite include Germany, Greece, Turkey, and China. (*Bentonite, Wyoming Geological Survey*)

2.6.1.2 How bentonite works as adsorbent?

Bentonite is very unusual in the fact that once it becomes hydrated, the electrical and molecular components of the clay are rapidly changed and produce an “electrical charge”. Its highest power lies in the ability to adsorb toxins, impurities, heavy metals and other contaminants. Bentonite clay’s structure assists it in attracting and soaking up poisons on its exterior wall and then slowly draw them into the interior center of the clay where it held in a sort of repository.

To state it in other way, “Bentonite is swelling clay. When it becomes mixed with water it rapidly swells open like a highly porous sponge. From here, toxins are drawn into the

sponge through electrical attraction and once there, they are bound. (*Bentonite, botanical.com*)

2.6.1.3 Application of bentonite

Much of bentonite's usefulness in the drilling and geotechnical engineering industry comes from its unique rheological properties. Relatively small quantities of bentonite suspended in water form a viscous, shear thinning material. Most often, bentonite suspensions are also thixotropic, although rare cases of rheopectic behavior have also been reported. At high enough concentrations (~60 grams of bentonite per liter of suspension), bentonite suspensions begin to take on the characteristics of a gel (a fluid with a minimum yield strength required to make it move). For these reasons it is a common component of drilling mud used to curtail drilling fluid invasion by its propensity for aiding in the formation of mud cake.

Bentonite can be used in cement, adhesives, ceramic bodies, and cat litter. Bentonite is also used as a binding agent in the manufacture of taconite pellets as used in the steelmaking industry. Fuller's earth, an ancient dry cleaning substance, is finely ground bentonite, typically used for purifying transformer oil. Bentonite, in small percentages, is used as an ingredient in commercially designed clay bodies and ceramic glazes. Bentonite clay is also used in pyrotechnics to make end plugs and rocket nozzles.

The ionic surface of bentonite has a useful property in making a sticky coating on sand grains. When a small proportion of finely ground bentonite clay is added to hard sand and wetted, the clay binds the sand particles into a moldable aggregate known as green sand used for making molds in sand casting. Some river deltas naturally deposit just such a blend of such clay silt and sand, creating a natural source of excellent molding sand that was critical to ancient metalworking technology. Modern chemical processes to modify the ionic surface of bentonite greatly intensify this stickiness, resulting in remarkably dough-like yet strong casting sand mixes that stand up to molten metal temperatures.

Bentonite also has the interesting property of adsorbing relatively large amounts of protein molecules from aqueous solutions. It is therefore uniquely useful in the process of winemaking, where it is used to remove excessive amounts of protein from white wines. Were it not for this use of bentonite, many or most white wines would precipitate undesirable flocculent clouds or hazes upon exposure to warmer temperatures, as these proteins denature. It also has the incidental use of inducing more rapid clarification of both red and white wines.

Aside from industrial uses, bentonite is also used as one of the most effective and powerful healing clay used to treat both internal and external maladies. Bentonite can be used externally as a clay poultice, mud pack or in the bath and in skin care recipes. Internally, it can be added to water or glazed upon food to help those with sensitive palates. (*Bentonite, botanical.com*)

2.6.1 Palm-oil empty fruit bunch and kernel.

This adsorbent has been considered as waste after they have extracted the oil from it. However, a lot of researches have shown that agricultural waste can be used as adsorbent when in the form of activated carbon.



Figure 2.5 - Palm-oil Empty Fruit Bunch

Malaysia as one of the main producers of palm-oil, has an abundant supply of this waste. Therefore, it is low cost (or more likely 'no cost'), as compared to commercial adsorbent. Its usage as adsorbent can become an alternative choice for today's toxin removal. Instead of dumping it to the landfills straight away, why don't we use it to the

fullest extend? Although its absorbency and capacity are being believed as to not rival the commercial adsorbent, it can be considered a wise choice due to its benefits.

2.6.2 Amberlite XAD4, XAD7 and XAD16™.

Amberlite XADs are the registered trademark of Rohm and Haas Co. It is a polymeric adsorbent supplied as insoluble white beads. It is nonionic, hydrophobic, cross-linked polymer which derives its adsorptive properties from its



patented macroreticular structure (containing both a continuous polymer phase and a continuous pore phase), is high surface area, and aromatic nature of its surface. Its characteristic pore size distribution makes them an excellent choice for the adsorption of organic substances of relatively low to medium molecular weight. It can be used in column or batch operation.

Table 2.7 shows the key properties of each Amberlite products and its price. (Rohm and Haas Co., sigmaaldrich.com)

Product	Amberlite XAD-4	Amberlite XAD-7	Amberlite XAD-16
Surface Area	725 m ² /g	450 m ² /g	800 m ² /g
Avg. pore diameter	40 Å	90 Å	100 Å
Wet Mesh Size	20 – 60	20 - 60	20 – 60
Price	USD160.50 / kg	USD148.00 / kg	USD212.50 / kg

Table 2.7 - Key properties of Amberlite

Based on the key properties shown above, Amberlite XAD-16 seems to be the best adsorbent due to its largest surface area and pore diameter. Even though they are claimed to be best in adsorbing contaminants, high price for this solvent will increase the operating cost in removing heavy metals and therefore, an alternative adsorbent that has comparable adsorption performance can be used and lower the cost.

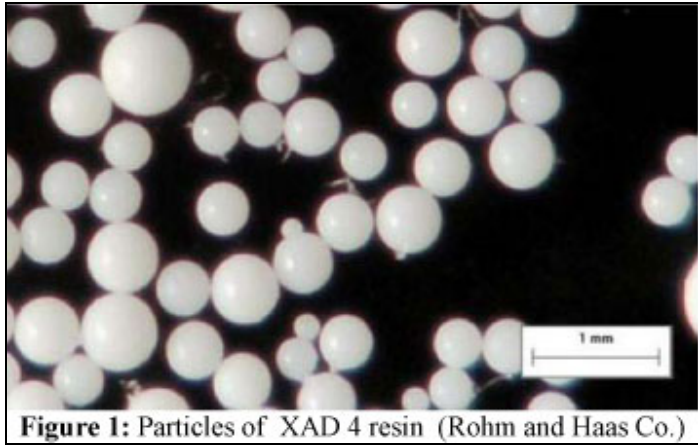


Figure 1: Particles of XAD 4 resin (Rohm and Haas Co.)

Figure 2.6 - Amberlite XAD 4 resin beads.

CHAPTER 3

METHODOLOGY

3.1 Resin and reagent

Three natural adsorbent and three synthetic adsorbent has been used in this work. Raw palm-oil empty fruit bunch and kernel were collected from the palm-oil mill in Tronoh (Perak, Malaysia) as waste in August 2009. Bentonite, a type of clay that consists of high montmorillonite content (75-85%) was also nature adsorbent used. Synthetic adsorbent, Amberlite XAD4, XAD7 and XAD16 were purchased from Sigma Aldrich Co.

Analytical reagent grade Cd^{2+} and Pb^{2+} as nitrates were purchase from Merck Co and System, respectively.

3.2 Adsorbent preparation and pre-treatment

Samples of palm-oil empty fruit bunch and kernel were washed with tap water for several times to remove impurities. Then, it was oven dried at 60°C for an overnight. The dried solids were then crushed and grinded with grinder, and sieved (size fraction of 0.5 – 1.0mm) and stored in polyethylene bottles until use.

To convert natural bentonite into sodium bentonite, 20g of bentonite was mixed with 750ml of 1M of NaCl solution, and continuously stirred for 12 hours. Then, the liquid was discarded and the solid was taken. Again, the solid sample was contacted with fresh 750ml of 1M NaCl solution and stirred for another 12 hour. This was performed to ensure complete conversion of the clay into its homoionic form.

To remove the excess NaCl and Cl^{-} ion (that could impregnated in the solid phase), the solid was filtered and wash several times with distilled water until a negative test for Cl^{-} was achieved (absence of Cl^{-} as detected by titrating the filtrate with AgNO_3). Finally, the pH of the dispersion was around 8 and Na^{+} -exchanged bentonite particles were

obtained. The material was then dried at room temperature for 24 hour or oven dried at 60°C.

3.3 Characterization of palm-oil waste biomass

FTIR (Fourier Transform Infrared) was used to identify the chemical groups present in the adsorbents (except for Amberlite XAD's). The samples were examined using a Shimadzu spectrophotometer within range of 400 - 4000cm⁻¹.



Figure 3.1 – FTIR (Shimadzu)

3.4 Kinetic studies

The experiments were carried out at natural pH (between 4 – 4.3 for lead and 4.6 – 5.3 for cadmium). 0.25g of adsorbent were mixed into 100ml of 2mmol/l solution of Pb(NO₃)₂ and Cd(NO₃)₂.4H₂O, separately. Both mixtures were stirred in rotary shaker at 150rpm for 4 hour. Then, the mixtures were filtered and the filtrate was analyzed for the remaining metal concentration by AAS. The experiment was repeated for each of the adsorbent.

The metal uptake at each moment was calculated from the equation:

$$Q_e = \frac{V(C_i - C_e)}{M} \quad (5)$$

Where V is the volume of metal solution, C_i is the initial metal concentration, C_e is the concentration of metal in solution at given time, and M is the mass of sorbent (dry weight).

3.5 Adsorption isotherm

Twelve lead (II) solution of several concentrations from 0.5 to 9.65 mmol/l (165.5 to 3080mg/l) and eight cadmium (II) solutions, from 0.1 to 2.9 mmol/l (30.8 to 894.5mg/l) in sample of 40 ml was prepared by dissolving $Pb(NO)_3$ and $Cd(NO)_3 \cdot 4H_2O$ respectively in distilled water. The samples (at $pH\ 4.5 \pm 0.1$) were then added with 0.1g of adsorbent and stirred in a rotary shaker at 150 rpm for 4 hours until equilibrium are reached. Then, the mixture was filtered and the filtrate was analyzed for the remaining metal concentration by AAS. The experiment was the repeated with the chosen adsorbent (based on metal uptake by previous experiment), which is one from palm-oil waste, bentonite and one from Amberlite.

The amount of metal adsorbed at equilibrium, Q_e , which represents the metal uptake, was calculated from the difference in metal concentration in the aqueous phase before and after adsorption, according to an equation formally identical to Eq. 3.



Figure 3.2 – AAS (Shimadzu)

3.6 Influence of pH on metal adsorption

A batch of 0.1g of adsorbent was mixed in 40ml of 2.41mmol/l solution of lead (II) and cadmium (II) separately. The pH of the solutions was varied with a range of 1 to 5.5, by addition of NaOH and HNO_3 solution. The mixture was stirred in a rotary shaker at

150rpm for 4 hour. It was filtered and the filtrate was analyzed by AAS. The experiment was repeated for the three adsorbent, as mention in the adsorption isotherm experiment.



Mixing adsorbents into Pb(II) and Cd(II) Nitrate solution



Shake at 150 rpm for 4 hour



Sample ready to be analyzed by AAS



Filtering samples

Figure 3.3 – Experimental procedures for kinetic studies, adsorption isotherm and effect of pH.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Kinetic Studies

Parameters:

pH (Natural pH) – Lead = 4 - 4.3; Cadmium = 4.6 – 5.3

Adsorbent = 0.25g of Na-Bentonite, OPEFB, OP Kernel and Amberlite XAD4, XAD7 and XAD16

Sorbate = 100ml of 662.4ppm of Pb(II)NO₃ and 616.9ppm of Cd(II)NO₃

Formula:

$$Q_e = \frac{V \times (C_i - C_e)}{M_s}$$

Q_e = metal adsorbed/adsorbent

Sorbate	Adsorbent	(C _i), ppm	(C _{me}), ppm	(Q _e), mg/g	% Adsorbed
Pb(II)	Na-Bentonite	662.4	149.444	205.1824	77.43
	OP Kernel	662.4	292.949	147.7804	55.77
	OPEFB	662.4	286.046	150.5416	56.82
	XAD 16	662.4	289.899	149.0004	56.24
	XAD 7	662.4	312.371	140.0116	52.84
	XAD 4	662.4	305.309	142.8364	53.91
Cd (II)	Na-Bentonite	616.9	222.189	176.0844	66.45
	OP Kernel	616.9	294.804	147.0384	55.49
	OPEFB	616.9	285.819	150.6324	56.85
	XAD 16	616.9	297.87	145.812	55.03
	XAD 7	616.9	301.83	144.228	54.43
	XAD 4	616.9	304.86	143.016	53.97

Table 4.1 - Kinetic Studies of Pb(II) and Cd(II) on adsorbents.

From the data shown in Table 4.1, we can compare the adsorbents based on metal uptake; Q_e , shown by these sequences:

Pb (II) : Bentonite > OPEFB > XAD16 > OP Kernel > XAD4 > XAD7

Cd(II) : Bentonite > OPEFB > OP Kernel > XAD16 > XAD7 > XAD4

From the sequences, we can determine that bentonite is the best adsorbent for both Pb(II) and Cd(II). Oil-palm solid wastes are comparable to Amberlite XAD's in adsorbance efficiency. Among Amberlite XAD, XAD16 are better than XAD4 and 7.

Surface area and pore size are the main factor of adsorption capacity. Pb(II) and Cd(II) ions are smaller (1.32 Å and 0.97 Å, respectively) than the pore size of XAD resins (100Å). Too large a pore diameter could render part of the inner adsorbent surface wasted, and the molecules ion initially adsorbed were prone to desorption at the same time, thus result in lower metal uptake than Na-Bentonite. In addition, the nature of XAD resins which is nonionic and hydrophobic may make the adsorption not favorable. Among XAD resins, XAD16 have the most surface area, 800m²/g.

4.2 Adsorption Isotherm

Parameters:

$$\text{pH} = 4.5 \pm 1$$

Adsorbent = 0.1g of Na-Bentonite, OPEFB and Amberlite XAD16

Sorbate =

Pb(II) = 12 samples in 40ml, range from 0.5mmol/l (165.6ppm) to 9.65mmol/l (3080ppm)

Cd(II) = 8 samples in 40ml, range from 0.1mmol/l (30.8ppm) to 2.9 mmol/l (894.5ppm)

Equation:

$$Q_e = \frac{K_L C_e}{1 + \alpha_L C_e} \quad : \text{general Langmuir equation (1)}$$

$$\frac{C_e}{Q_e} = \frac{\alpha_L C_e}{K_L} + \frac{1}{K_L} \quad : \text{linearized Langmuir equation (2)}$$

$$Q_e = K_F C_e^{1/n} \quad : \text{general Freundlich equation (3)}$$

$$\text{Log } Q_e = \text{log} K_F + (1/n) \text{log} C_e \quad : \text{linearized Freundlich equation (4)}$$

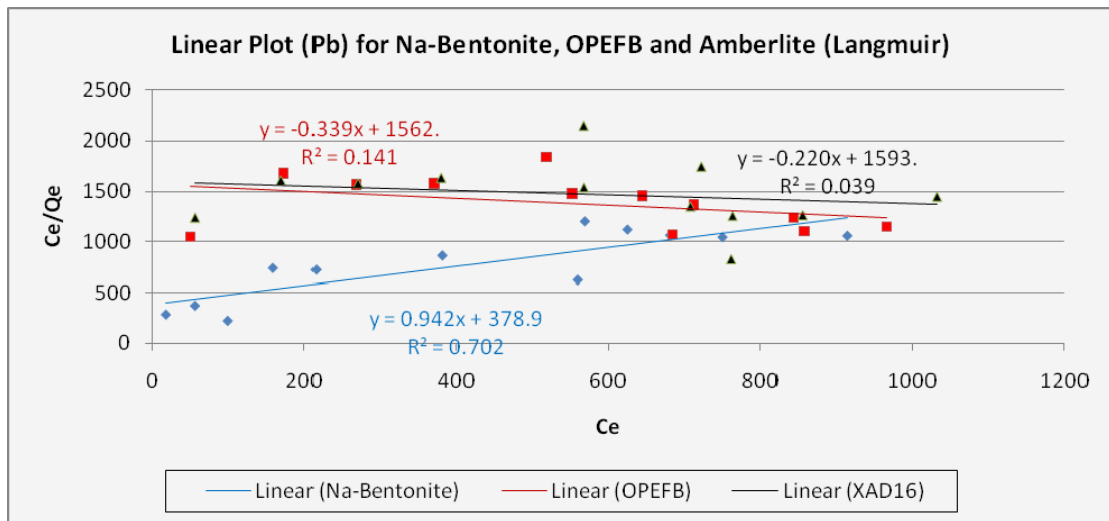
Pb(II) (C _i), ppm	Na-Bentonite		OPEFB		Amberlite XAD16	
	(C _e), ppm	(Q _e), ppm	(C _e), ppm	(Q _e), ppm	(C _e), ppm	(Q _e), ppm
165.6	16.694	59.2624	48.798	46.7208	54.737	44.3452
430.5	55.219	150.1124	172.559	103.1764	168.385	104.846
695.5	158.433	214.8268	267.426	171.2296	269.192	170.5232
960.4	215.097	298.1212	370.961	235.7756	379.469	232.3724
1225.4	98.559	450.7364	518.318	282.8328	566.956	263.3776
1490.3	381.877	443.3692	552.188	375.2448	567.277	369.2092
1755.2	569.364	474.3344	643.684	444.6064	721.376	413.5296

2020.2	624.422	558.3112	712.066	523.2536	707.09	525.244
2285.1	680.925	691.67	683.814	640.5144	762.951	608.8596
2550.1	750.43	719.868	842.889	682.8844	854.286	678.3256
2815.0	559.893	902.0428	857.336	783.0656	1031.019	713.5924
3080.0	914.481	866.2076	966.65	845.34	761.024	927.5904

Table 4.2 - Experimental Data of Pb(II) sorption on Na-Bentonite, OPEFB and Amberlite XAD16.

Langmuir			
Parameter	Na-Bentonite	OPEFB	Amberlite XAD16
K_L	0.002639	0.00064	0.000628
α_L	0.002486	-0.00022	-0.00014
R^2	0.702	0.141	0.0039
Freundlich			
Parameter	Na-Bentonite	OPEFB	Amberlite XAD16
$1/n$	0.599	1.008	1.017
K_F	0.01367	0.000703	0.000639
R^2	0.863	0.954	0.929

Table 4.3 – Langmuir and Freundlich isotherm parameters for Pb(II) sorption on Na-Bentonite, OPEFB and Amberlite XAD16.



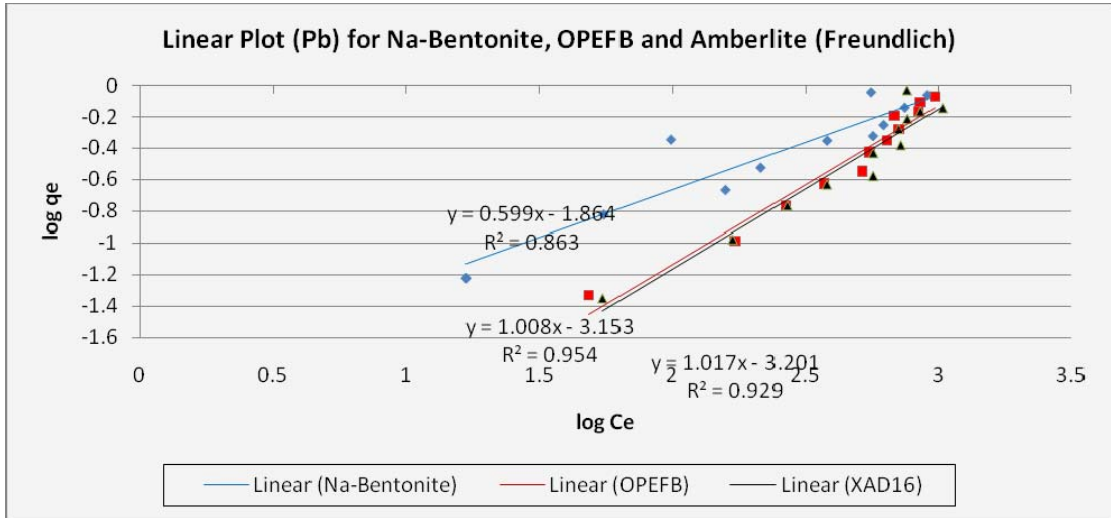
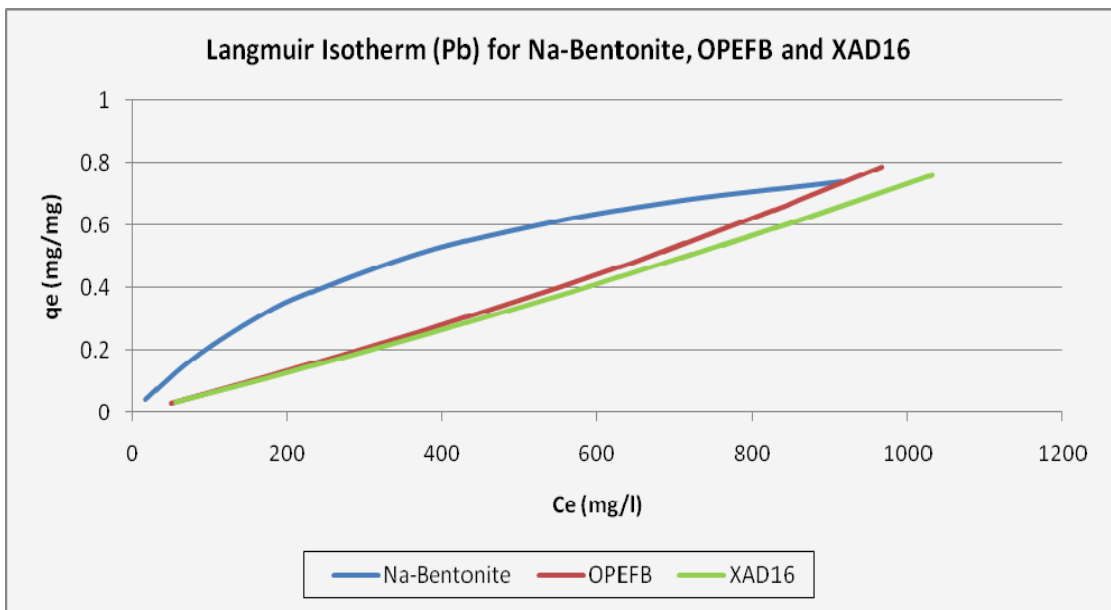


Figure 4.1 - Linear plot for the sorption of Pb(II) onto Na-Bentonite, OPEFB and Amberlite XAD16 (Langmuir and Freundlich).



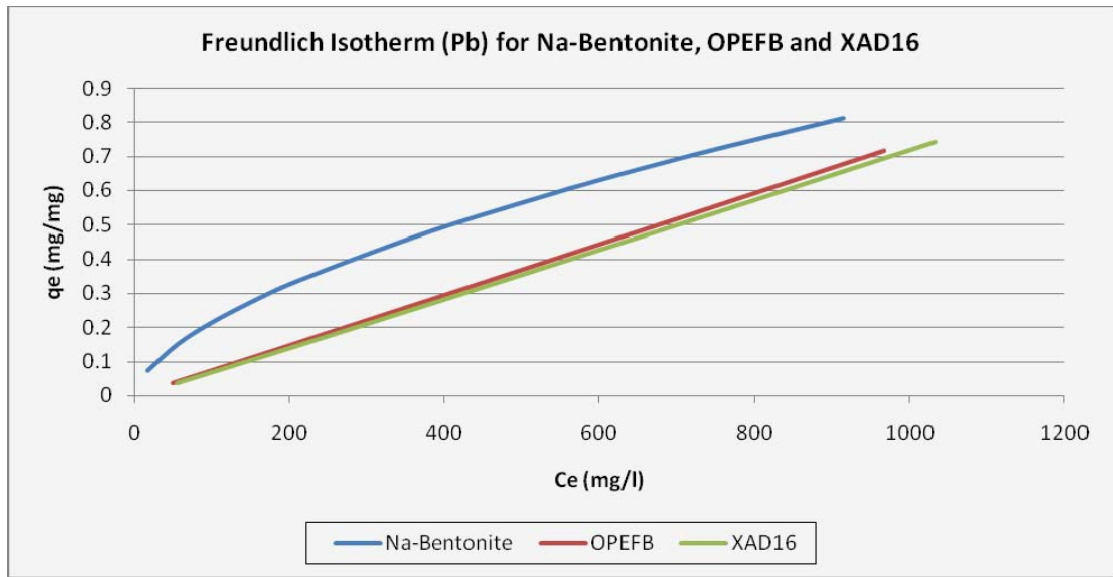


Figure 4.2 – Langmuir and Freundlich equilibrium curves for sorption of Pb(II) onto Na-Bentonite, OPEFB and Amberlite XAD16.

Cd(II) (C_i), ppm	Na-Bentonite		OPEFB		Amberlite XAD16	
	(C_e), ppm	(Q_e), ppm	(C_e), ppm	(Q_e), ppm	(C_e), ppm	(Q_e), ppm
30.8	5.718	10.0328	1.7755	11.6098	6.3815	8.5674
154.2	23.48115	52.2875	54.42976	39.908	54.96029	39.6958
277.6	50.792	90.7232	131.1478	58.508	126.1036	60.5986
401	84.84	126.464	139.54	104.584	153.704	98.9184
524.4	126.415	159.194	219.1525	122.099	239.3003	114.0398
647.74	211.3679	174.5488	282.5053	146.0938	289.0501	143.47596
771.12	294.877	190.4972	373.6905	158.9718	372.4475	159.469
894.5	341.5795	221.1682	395.291	199.6836	426.1251	187.34996

Table 4.4 - Experimental Data of Cd(II) sorption onto Na-Bentonite, OPEFB and Amberlite XAD16.

Langmuir			
Parameters	Na-Bentonite	OPEFB	Amberlite XAD16
K_L	0.002379	0.001097	0.00077
α_L	0.00832	0.004021	0.002051
R^2	0.968	0.559	0.765
Freundlich			
Parameters	Na-Bentonite	OPEFB	Amberlite XAD16
1/n	0.708	0.512	0.8
K_F	-2.364	0.0073	0.00148
R^2	0.934	0.933	0.990

Table 4.5 – Langmuir and Freundlich isotherm parameters for Cd(II) onto Na-Bentonite, OPEFB and Amberlite XAD16.

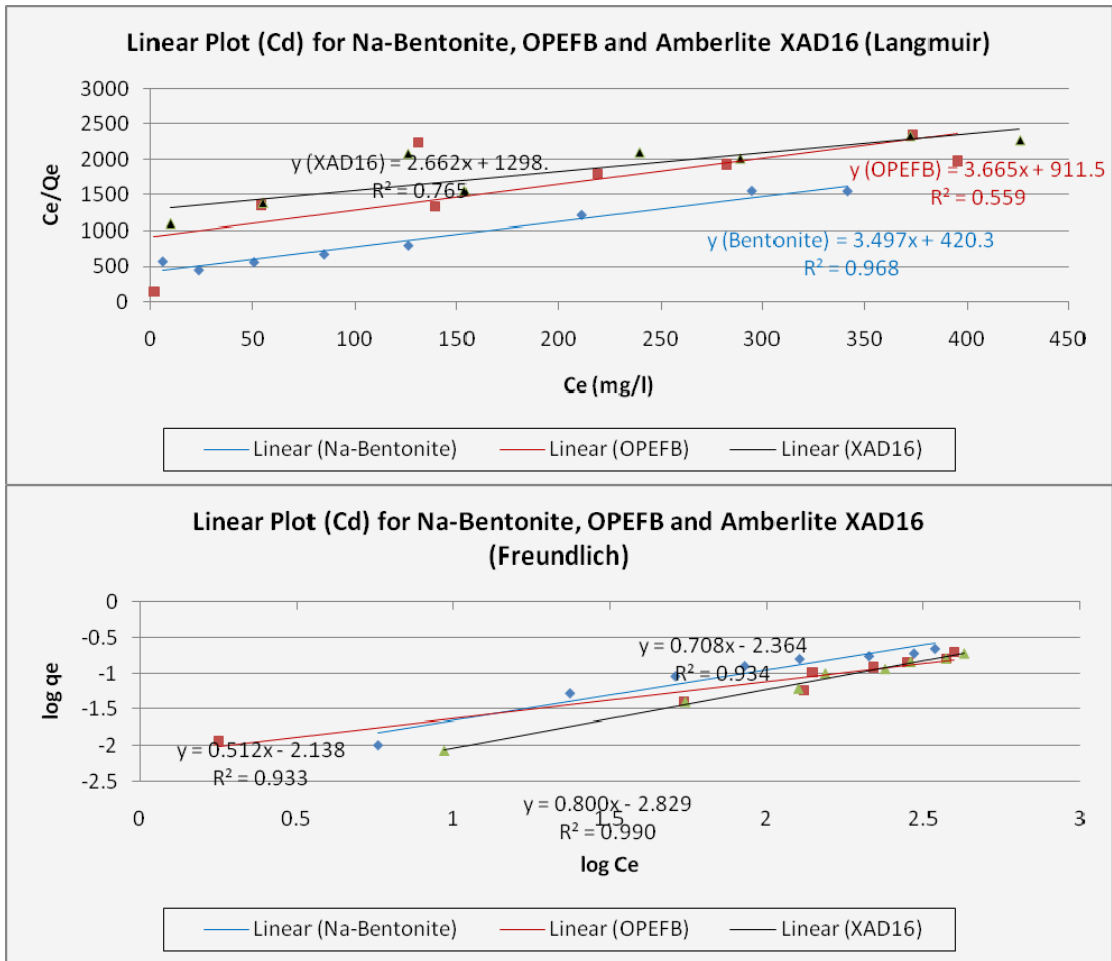


Figure 4.3 - Linear plot for the sorption of Cd(II) onto Na-Bentonite, OPEFB and Amberlite XAD16 (Langmuir and Freundlich).

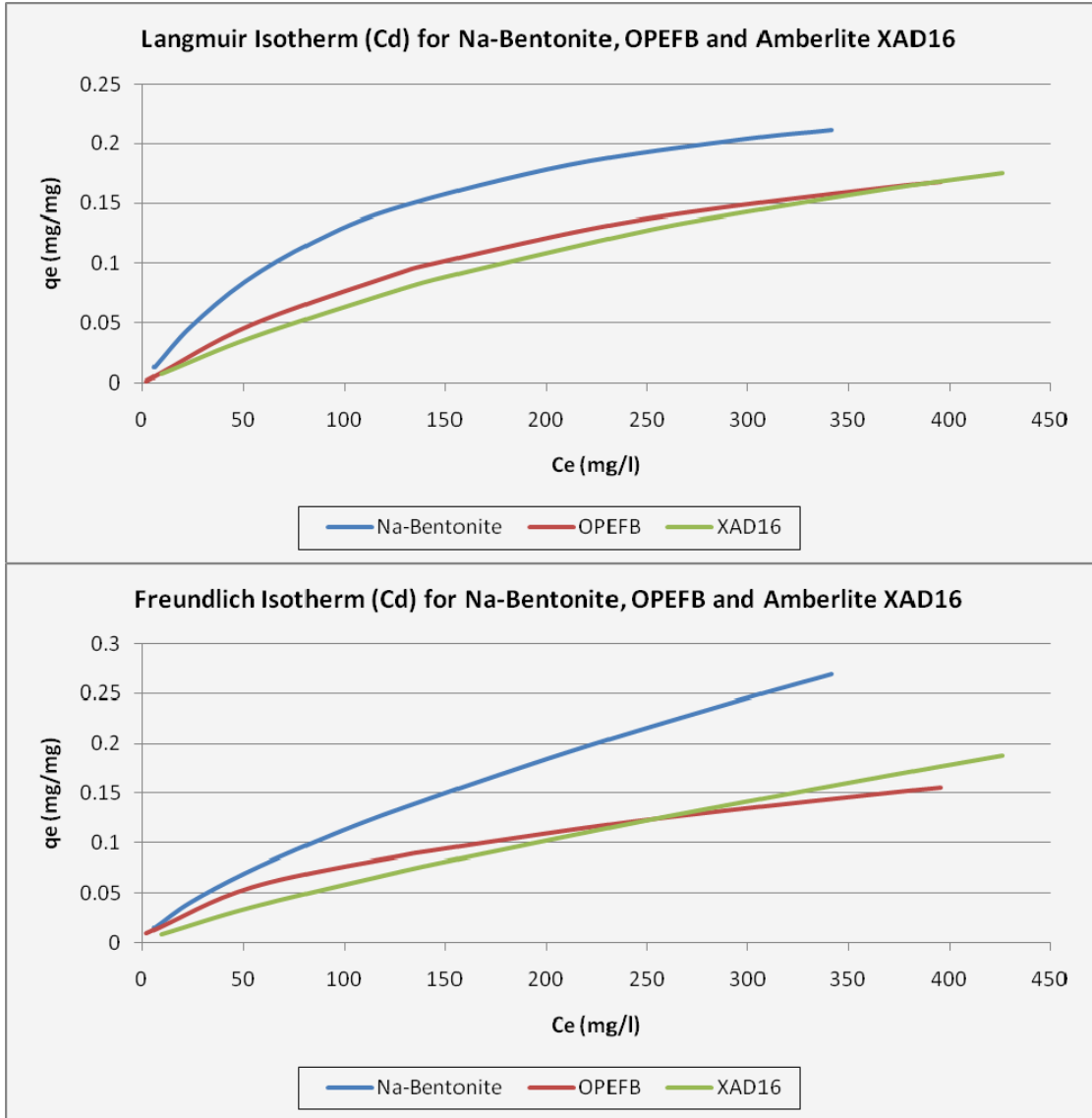


Figure 4.4 – Langmuir and Freundlich equilibrium curves for sorption of Cd(II) onto Na-Bentonite, OPEFB and Amberlite XAD16.

Table 4.2 and 4.4 shows the experimental data of Pb(II) and Cd(II) respectively. Table 4.3 and 4.5 shows the isotherm parameters (Langmuir and Freundlich) for Pb(II) and Cd(II) respectively, achieved by plotting the linearized Langmuir equation (2) and linearized Freundlich equation (4) (Figure 4.1 and 4.3). Then, the isotherm parameters were put into the general Langmuir equation (1) and Freundlich equation (3) to get the theoretical q_e . The Langmuir and Freundlich isotherm model was shown in Figure 4.2 and 4.4.

Based on these results, Freundlich isotherm show the highest degree of fit on all adsorbent compared to Langmuir isotherm. These proves that all of the adsorptions can be best described by Freundlich isotherm. XAD16 shows the highest degree fits for Cadmium (0.99) and OPEFB shows the highest degree fits for Lead (0.954). These results also shows that the adsorption happen in multilayer and removed the assumption of monolayer adsorption.

4.3 Effect of pH

Parameters:

pH = 1 - 5.5

Adsorbent = 0.1g of Na-Bentonite, OPEFB and Amberlite XAD16

Sorbate = 2.41mmol/l of Pb(II)NO₃ (798.1ppm) and Cd(II)NO₃ (743.4ppm) in 40ml

Sorbate	pH	Na-Bentonite		OPEFB		XAD16	
		(C _{me}), ppm	(Q _m), ppm	(C _{me}), ppm	(Q _m), ppm	(C _{me}), ppm	(Q _m), ppm
Pb(II)	1	87.419	284.2724	337.629	184.1884	415.728	152.9488
	2	148.997	259.6412	341.692	182.5632	409.841	155.3036
	3	186.788	244.5248	355.476	177.0496	401.084	158.8064
	4	234.572	225.4112	360.456	175.0576	390.952	162.8592
	4.5	257.736	216.1456	377.196	168.3616	389.504	163.4384
Cd(II)	1	396.299	138.8404	385.6673	143.0931	391.3886	140.8046
	2	367.6922	150.2831	394.8036	139.4386	393.0961	140.1216
	3	288.8357	181.8257	368.0345	150.1462	394.1638	139.6945
	4	316.788	170.6448	361.331	152.8276	366.6246	150.7102
	5.5	N/A	N/A	357.146	154.5016	355.3976	155.201

Table 4.6 - Experimental data for the sorption of Pb(II) and Cd(II) onto Na-Bentonite, OPEFB and Amberlite XAD16 in the function of pH.

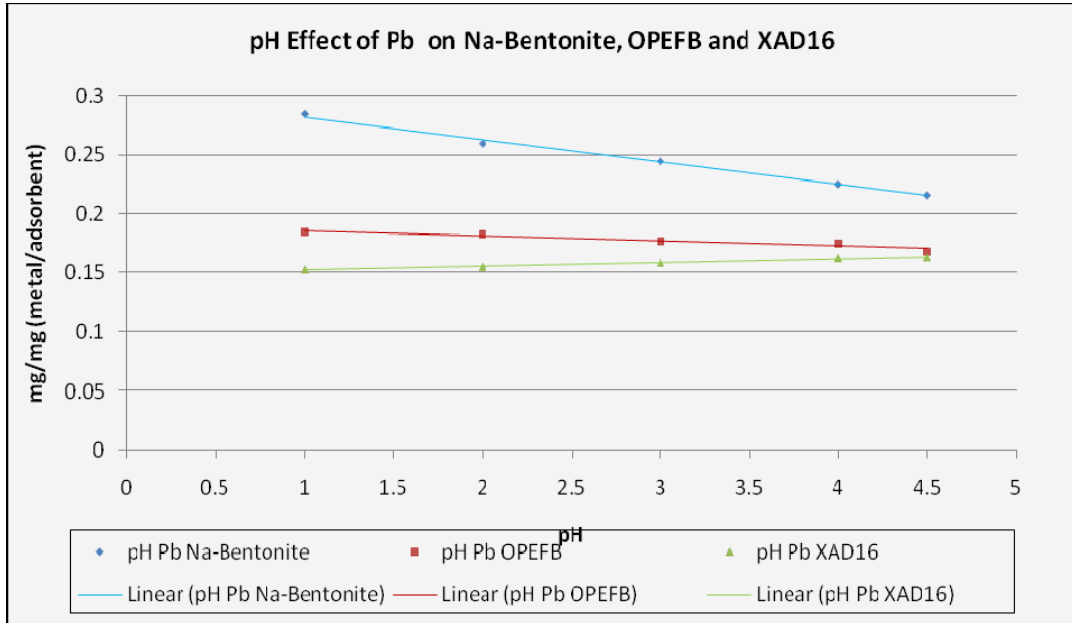


Figure 4.5 - Effect of pH on Pb(II) sorption onto Na-Bentonite, OPEFB and Amberlite XAD16.

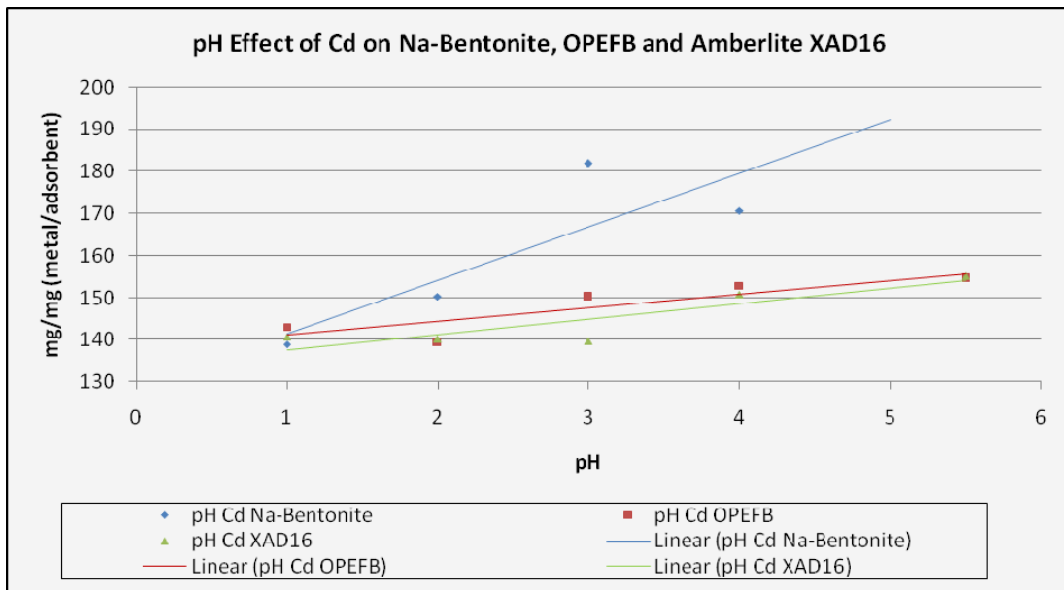


Figure 4.6 - Effect of pH on Cd(II) sorption onto Na-Bentonite, OPEFB and Amberlite XAD16.

The adsorption of Pb(II) and Cd(II) onto Na-Bentonite, OPEFB and Amberlite XAD16 as a function of pH are shown in Figure 4.5 and 4.6. It can be seen that the adsorption of Pb(II) and Cd(II) are pH-dependent, mostly on Na-Bentonite. The uptake of Pb(II) and Cd(II) on Na-Bentonite is better at all pH compared to OPEFB and XAD16.

For Na-Bentonite, the adsorption of Pb(II) and Cd(II) increase with increasing pH. This is due to at lower pH, more H⁺ exist and compete with metal ions. This means that at higher H⁺ concentration, the bentonite surface becomes more positively charged thus reducing the attraction between surface and metal cations. In addition, due to removal of metals by recipitation above pH5, metals were removed by both adsorption and precipitation. (*Liu Yun et. al, 2006*)

4.4 Adsorbent Characterization

Adsorbents functional group has been observed by analyzing with FTIR. Infrared spectra for Amberlite XAD4, 7, and 16 were taken from product data sheet issued by Rohm and Haas. The infra-red spectrums are shown in Figure 4.7 – 4.12. Table 4.7 list the functional group for OPEFB, OP Kernel and Na-Bentonite.

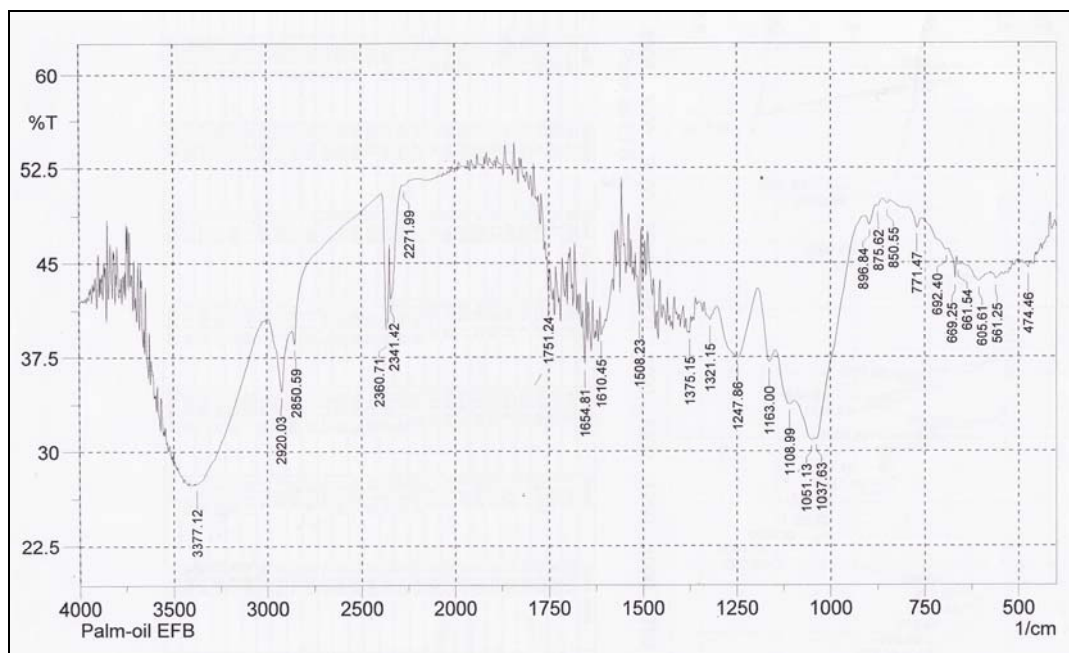


Figure 4.7 - FTIR spectra for OPEFB

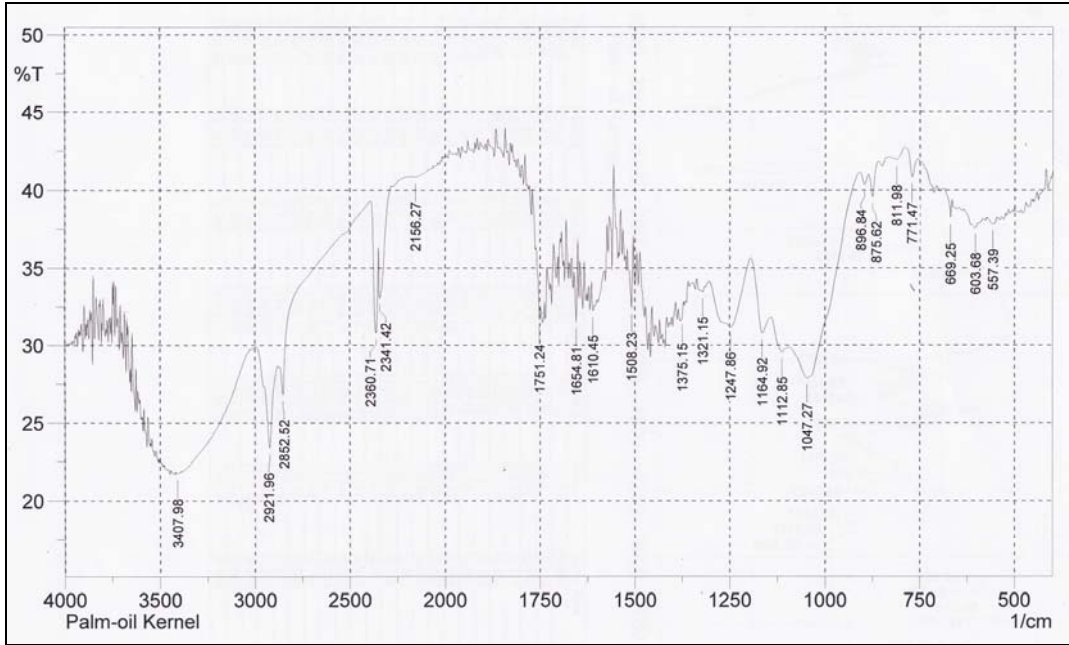


Figure 4.8 - FTIR Spectra for OP Kernel

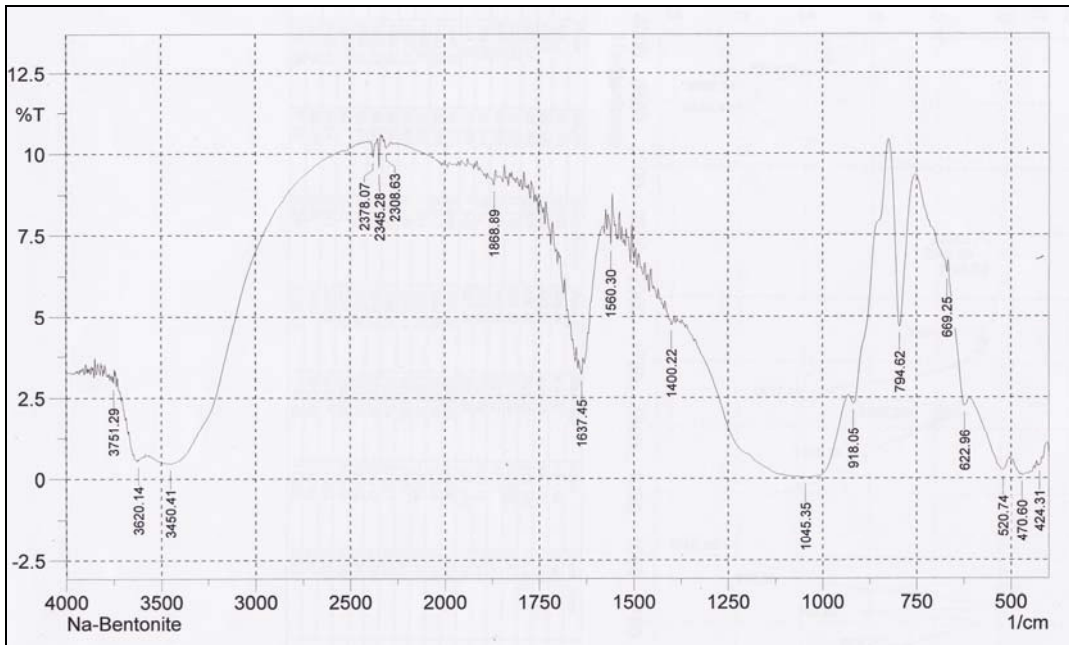


Figure 4.9 - FTIR Spectra for Na-Bentonite

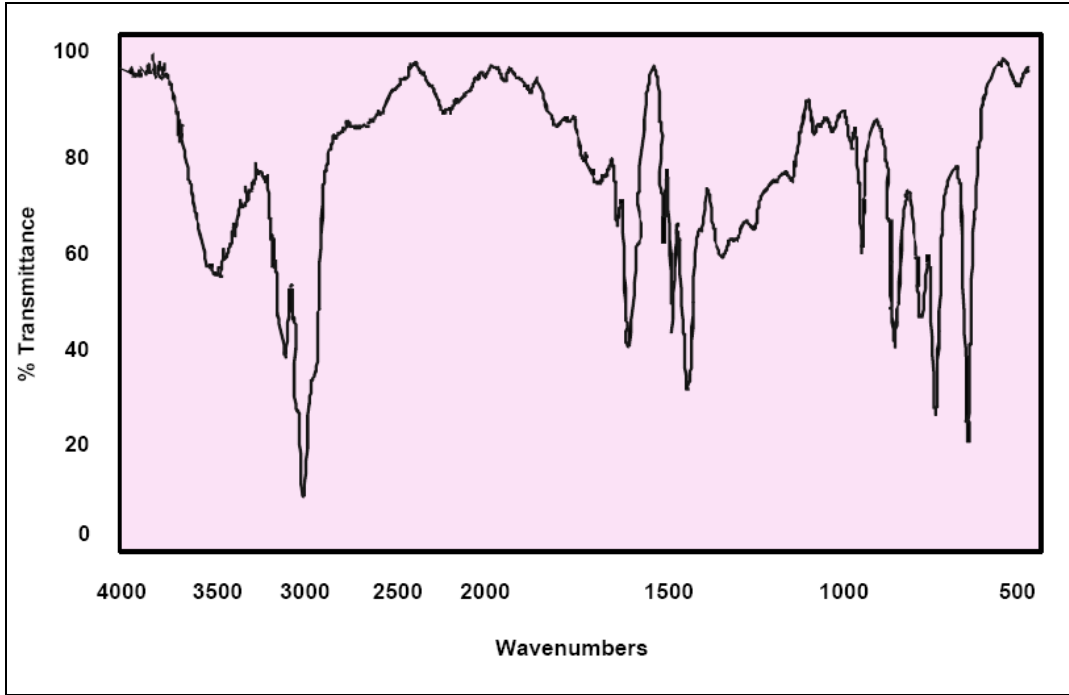


Figure 4.10 - IR Spectra for XAD4 (XAD PDS)

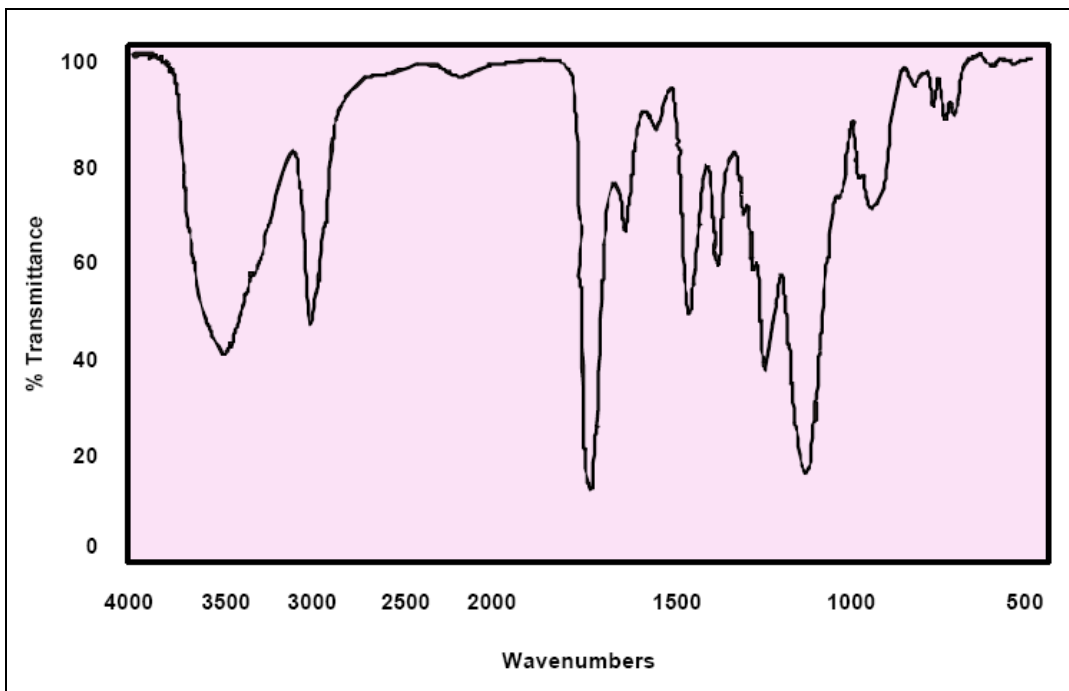


Figure 4.11 - IR Spectra for XAD7 (XAD7 PDS)

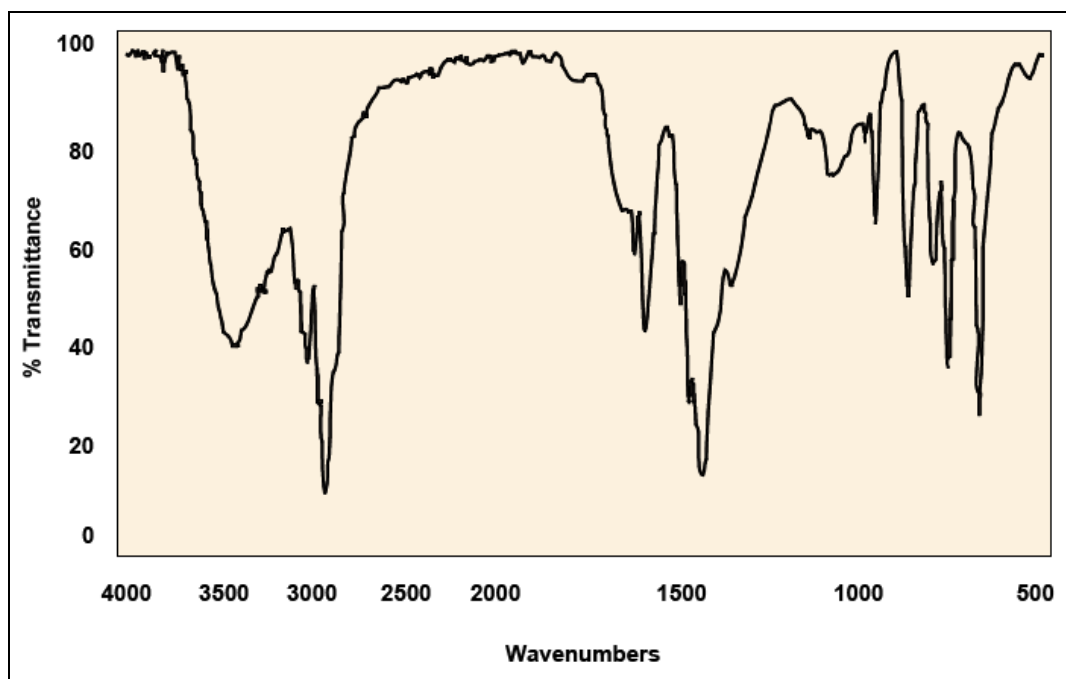


Figure 4.12 - IR Spectra for XAD16 (XAD16 PDS)

OPEFB			OP Kernel		
cm ⁻¹	Functional Group	Bond	cm ⁻¹	Functional Group	Bond
669.25	acid chlorides	C-Cl stretch	669.25	acid chlorides	C-Cl stretch
771.47	aromatics	C-H bend (mono)	771.47	aromatics	C-H bend (mono)
896.84	anhydrides	C-O stretch	875.62	aromatics	C-H bend (meta)
1051.13	alcohols	C-O stretch	1047.27	alcohols	C-O stretch
1247.86	ketones	C-C stretch	1247.86	ketones	C-C stretch
1654.81	alkenes	C=C stretch (isolated)	1751.24	esters	C=O stretch
2360.71	Carboxylic acid	O-H stretch	2360.71	Carboxylic acid	O-H stretch
2920.03	alkanes	C-H stretch	2921.96	alkanes	C-H stretch
3377.12	alcohols	O-H stretch	3407.98	alcohols	O-H stretch
Na-Bentonite					
cm ⁻¹	Functional Group		Bond		
520.74	alkyl halides		C-Br stretch		
794.62	amines		N-H (oop)		
1045.35	alcohols		C-O stretch		
1637.45	alkenes		C=C stretch (isolated)		
3450.41	amines		N-H stretch		

Table 4.7 - Functional Groups

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

The equilibrium adsorption for Pb(II) and Cd(II) onto bentonite, oil-palm solid waste and Amberlite XAD polymeric adsorbents has been studied and the comparison between the adsorbent has done. Bentonite has proved to be the best adsorbent to remove lead and cadmium from waste stream, while oil-palm solid wastes are comparable to Amberlite XAD polymeric adsorbents. However, as the polymeric adsorbents incur high cost, oil-palm solid wastes are more preferable.

Based on linear method, all adsorption can be best described by Freundlich isotherm means multilayer adsorptions occur. For lead, OPEFB shows the highest degree of fit (0.954) and for cadmium, XAD16 shows the highest degree of fit (0.99)

pH has proved to pose significantly as a function as the metal uptake increase with increasing pH. Furthermore, at higher pH than 5.0, metal precipitation will also occur.

The functional group of the adsorbents had been identified by FTIR analysis.

5.2 Recommendation

Improvement can be done to make the experiment more efficient and produces good results:

- The initial concentration variation for adsorption isotherm studies should be lowered, so that the samples concentration (equilibrium) will be lower than the standards prepared for AAS and AAS can give more accurate readings.
- If the samples concentration are high, dilution should be done to make sure that the samples concentration should be lower than standards.

- pH meter must be calibrated correctly, to avoid inaccurate pH reading, and thus effect the experiments.
- The adsorption of metals as a function of time should be carried out to determine the maximum capacity of each adsorbent.
- More studies on oil-palm solid waste to be carried out in order to further characterize it such as pore size, surface area etc.

REFERENCES

- M. Ursinyova, V. Hladioka, *Cadmium in the environment of Central Europe*, Elsevier Science BV, 2000.
- M. Ursinyova, V. Hladioka, *Lead in the environment of Central Europe*, Elsevier Science BV, 2000.
- No author, *Chemical properties of cadmium-Health effect of cadmium-Environmental effect of cadmium*, [http://www. lenntech.com/periodic-chart-elements/cd-en.htm](http://www.lenntech.com/periodic-chart-elements/cd-en.htm).
- No author, *Chemical properties of lead, Health effect of lead-Environmental effect of lead*, <http://www.lenntech.com/periodic-chart-elements/pb-en.htm>.
- Agency for Toxic Substances and Disease Registry, *Cadmium Toxicity Case Studies in Environmental Medicine*, USA, 1990.
- No author, *Amberlite XAD-4, XAD-7, XAD-16 Product Data Sheet*, <http://www.rohmmaas.com/ionexchange/pharmaceuticals/xad.htm>.
- No author, *Bentonite Clay Profile*, <http://www.botanical.com/products/learn/bentonite.html>
- Wyoming Geological Survey, *Bentonite*, <http://www.wsgs.uwyo.edu/Topics/IndustrialMinerals/bentonite.aspx>
- No author, *Bentonite Clay Powder Product Data Sheet*, <http://www.bentonites.co.uk/products.html>.
- T. A. Kurniawan, Gilbert Y.S Chan, Wai Hung Lo, Sandhya Babel, *Physico-chemical treatment techniques for wastewater laden with heavy metals*, Chemical Engineering Journal 118, 2006, pg. 83-98.
- S.R.K Yadanaparthi, David Graybil, Ray von Wandruzka, *Adsorbents for the removal of arsenic, cadmium, and lead from contaminated waters*, I. Hazard. Mater. (2009). doi: 10.106/i.ihazmat.2009.05.103.

Liu Yun, Shen Xing, Xian Qiming, Chen Haidong, Zou Huixian, Gao Shixiang,
Adsorption of copper and lead in aqueous solution onto bentonite modified by 4-
methylbenzo-15-crown-5, Journal of Hazardous Materials B137 (2006) 1149-
1155.

M.A Abdullah, L. Chiang, M. Nadeem, *Comparative evaluation of adsorption kinetics*
and isotherms of a natural product removal by Amberlite polymeric adsorbents,
Chemical Engineering Journal 146 (2009) 370-376

No author, *Adsorption*, <http://en.wikipedia.org/wiki/Adsorption.html>.

F. Helfferich, *Ion Exchange*, McGraw Hill, New York, 1962

A. Mockovčiaková, Z. Orolinová, *Adsorption properties of modified bentonite clay*,
ISSN 1392 – 1231, CHEMINE TECHNOLOGIJA, 2009, Nr. 1 (50)

No author, Amberlite XAD Price, www.sigmaaldrich.com

APPENDICES

(A) Infrared Spectroscopy

IR Absorptions for Representative Functional Groups

Functional Group	Molecular Motion	Wavenumber (cm ⁻¹)
alkanes	C-H stretch	2950-2800
	CH ₂ bend	~1465
	CH ₃ bend	~1375
	CH ₂ bend (4 or more)	~720
alkenes	=CH stretch	3100-3010
	C=C stretch (isolated)	1690-1630
	C=C stretch (conjugated)	1640-1610
	C-H in-plane bend	1430-1290
	C-H bend (monosubstituted)	~990 & ~910
	C-H bend (disubstituted - E)	~970
	C-H bend (disubstituted - 1,1)	~890
	C-H bend (disubstituted - Z)	~700
	C-H bend (trisubstituted)	~815
alkynes	acetylenic C-H stretch	~3300
	C,C triple bond stretch	~2150
	acetylenic C-H bend	650-600
aromatics	C-H stretch	3020-3000
	C=C stretch	~1600 & ~1475
	C-H bend (mono)	770-730 & 715-685
	C-H bend (ortho)	770-735
	C-H bend (meta)	~880 & ~780 & ~690
	C-H bend (para)	850-800
alcohols	O-H stretch	~3650 or 3400-3300

	C-O stretch	1260-1000
ethers	C-O-C stretch (dialkyl)	1300-1000
	C-O-C stretch (diaryl)	~1250 & ~1120
aldehydes	C-H aldehyde stretch	~2850 & ~2750
	C=O stretch	~1725
ketones	C=O stretch	~1715
	C-C stretch	1300-1100
carboxylic acids	O-H stretch	3400-2400
	C=O stretch	1730-1700
	C-O stretch	1320-1210
	O-H bend	1440-1400
esters	C=O stretch	1750-1735
	C-C(O)-C stretch (acetates)	1260-1230
	C-C(O)-C stretch (all others)	1210-1160
acid chlorides	C=O stretch	1810-1775
	C-Cl stretch	730-550
anhydrides	C=O stretch	1830-1800&1775-1740
	C-O stretch	1300-900
amines	N-H stretch (1 per N-H bond)	3500-3300
	N-H bend	1640-1500
	C-N Stretch (alkyl)	1200-1025
	C-N Stretch (aryl)	1360-1250
	N-H bend (oop)	~800
amides	N-H stretch	3500-3180
	C=O stretch	1680-1630
	N-H bend	1640-1550
	N-H bend (1°)	1570-1515
alkyl halides	C-F stretch	1400-1000

	C-Cl stretch	785-540
	C-Br stretch	650-510
	C-I stretch	600-485
nitriles	C,N triple bond stretch	~2250
isocyanates	-N=C=O stretch	~2270
isothiocyanates	-N=C=S stretch	~2125
imines	R ₂ C=N-R stretch	1690-1640
nitro groups	-NO ₂ (aliphatic)	1600-1530&1390-1300
	-NO ₂ (aromatic)	1550-1490&1355-1315
mercaptans	S-H stretch	~2550
sulfoxides	S=O stretch	~1050
sulfones	S=O stretch	~1300 & ~1150
sulfonates	S=O stretch	~1350 & ~11750
	S-O stretch	1000-750
phosphines	P-H stretch	2320-2270
	PH bend	1090-810
phosphine oxides	P=O	1210-1140