ADSORPTION OF LEAD USING RICE HUSKS

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SUPERVISOR'S DECLARATION

I hereby declare that I have checked this thesis and in my opinion this thesis is adequate in terms of scope and quality for the award of the degree of Bachelor of Chemical Engineering.

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I hereby declare that the work in this thesis is my own except for quotations and summaries which have been duly acknowledged. The thesis has not been accepted for any degree and is not concurrently submitted for award of other degree.

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ABSTRACT

Excessive release of heavy metals into environment due to industrialization and urbanization has posed a great problem to the world. Heavy metal ions do not degrade, so it can give bad effect to human body and environment itself. Adsorption is one of the most effective techniques to remove heavy metals. Activated carbon is the common adsorbent to remove heavy metals from wastewater but it is expensive material. The purpose of this study is to investigate the effectiveness of rice husks as adsorbent for the removal of lead ions. The lead ions removal from aqueous solution was studied using batch method. The main parameters that influenced lead sorption on rice husk were contact time, adsorbent dosage and pH value. The rice husks were modified using tartaric acid before proceeds with batch studies. Using the initial concentration of lead solutions at 400mg/L, the analysis was continued using different contact time in range of 5 minutes to 70 minutes. Besides that, the influences of adsorbent dosage also been studied in range of 0.5g to 3.0g. Then, for the pH parameter, the experiment was run using the value between 2 and 6. After that, contains of lead ions were analyzed using Atomic Absorption Spectrometer (AAS). For the contact time, the adsorption increased when the contact time increased and the maximum adsorption is 71% at 70 min. The research also gave similar results with the adsorbent dosage, where the adsorption of lead increased with increasing of adsorbent because of greater surface area with maximum value of 80% at 3.0 g. The adsorption of lead using rice husk was increased when the pH increased from 2 to 6 and the percentage adsorption is 86% at pH 6. As the conclusion, the rapid uptake and high sorption capacity achieved when the experiments were conducted at contact time, adsorbent dosage and effective pH. It shown that rice husk is an attractive alternative adsorbent material for the lead ions removal.

ABSTRAK

Pembuangan logam berat secara berlebihan ke persekitaran yang berpunca dari sektor perindustrian dan pembangunan telah memberi masalah yang besar kepada dunia. Ion logam berat yang tidak boleh terurai akan membawa kesan buruk kepada tubuh manusia dan alam sekitar. Penjerapan adalah salah satu teknik yang paling berkesan untuk menyingkirkan logam berat. Karbon aktif merupakan penjerap yang biasa digunakan dalam penyingkiran logam berat dari sisa air buangan tetapi bahan ini sangat mahal. Tujuan penyelidikan ini dijalankan adalah untuk mengkaji keberkesanan sekam padi sebagai penjerap dalam penyingkiran ion plumbum menggunakan kaedah berperingkat. Antara pembolehubah yang mempengaruhi penjerapan ion plumbum adalah masa sentuhan, dos penjerap dan pH. Sekam padi telah dibaikpulih menggunakan asid tartarik sebelum kajian diteruskan. Dengan menggunakan larutan plumbum pada kepekatan awal 400 mg/L, analisis diteruskan dengan pembolehubah masa sentuhan antara 5 hingga 70 minit. Selepas itu, dos penjerap diubah antara nilai 0.5 dan 3.0 g. Kemudian, untuk pH, eksperimen telah dilakukan menggunakan nilai antara 2 dan 6. Selepas kajian berperingkat dilakukan, baki ion plumbum yang tinggal dianalisis menggunakan Spektrometer Penyerapan Atom (AAS). Bagi keputusan masa sentuhan, kadar penjerapan plumbum meningkat dengan peningkatan masa dan nilai maksimum adalah 71% pada minit ke-70. Begitu juga dengan dos penjerap dimana penjerapan bertambah dengan pertambahan dos disebabkan pertambahan luas permukaan dengan nilai tertinggi adalah 80% apabila dos 3.0 g. Kadar penjerapan plumbum menggunakan sekam padi telah meningkat apabila pH meningkat dari 2 ke 6 dan peratus penjerapan maksimum ialah 86% pada pH 6. Sebagai kesimpulan, kadar penjerapan yang bagus dicapai apabila kajian dijalankan pada masa sentuhan, dos penjerap dan pH yang sesuai. Hasil menunjukkan bahawa sekam padi merupakan bahan penjerap alternatif untuk penyingkiran ion plumbum dalam larutan.

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M	Molarity of solutions
V	Volume of solutions
C_o	Initial concentration
C_e	Equilibrium concentration

CHAPTER 1

INTRODUCTION

1.1 Heavy Metals

With rapid development in agriculture, industry, commerce, hospital and health-care facilities, many activities are consuming significant quantities of toxic chemicals and generating a large amount of hazardous waste. Currently, there are about 110 000 types of toxic chemicals commercially available. Each year, another 1 000 new chemicals are added into the market for industrial and other uses. One of the most hazardous pollutants in environment is heavy metals (Sud *et al*., 2008).

Heavy metals are elements having atomic weights between 63.5 and 200.6, and a specific gravity greater than 5.0 (Fu and Wang, 2011). Heavy metals generally refers to the elements such as Cd (cadmium), Cr (chromium), Cu (copper), Hg (mercury), Ni (nickel), Pb (lead), Fe (ferum) and Zn (zinc) which are commonly associated with pollution and toxicity problems. Heavy metals occur naturally in rock formation and ore minerals and so a range of normal background concentration is associated with each of these elements in soils, sediments, waters and living organisms. These heavy metals are of specific concern due to their toxicity, bio-accumulation tendency and persistency in nature. Several past disasters due to the contamination of heavy metals in aquatic streams are Minamata tragedy in Japan due to methyl mercury contamination and ''Itai-Itai'' due to contamination of cadmium in Jintsu river of Japan (Sud *et al*., 2008).

Industrial uses of metals and other domestic processes have introduced substantial amounts of potentially toxic heavy metals into the atmosphere and into the aquatic and terrestrial environments. In small quantities, certain heavy metals are nutritionally essential for healthy life. Some of these are referred to as the trace elements (e.g., iron, copper, manganese, and zinc). These elements, or some form of them, are commonly found naturally in foodstuffs, in fruits and vegetables, and in commercially available multivitamin products. Heavy metals are also common in industrial applications such as in the manufacture of pesticides, batteries, alloys, electroplated metal parts, textile dyes, steel, mining, refining ores, fertilizers industries, paper industries and so forth (Sud *et al*., 2008). Many of these products are in our homes and actually add to our quality of life when properly used.

However, high concentrations of heavy metals are known to produce a range of toxic effect and also have a potentially damaging effect on human physiology and other biological systems. For example, lead can cause encephalopathy, cognitive impairment, behavioral disturbances, kidney damage, anemia, and toxicity to the reproductive system. At high exposure level, cadmium can cause nephrotoxic effect, while after long term exposure it can cause bone damage. Other study reported that copper can cause weakness, lethargy, anorexia, and gastrointestinal tract (Dewayanto, 2010).

1.2 Adsorption Process

Adsorption is the adhesion of a chemical species onto the surface of particles. In general, adsorption can be defined as accumulation or depletion of solute molecules at an interface. Adsorption process can be a physical adsorption which involve only relatively weak intermolecular forces, and chemisorptions which involve the formation of a chemical bond between the sorbate molecule and the surface of the adsorbent. Chemical adsorption results in the formation of a monomolecular layer of the adsorbate on the surface through forces of residual valence of the surface molecules. Physical adsorption is results from molecular condensation in the capillaries of the solid (Khan *et al*., 2004).

Khan *et al.* (2004) investigated that the adsorption process is being widely used by various researchers for the removal of heavy metals from waste streams. Activated carbon has been frequently used as and adsorbent but it is so expensive material. Hence, there are necessary to make the research towards the production of low cost and more effective alternatives for activated carbon. The adsorption process offers flexibility in design and operation and in many cases will produce high-quality treated effluent. In addition, because it is sometimes reversible, adsorbents can be regenerated by suitable desorption process.

Adsorption has been proved to be an excellent way to treat industrial waste effluents, offering significant advantages like the low-cost, availability, profitability, ease of operation and efficiency, in comparison with conventional methods especially from economical and environmental points of view. A search for a low-cost and easily available adsorbent has led to the investigation of materials of biological origin as potential metal biosorbents. Biosorption is becoming a potential alternative to the existing technologies for the removal and/or recovery of toxic metals from wastewater (Demirbas, 2008).

1.3 Agricultural Adsorbent

In recent years, more attentions have been gained by the biomaterials which are byproducts or the wastes of large-scale industrial processes and agricultural waste materials. A range of adsorbents such as orange peel, grass, leaf, wheat shells, heartwood, rice husk, saw dust of various plants, bark of the trees, groundnut shells, coconut shells, black gram husk, hazelnut shells, walnut shells, cotton seed hulls, waste tea leaves, Cassia fistula leaves, maize corn cob, jatropa deoiled cakes, apple, banana, soybean hulls, grapes stalks, water hyacinth, sugar beet pulp, sunflower stalks, coffee beans, arjun nuts, and sugarcane bagasse have been reported to be used to remove or recover heavy metals from aqueous solutions (Sud *et al.*, 2008).

Effective use of biomass wastes has become one of the promising fields of the treatment of heavy metals due to the low cost as well as their environmentally friendly nature (Shao *et al*., 2011). Wong *et al*. (2003) investigated this agricultural wastes were extensively used for the removal of heavy metals due to their abundance in nature. Besides that, it has been used for adsorbing metal ions due to the characteristic functional groups (Tarley *et al*., 2004).

Agricultural waste materials being economic and eco-friendly due to their unique chemical composition, availability in abundance, renewable, low in cost and more efficient are seem to be viable option for heavy metal remediation. These promising agricultural waste materials are used in the removal of metal ions either in their natural form or after some physical or chemical modification (Sud *et al*., 2008). But, many studies have shown that the adsorption capacity of these adsorbents may be increased by their treatment with chemical reagents (Tarley *et al*., 2004). In general, raw lignocellulosic biosorbents were modified by various methods to increase their sorption capacities because metal ion binding by lignocellulosic biosorbents is believed to take place through chemical functional groups such as carboxyl, amino, or phenolics. More recently, great effort has been contributed to develop new adsorbents and improve existing adsorbents. Many investigators have studied the feasibility of using low-cost agro-based waste materials (Demirbas, 2008).

1.4   Problem Statement

Excessive release of heavy metals into the environment due to industrialization and urbanization has posed a great problem worldwide. Unlike organic pollutants, the majority of which are susceptible to biological degradation, heavy metal ions do not degrade into harmless end products. So, heavy metals can give bad effect to human body and environment itself. Many researchers have done the research and found that adsorption is the most effective technique to remove heavy metals. The common adsorbent that has been used before to remove heavy metals from wastewater is activated carbon but it is expensive material. So, this research is aiming to solve the problem by using a low cost material from

agricultural waste as an effective adsorbent to remove heavy metal ion from aqueous solution.

1.5   Objective

The purpose of this study is to investigate the effectiveness of rice husks as adsorbent for the removal of lead ions from solutions.

1.6   Scope of Study

This research is focusing on the following scope of study:

1.   The modification of rice husks using tartaric acid to enhance the adsorption capacity.

2.   Lead ions from synthetic solutions that were prepared in laboratory are employed in investigation of metal ion adsorption parameter like contact time, adsorbent dosage amount and pH effect using rice husks.

3.   Batch experiments in laboratory scale are carried out to obtain all data in this study.

CHAPTER 2

LITERATURE REVIEW

2.1   Lead

In cooperation with the U.S. Environmental Protection Agency, the Agency for Toxic Substances and Disease Registry (ATSDR) has compiled a Priority List for 2011 called the ATSDR 2011 Substance Priority List. Based on the list, lead is ranked as second hazardous heavy metals among the substances after arsenic (ATSDR, 2011).

Lead, one of the most toxic heavy metals, is attracting wide attention of environmentalists due to its acute and chronic toxic effects in animal and human health. In addition, lead poisoning in human causes severe damage to the kidney, liver, reproductive system and nervous system. According to US EPA (1986), the current Environmental Protection Agency (EPA) standard for lead in wastewater and drinking water is 0.5 and 0.05 mg/L, respectively. However the lead ions are being added to the water stream at a much higher concentration than the prescribed limits by EPA, thus leading to the health hazards and environmental degradation (Shao *et al.*, 2011).

2.1.1 Properties of Lead

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. Lead has atomic mass 207.2 g/mol. Density of lead at 20 ^{o}C is 11.34 g/cm^3. Lead will melt at 327 ^{o}C and boil at 1755 ^{o}C as shown in **Table 2.1**.

Table 2.1: Physical and Chemical Properties of Lead

Property	Description/Value
Physical state	Soft metal
Atomic number	82
Atomic mass	207.2 g/mol
Density	11.34 g/cm3 at 20 ^{o}C
Melting point	327 ^{o}C
Boiling point	1755 ^{o}C

Source: WHO (1989)

2.1.2 Source and Usage of Lead

The major source of lead in the environment is from plastics, finishing tools, cathode ray tubes, ceramics, solders, pieces of lead flashing and other minor product, steel and cable reclamation. Lead can result in the wide range of biological effects depending upon the level and duration of exposure. In the environment lead binds strongly to particles such as oil, sediments and sewage sludge so its removal is of great concern (Sud *et al*., 2008).

Lead is used in the production of lead acid batteries, solder, alloys, cable sheathing, pigments, rust inhibitors, ammunition, glazes, and plastic stabilizers (WHO, 1989). Tetraethyl and tetra methyl lead were important because of their extensive use in the past as antiknock compounds in petrol, but their use for this purpose has been almost completely phased out in the world. From a drinking-water perspective, the almost universal use of lead compounds in plumbing fittings and as solder in water-distribution systems is important. Lead pipes may be used in older distribution systems and plumbing (Dewayanto, 2010). **Figure 2.1** showed the Percentage of Lead Usage.
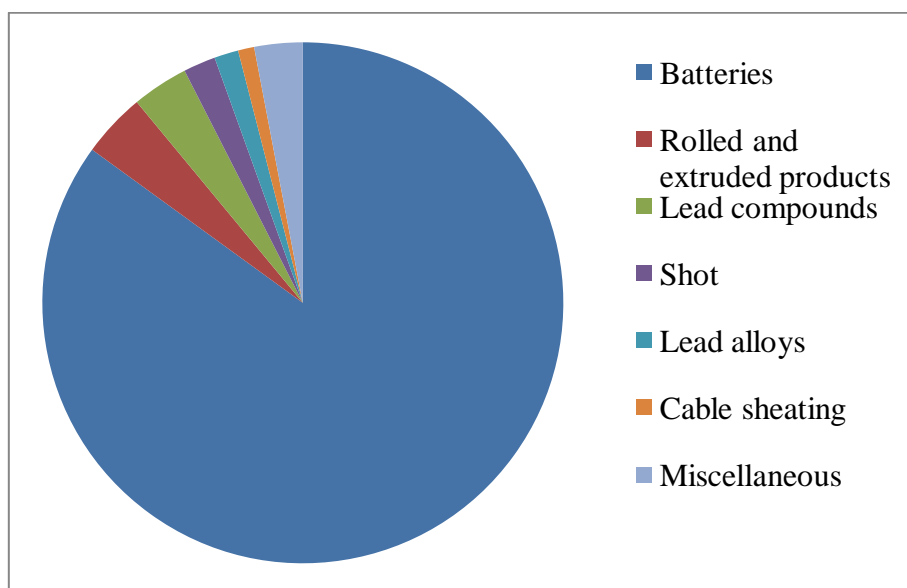
Figure 2.1: Percentage of Lead Usage

Source: International Lead and Zinc Study Group (2010)

2.1.3   Effects of Lead

Lead can enter the human body through uptake of food, water and air. It is a cumulative general poison. Infants, children up to 6 years of age, the fetus, and pregnant women are the most susceptible to adverse health effects of lead. Its effects on the central nervous system can be particularly serious. In acute and long-term exposure, lead can cause several unwanted effects, such as gastrointestinal symptoms, sleeplessness, headaches, abdominal cramps, kidney damages and loss of memory (US EPA, 1986). Renal diseases and increased of blood hypertension also have long been associated with lead poisoning.

2.2   Heavy Metals Treatment Technique

Concerning the health hazard, heavy metals are among the most detrimental pollutants in source and treated water, and are becoming a severe health problem. Since the damaging effects of heavy metals in environment are known, many methods have been developed for removal of heavy metals from waste discharges. Various chemical treatment methods have been developed for the removal and recovery of heavy metals from wastewater.

There are four major classes of conventional chemical separation technologies: chemical precipitation, electrolytic recovery, adsorption/ion exchange, and solvent extraction/liquid membrane separation. These major classes involves various methods including chemical treatment with lime, caustic oxidation and reduction, ion exchange, adsorption, reverse osmosis, solvent extraction, membrane filtration, electrochemical treatment and evaporative recovery (Dewayanto, 2010).

In order to increase the performance of chemical precipitation process, many techniques of chemical precipitation were developed. As an alternative to hydroxide precipitation, numerous companies have developed and marketed chemical products which react with metal species to form insoluble compounds such as sulfides, carbonates and carbamates. Sodium decanoate, polymers and other reagents can be used to precipitate

metal ion. However, chemical precipitation is not very suitable when the pollutants are present in trace amounts. Other disadvantage of this method is generation on of a large amount of sludge. Precipitation is accompanied by flocculation or coagulation, and one major problem is the formation of large amounts of sediments containing heavy metal ions.

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 exchange materials. Ion exchanged may facilitate an adsorption process. The exchange of ions occurs at the surface of the solid and ions are being transferred through an interphase from the liquid to the surface of the solid. Exchange materials can be comprised of resins, membranes, minerals, and clays. Major disadvantage of ion exchange is that it is expensive in capital and operating cost (Dewayanto, 2010).

Electrolytic recovery technique uses lesser chemical consumption and recover pure metal as an added economic value, but requires high capital cost and less efficient at dilute concentrations (Dewayanto, 2010).

Nevertheless the process of adsorption has become one of the preferred methods for removal of toxic contaminants from water as it has been found to be very effective, economical, versatile and simple. Adsorption has the additional advantages of applicability at very low concentrations, suitability for using batch and continuous processes, ease of operation, little sludge generation, possibility of regeneration and reuse, and low capital cost. Agricultural by-products and in some cases appropriately modified have shown to have a high capacity for heavy metal adsorption. Toxic heavy metals such as Pb^{2+}, Cd^{2+}, Hg^{2+}, Cu^{2+}, Ni^{2+}, Cr^{3+}, and Cr^{6+}, as well as some elements from lanthanide and actinides groups have been successfully removed from contaminated industrial and municipal waste waters using different agro waste materials (Lewinsky, 2007).

2.2.1   Current Adsorption Technology

The research for the new technologies adsorption involving the removal of toxic metals from wastewaters has directed attention to biosorption, based on metal binding capacities of various biological materials. Biosorption can be defined as the ability of biological materials to accumulate heavy metals from wastewater through metabolically mediated or physic-chemical pathway of uptake. The major advantages of biosorption over conventional treatment methods include low cost, high efficiency, minimization of chemical or biological sludge, no additional nutrient requirement, and regeneration of biosorbents and possibility of metal recovery. Agricultural materials mainly those containing cellulose and lignin show potential metal binding capacity. The basic components of the agricultural waste biomass include hemicelluloses, lignin, extractives, lipids, proteins, simple sugars, water hydrocarbons, and starch containing variety of functional groups that facilitates metal complexation or precipitation and which assists the heavy metals sequestration process (Yeneneh *et al*, 2010).

2.2.2   Mechanism of Biosorption

Sud *et al*. (2008) reported that the removal of metal ions from aqueous streams using agricultural materials is based upon metal biosorption. The process of biosorption involves a solid phase (sorbent) and a liquid phase (solvent) containing a dissolved species to be sorbed. Due to high affinity of the sorbent for the metal ion species, the latter is attracted and bound by rather complex process affected by several mechanism involving chemisorptions, complexation, adsorption on surface and pores, ion exchange, microprecipitation, heavy metal hydroxide condensation onto the biosurface, and surface adsorption, chelation, adsorption by physical forces, entrapment in inter and intrafibrillar capillaries and spaces of the structural polysaccharides network as a result of the concentration gradient and diffusion through cell wall and membrane (Sud *et al*., 2008).

In order to understand how metals bind to the biomass, it is essential to identify the functional groups responsible for metal binding. Most of the functional groups involved in the binding process are found in cellwalls. Plant cellwalls are generally considered as structures built by cellulose molecules, organized in microfibrils and surrounded by hemicellulosic materials (xylans, mannans, glucomannans, galactans, arabogalactans), lignin and pectin along with small amounts of protein (Dewayanto, 2010).

2.3   Properties of Agricultural Adsorbent

Agricultural materials particularly those containing cellulose shows potential metal biosorption capacity. The materials are usually composed of lignin and cellulose as the main constituents. Other components are hemicellulose, extractives, lipids, proteins, simple sugars, starches, water, hydrocarbons, ash and many more compounds that contain a variety of functional groups present in the binding process. Cellulose is a crystalline homo-polymer of glucose with ß1- 4 glycosidic linkage and intra-molecular and intermolecular hydrogen bonds. Hemicellulose is a heteropolymer of mainly xylose with ß1- 4 glycosidic linkages with other substances of acetyl feruoyl and glycouronyl groups. Lignin is three dimensional polymer of aromatic compounds covalently linked with xylans in hardwoods and galactoglucomannans in softwoods (Dewayanto, 2010).

The functional groups present in biomass molecules acetamido groups, carbonyl, phenolic, structural polysaccharides, amido, amino, sulphydryl carboxyl groups alcohols and esters. These groups have the affinity for metal complexation. Some biosorbents are non-selective and bind to a wide range of heavy metals with no specific priority, whereas others are specific for certain types of metals depending upon their chemical composition. The presence of various functional groups and their complexation with heavy metals during biosorption process has been reported by different research workers using spectroscopic techniques that facilitate metal complexation which helps for the sequestering of heavy metals (Sud *et al*., 2008).

Agricultural waste usually has high moisture content. Physical treatments on it are required to remove the moisture include natural drying under the direct sunlight, room drying, and oven drying at certain temperature. Dried materials are normally ground to obtain the specific granular size of it before employed as adsorbent. Dried materials can directly be applied as adsorbent or transformed into carbonaceous adsorbent by pyrolysis (Dewayanto, 2010).

Chemical treatment of agricultural wastes can extract soluble organic compounds and enhance chelating efficiency. Chemical treatment methods using different kinds of modifying agents such as base solutions (sodium hydroxide, calcium hydroxide, sodium carbonate) mineral and organic acid solutions (hydrochloric acid, nitric acid, sulfuric acid, tartaric acid, citric acid, thioglycollic acid), organic compounds (ethylenediamine, formaldehyde, epichlorohydrin, methanol), oxidizing agent (hydrogen peroxide), and dye (Reactive Orange 13). Chemically modified adsorbents can provide better performance for removing soluble organic compounds, eliminating coloration of the aqueous solutions and increasing efficiency of metal adsorption (Dewayanto, 2010).

2.4   Rice Husks

Many researchers have done the research on using agricultural waste in adsorption of heavy metals. They had reported that the modified rice husks are a potentially useful material for the removal of lead from aqueous solutions. The rapid uptake and high adsorption capacity make it very attractive alternative adsorption material (Khan *et al.*, 2004). Rice husks contain a high proportion of cellulose (28-36%), thus it appears to be a good candidate for modification with carboxylic acids. The addition of carboxyl fuctional groups may enhance the sorption capacities of the rice husks. Wong *et al.* (2003) showed that tartaric acid modified rice husks had the highest binding capacities for lead.

Removal of the heavy metal from solutions was possible using low cost agricultural waste by-products for example rice husks as adsorbent. Plant wastes are inexpensive as they have no or very low economic value. Abdel Ghani *et al.* (2007) had using rice husks, maize cobs and sawdust as adsorbent. They found that rice husks was the most effective adsorbent for many metals for which the removal reached 98.15% of lead at room temperature. Rice husks as shown in **Figure 2.2** can be used to treat heavy metals in the form of either untreated or chemically and thermally modified forms using different modification methods. Pretreatment of plant wastes can extract soluble organic compounds and enhance adsorption efficiency.

Figure 2.2: Rice Husks

2.4.1   Properties of Rice Husks

Rahman *et al.* (1997) investigated that rice husks consists of cellulose (32.24%), hemicelluloses (21.34%), lignin (21.44%) and mineral ash (15.05%) as well as high percentage of silica in its mineral ash, which is approximately 96.34%. Rice husks are insoluble in water, has good chemical stability, has high mechanical strength and possesses a granular structure, unique chemical composition, availability in abundance, renewable,

low in cost and more efficient are seem to be viable option for heavy metals remediation making it a good adsorbent material for treating heavy metals from wastewater (Abdel Ghani *et al.,* 2007). There are many ions studied but this research is more focus on lead.

2.4.2 Statistic of Rice Husks Production

The annual world rice production is approximately 500 million metric tons, of which 10 – 20% is rice husk. Dry rice husk contains 70 – 85% of organic matter (lignin, cellulose, sugars, etc) and the remainder consists of silica, which is present in the cellular membrane. In 2008, the world paddy production was 661 million tons and consequently 132 million tons of rice husks were also produced. According to the statistics compiled by the Malaysian Ministry of Agricultural, 408 thousand metric tons of rice husks, a commodity crop residue, is produced in Malaysia each year (Wong *et al*., 2003). **Table 2.2** showed the production of paddy by state in Malaysia for year 2006-2008.

Table 2.2: Production of Paddy in Malaysia for 2006-2008

State	Production of Paddy, Metric Tons		
	2006	2007	2008
Johor	5739	9221	8128
Kedah	776490	911295	867335
Kelantan	238433	249440	232309
Melaka	8640	7225	4158
Negeri Sembilan	6864	5091	5437
Pahang	22282	22673	21384
Perak	233923	259081	280237
Perlis	170542	198025	233144
Penang	114488	120286	120075
Selangor	176794	186951	177444
Terengganu	59671	62253	63490
Peninsular Malaysia	**1813867**	**2031541**	**2013142**
Sabah	133858	134384	133138
Sarawak	239794	209679	206753
Malaysia	**2187519**	**2375604**	**2353032**

Source: Ministry of Agricultural and Agro-based Industry (2009)

2.4.3   Modification of Rice Husks

In recent years, attention has been focused on the utilization of unmodified or modified rice husk as an adsorbent for the removal of pollutants. Researcher using tartaric acid modified rice husk as adsorbent have carried out batch studies for the removal of lead and copper and reported the effects of various parameters such as pH, initial concentration of adsorbate, particle size, temperature etc. It was reported that modified rice husk is a potentially useful material for the removal of Cu and Pb from aqueous solutions. The rapid

uptake and high adsorption capacity make it a very attractive alternative adsorption material (Khan *et al.*, 2004).

Chemical modification became popular and many researchers devised elaborate modification procedures. Biomass chemical modifications include delignification, esterification of carboxyl and phosphate groups, methylation of amino groups, and hydrolysis of carboxylate groups (Demirbas, 2008).

Wong *et al.* (2008) reported that tartaric acid is commonly used in the chemical treatment of rice husks. Pretreatment of rice husks using tartaric acid can remove lignin, hemicelluloses, reduce cellulose crystallinity and increase the porosity of surface area. In general, chemically modified or treated rice husks exhibited higher adsorption capacities on heavy metal ions than unmodified rice husks. Wong *et al.* (2008) carried out an adsorption study of lead on modified rice husks by various kinds of carboxylic acids such as tartaric acid, acetic acid, formic acid and benzoic acid. It was reported that the highest adsorption capacity was achieved by tartaric acid modified rice husks. The carboxyl groups on the surface of the modified rice husks were primarily responsible for the sorption of metal ions. The maximum adsorption capacities for lead were reported as 108 mg/g, respectively (Wong *et al.*, 2008). **Figure 2.3** shows the carboxyl groups on structure of tartaric acid.
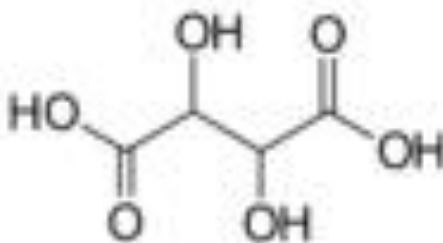
Figure 2.3: Structure of Tartaric Acid

Source: www.ask.com (2011)

2.5   Utilization of Atomic Absorption Spectrometry in Heavy Metal Analysis

2.5.1   Basic Principles of Atomic Absorption Spectrometry

The analysis of metal ion in environment is currently dominated by techniques which can be grouped together under the atomic spectrometry. The main techniques are Flame Atomic Absorption Spectrometry (Flame AAS), Graphite Furnace Atomic Absorption Spectrometry (GFAAS), Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES), and Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) (Reeve, 2002). Flame atomic absorption as shown in **Figure 2.4** is a very common technique for detecting metals and metalloids in environmental samples. It is very reliable and simple to use. The technique is based on the fact that ground state metals absorb light at specific wavelengths. Metal ions in a solution are converted to atomic state by means of a flame. Light of the appropriate wavelength is supplied and the amount of light absorbed can be measured against a standard curve. The general construction of an AAS instrument is simple and is shown schematically in **Figure 2.5**. The most important components are radiation source, which emits the spectrum of the analyte element, an atomizer in which the atoms of the analyte element are formed, a monochromator for the spectral dispersion of the radiation and separation of the analytical line from other radiation, a detector permitting measurement of radiation intensity, followed by an amplifier and a signal processing unit with a readout device (Dewayanto, 2010).

Figure 2.4: Atomic Absorption Spectrometer (AAS)
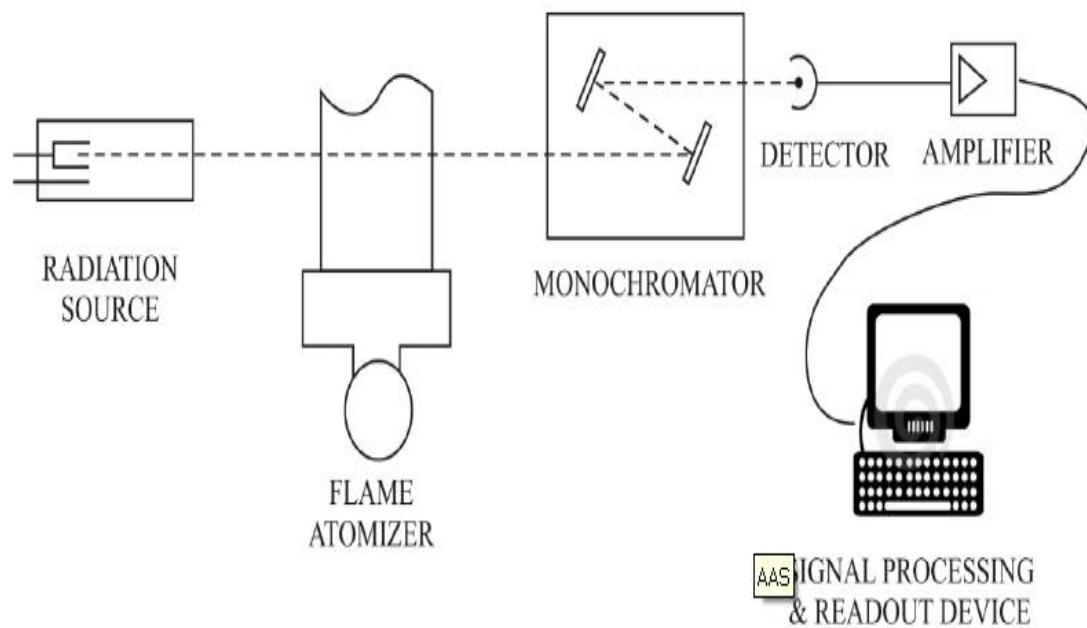
Figure 2.5: Schematic Design of an Atomic Absorption Spectrometry

Source: Dewayanto (2010)

A hollow cathode lamp is a stable light source, which is necessary to emit the sharp characteristic spectrum of the element to be determined. A different cathode lamp is needed for each element, although there are some lamps that can be used to determine more than one elements if the cathode contains all of them. The flame atomizer is the part with two major functions: nebulization of sample solution into a fine aerosol solution, and dissociation of the analyte elements into free gaseous ground state form. The monochromator isolates the specific spectrum line emitted by the light source through spectral dispersion, and focuses it upon a detector, whose function is to convert the light signal into electrical signal.

2.5.2   Quantitative Analysis

Different concentration of sample solution will give different level of absorbance. The atomic absorption spectrometry determines the contents of the elements contained in samples not as absolute values but as values relative to the contents in standard solution. Series of standard solutions at different concentration are used to establish a calibration curve. They are introduced into AAS and the absorbances of standard solution are plotted versus concentration in a calibration curve. The absorbance value of an unknown sample is fitted to the curve to obtain the concentration. **Figure 2.6** shows the typical of calibration curve.
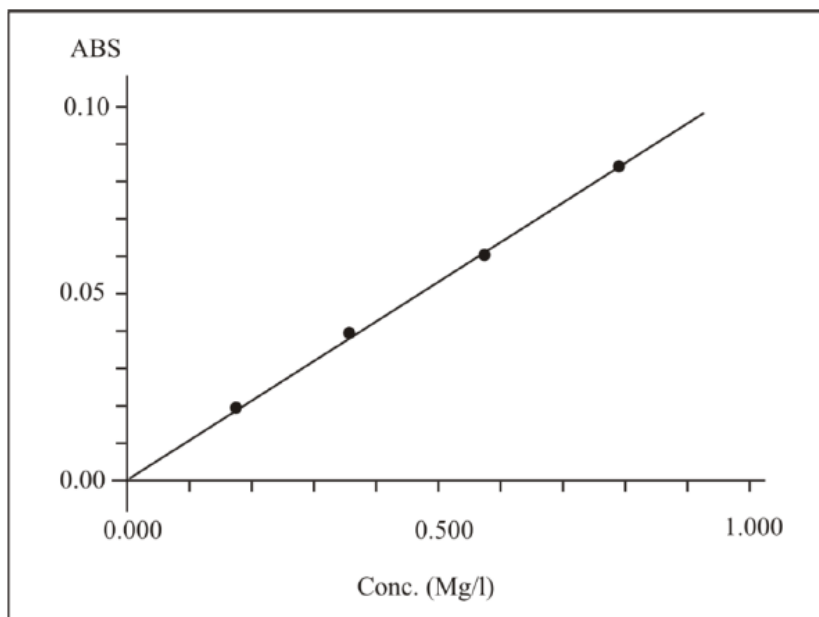
Figure 2.6: Typical Calibration Curve of AAS Analysis

Source: Dewayanto (2010)

2.5.3 Analytical Condition for Lead ion Analysis

To set up conditions optimum for analysis, some analytical conditions must be adjusted carefully for each analyte. The parameters are type of radiation source include the lamp current and wavelength, type of burner head, burner height, flame source, and fuel gas flow. Some types of AAS instrument have capability to adjust the parameters automatically. The analytical condition for lead analysis is shown in **Table 2.3**.

Table 2.3: Analytical Conditions for Lead Analysis

wavelength	283.3 nm
Slit width	1.3 nm
Time constant	1
Lamp current	9 mA
PMT voltage	540 V
Flame type	Air-C_2H_2
Fuel flow	2.21 L/min
Oxidant	160 kPa
Burner height	7.5 mm
Delay time	5 s
Measurement time	5 s

Source: AAS Manual Book

CHAPTER 3

METHODOLOGY

3.1   Material Preparation

3.1.1 Adsorbent Preparation

Raw rice husks used in this study were collected from a mill located at Kedah, Malaysia. The rice husks were washed using distilled water to remove soil and clay then were dried in an oven at 105°C for 24 hour to remove moisture. Dried rice husks were grounded to pass through a 1 mm sieve. After that, the rice husks were modified with tartaric acid using the method that adapted from Wong *et al.* (2003). The modification of rice husks were conducted by mixed the husks with tartaric acid in a ratio of 1 g rice husks to 7 mL of 0.1 M tartaric acid. The mixture was stirred for 1 hour. Then, the acid/slurry was dried in an oven at 50°C overnight. The flowchart of adsorbent preparation is shown in **Figure 3.1.**

```
┌─────────────────────────────────────────────┐
│        collected raw rice husks from mill    │
└─────────────────────────────────────────────┘
                      ↓
┌─────────────────────────────────────────────┐
│      washed rice husks using distilled water │
└─────────────────────────────────────────────┘
                      ↓
┌─────────────────────────────────────────────┐
│    dried rice husks in oven at 105 C for 24 hour │
└─────────────────────────────────────────────┘
                      ↓
┌─────────────────────────────────────────────┐
│             grounded rice husks              │
└─────────────────────────────────────────────┘
                      ↓
┌─────────────────────────────────────────────┐
│       modified rice husk with tartaric acid  │
└─────────────────────────────────────────────┘
                      ↓
┌─────────────────────────────────────────────┐
│   dried modified rice husks in oven at 50 C overnight │
└─────────────────────────────────────────────┘
```
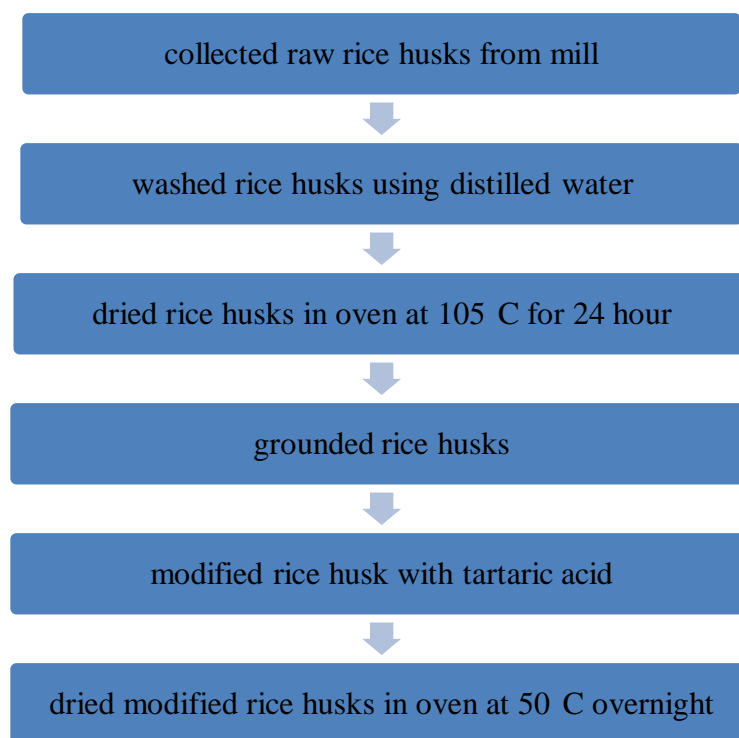
Figure 3.1: Flowchart of Adsorbent Preparation

3.1.2   Reagents Preparation

The synthetic solutions were prepared from analytical reagent grade $Pb(NO_3)_2.H_2O$. The lead powder was mixed with distilled water in ratio of 400 mg: 1 L respectively. The other chemicals that were used are dilute 0.1 M hydrochloric acid and 0.1 M sodium hydroxide to adjust the pH of metal solution.

3.2   Equipment

The equipments that were used in this research are oven to dry the rice husks, pH meter to measure the pH of solution and the orbitary shaker to speed up the separation of heavy metal ions from the solution. Besides that, Atomic Absorption Spectrometer (AAS) also was used to detect the concentration of lead ion in the samples.

3.3   Batch Study

3.3.1   Effect of Contact Time

The effect of adsorption time on adsorption efficiency has been investigated by many researchers. Generally, adsorption rate is very fast initially and increased with time but with small increasing value. The initial faster rate of metal sorption may be explained by the large number of sorption sites available for adsorption. For the initial bare surface, the sticking probability is large, and consequently adsorption proceeded with a high rate. The slower adsorption rate at the end is probably due to the saturation of active sites and attainment of equilibrium (Asrari *et al.*, 2010).

For this research, 1 g of rice husks was placed in a 100-mL conical flask with 30 mL of lead solution at a fixed initial concentration of 400 mg/L and pH value is 5. Then it was shaking on an orbitary shaker at 150 rpm. The contact times were varied at the intervals of 5 to 70 minutes as shown in **Table 3.1**. After that, the samples were taken and the final concentrations of lead were determined using AAS. This method was adopted from Asrari *et al.* (2010).

Table 3.1: Contact Time Range

Contact Time, min
5
15
30
50
70

3.3.2   Effect of Adsorbent Dosage

Asrari *et al*. (2010) had run the research on the effect of variation of adsorbent dosage/amount on the removal of metal ions by rice husks and found that it is apparent that the metal ion concentration in solution decreases with increasing adsorbent dosage for a given initial metal concentration. So, the percentage adsorption was increased with adsorbent amount. This result was anticipated because for a fixed initial solute concentration, increasing amount of adsorbent provides greater surface area.

The effect of adsorbent dosage was studied by adding the rice husks amount varying from 0.5 to 3.0 g as shown in **Table 3.2** in the 30 mL lead solution. For all these runs, the initial concentration of lead solution were fixed at 400 mg/L with pH are 5. After that, the samples were placed in the conical flasks and were shaking at 150 rpm for 1 hour on orbitary shaker. Then, all the samples were analyzed using AAS. This method was adopted from Asrari *et al*. (2010).

Table 3.2: Adsorbent Dosage Range

| Adsorbent Dosage, g |
|:---:|
| 0.5 |
| 1.0 |
| 1.5 |
| 2.0 |
| 3.0 |

3.3.3 Effect of pH

Effect of pH in metal adsorption is an important field to be studied. Most of previous studies had stated that pH significantly influence the adsorption process. Generally, in very low pH (<3) adsorption capacity of metal ion on adsorbent is low. The adsorption capacity will increase sharply in pH range of 4 – 6, and tend to be decreased or relatively constant at higher pH. Below pH 3, conditions were considered to be too acidic for adsorption to take place. Lowering the solution pH caused the surface charge on the cells to become positive, thus inhibiting the uptake of positively charged lead cations. The researcher suggested that the smaller adsorption values observed at low pH are attributed to competition between the protons and cations released by adsorbent into the solution. Protonation of negative oxygen functions on adsorbent reduces their ability to coordinate with metal ions, so at low pH metal ions are released. Most of metal ion speciation in the solution with pH up to 5 - 8 is dominated by Me2+. At pH above that, the hydrolysis of metallic ions could take place, leading to a decrease in the adsorption process (Dewayanto, 2010).

50 mL of lead solution with initial concentration was fixed at 400 mg/L were prepared in a beaker. To study the effect of pH on lead adsorption, the pH of the solution were adjusted to values in the range of 2-6 as shown in **Table 3.3** by the addition of 0.1 M HCL or 0.1 M NaOH prior to experiment. After that, 30 mL of this solution were put in the conical flask and were treated with 1 g of rice husks. Then, all the samples were shaking on orbitary shaker at 150 rpm for 1 hour before analyzed the final concentration using AAS. This method was adopted from Wong *et al*. (2003).

Table 3.3: pH Range

pH
2
3
4
5
6

2.3 Preparation for AAS Analysis

filtered the samples

diluted the samples

dropped nitric acid

prepared standard solutions
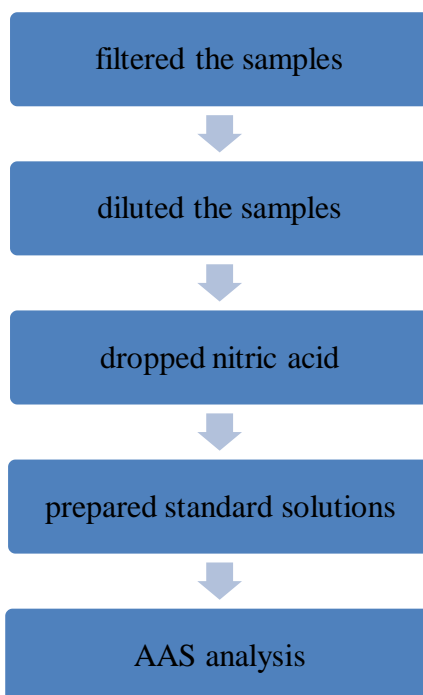
AAS analysis

Figure 3.2: Flowchart of AAS Analysis

3.4.1 Sample Preparation

As shown in **Figure 3.2, t**he samples were filtered immediately after shaking to remove rice husks. Then, the solutions were dilute a few times to get the concentration between the ranges of standard solutions. A few drops of nitric acid were added into all samples to avoid production of hydroxide precipitates.

3.4.2 Standard Solution Preparation

Standard solutions for tracing calibration curve are generally prepared by diluting a stock standard solution which was prepared at 1000 mg/L for minimizing concentration variation. Series of standard solution were prepared at concentrations of 0, 1.56, 3.13, 6.25, 12.50 and 25.00. In addition, a diluted acid is added as a stabilizer to the solutions to minimize the concentration variation caused by adsorption of the container wall and production of hydroxide. In a neutral pH, most types of elements produce hydroxide precipitates or are absorbed on the container wall. Standard solutions for tracing a calibration curve are being prepared immediately before measurement and then discarded after completing the measurements.

3.5 Analysis using Atomic Absorption Spectrometry (AAS)

A Flame Atomic Absorption Spectrometry was employed to determine the concentration of lead ion in the sample solutions. Hollow cathode lamps were used as radiation source. The other characteristics of AAS are as **Table 3.4**.

Table 3.4: Characteristic of AAS

wavelength	283.3 nm
Slit width	1.3 nm
Time constant	1
Lamp current	9 mA
PMT voltage	540 V
Flame type	Air-C_2H_2
Fuel flow	2.21 L/min
Oxidant	160 kPa
Burner height	7.5 mm
Delay time	5 s
Measurement time	5 s

AAS analysis was conducted using standard solutions followed by the samples. After that, the standard curve was got and the concentration of the samples can be found. With initial concentration, C_o is equal to 400 mg/L and final concentration, C_e that were got from AAS analysis, the percentage adsorption of Pb can be found using **Eq. 3.1**:

$$\% \ Adsorption = \frac{C_o - C_e}{C_o} \times 100\% \qquad \textbf{Eq. (3.1)}$$

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Introduction

For the research of adsorption of lead using rice husks, the rice husks that were used are waste product from the rice mill. The color of the rice husks is yellow and grounded to pass 1 mm sieve. The study was focused on three parameters only; contact time, adsorbent dosage and pH. It is well known that adsorbent dosage affected adsorption capacity by the surface area availability. For the contact time, longer the adsorbent attached the solutions, more percentage of adsorption were achieved. Besides, adsorption of heavy metal ions by solid substrates depends on the pH of the solution due to charge ions. The percentage of adsorption can be found using this equation:

$$\% \text{ Adsorption} = \frac{C_o - C_e}{C_o} \times 100\%$$

Where:

C_o is initial concentration of lead solution (400 mg/L)

C_e is equilibrium concentration got from AAS analysis

4.2 Effect of Contact Time

Table 4.1: Effect of Contact Time

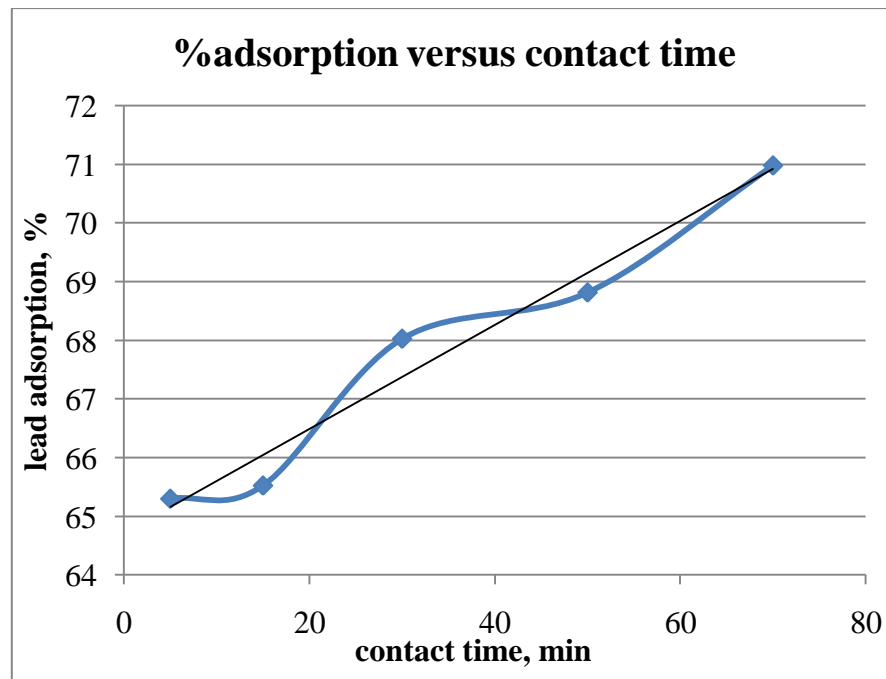| Contact Time, min	Equilibrium Concentration, mg/L	Lead Adsorption, %
5	138.8	65.3
15	137.9	65.525
30	127.9	68.025
50	124.75	68.8125
70	116.1	70.975

Figure 4.1: Effect of Contact Time

The effect of adsorption time on adsorption efficiency has been showed in **Table 4.1** and **Figure 4.1**. Adsorption rate is very fast initially; about 65% of lead is removed within 5 min. The adsorption capacity increased with time but with small increasing value from time of 5 min to maximum adsorption about 71% at 70 min. The initial faster rate of metal sorption may be explained by the large number of sorption sites available for adsorption. For the initial bare surface, the sticking probability is large, and consequently adsorption proceeded with a high rate. The slower adsorption rate at the end is probably due to the saturation of active sites and attainment of equilibrium (Asrari *et al*., 2010). If the experiment are continue, the percentage of adsorbent will increase until equilibrium time due to unavailable of sorption site.

4.3   Effect of Adsorbent Dosage

Table 4.2: Effect of Adsorbent Dosage

Adsorbent Dosage, g	Equilibrium Concentration, mg/L	Lead Adsorption, %
0.5	151.85	62.0375
1.0	139.9	65.025
1.5	106.2	73.45
2.0	89.4	77.65
3.0	79.25	80.1875

Figure 4.2: Effect of adsorbent dosage

The effect of variation of adsorbent dosage/amount on the removal of metal ions by rice husks is shown in **Table 4.2** and **Figure 4.2**. Amount of rice husks were varied from 0.5 to 3 g. It is apparent that the metal ion concentration in solution decreases with increasing adsorbent dosage for a given initial metal concentration. So, the percentage adsorption was increased with adsorbent amount. From 0.5 g to 1.0 g, the difference in percentage was small then from 1.5 g to 2.0 g, the increasing of adsorption is quite large. After that, the adsorption is still increase but in small value. The maximum percentage of adsorption is at 3.0 g with 80%. This result was anticipated because for a fixed initial solute concentration, increasing amount of adsorbent provides greater surface area (Asrari *et al*., 2010). If the dosage is increase more, the adsorption percentage will increase until equilibrium concentration.

4.4   Effect of pH

Table 4.3: Effect of pH

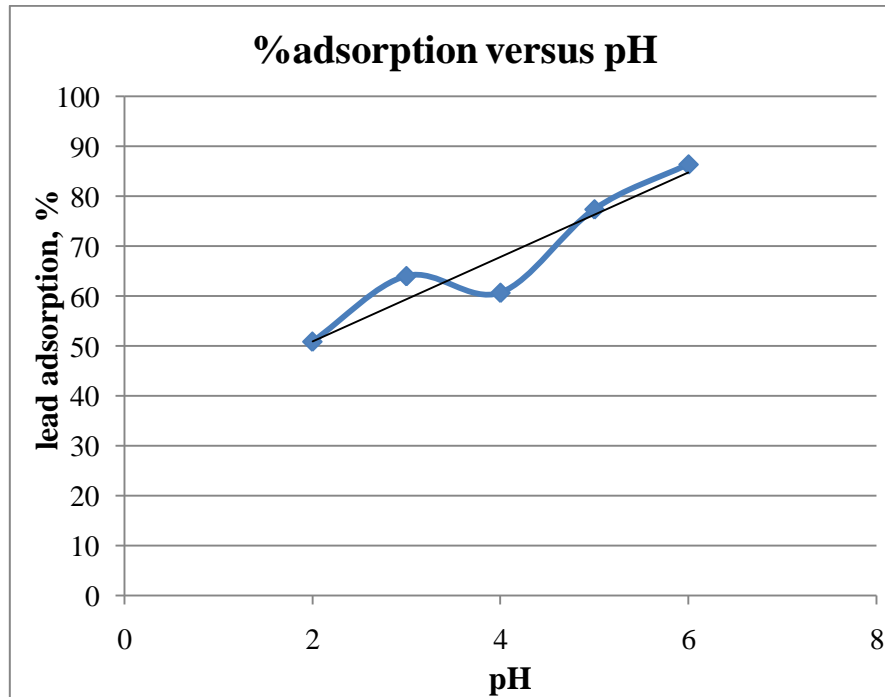| pH of solution	Equilibrium Concentration, mg/L	Lead Adsorption, %
2	196.4	50.9
3	143.9	64.025
4	157.25	60.6875
5	90.4	77.4
6	54.4	86.4

Figure 4.3: Effect of pH

Changes in solution pH can alter the chemical nature of the functional groups on the rice husks and then the metal adsorption capacity of the adsorbent. **Table 4.3** and **Figure 4.3** displayed the lead ion adsorption on the rice husks as a function of solution pH. It showed that the adsorption amount of lead increases with the increase of solution pH from 2 until 3, then decrease at pH 4 before increase again from 4 to 6. It means the adsorption process is pH-dependent. At low solution pH, the carboxyl functional groups on the rice husks are positively-charged; the adsorption capacity is lower; while at higher pH, the deprotonated groups are involved in lead ion adsorption and form carboxylate anion. It is also known that heavy metal cations are completely released under circumstances of extreme acidic conditions. Metal biosorption is a rather complex process affected by several factors. Mechanisms involved in the biosorption process include adsorption (chemisorption), complexation on surface and pores, ion exchange, microprecipitation, heavy metal hydroxide condensation onto the biosurface, and surface adsorption (Asrari *et al.*, 2010). The exclusion for pH 4 is related to a few factors such as precipitation and contamination.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

Rice husks are one of the agricultural waste products. Besides can reduce the amount of it as a waste itself, rice husks also can be useful material to reduce another waste that is heavy metals from solution. The rice husks were modified with 0.1 M tartaric acid with ratio 1 g rice husks to 7 mL tartaric acid before have been used as adsorbent in batch study to treat lead solution. Adsorption is highly dependent on the contact time, adsorbent dose and pH. The rapid uptake and high sorption capacity when the experiment was conducted at effective contact time, adsorbent dosage and pH value made it very attractive alternative sorbent materials.

In this study, when the contact time increased, the percentage adsorption also increased and the maximum adsorption is 71% at 70 min. The adsorption capacity also increased with increasing of adsorbent dosage due to higher surface area with maximum value of 80% at 3.0 g. This research also indicated that the percentage adsorption of lead ion increased when pH was increased because the increasing of sorption capacity and the maximum percentage adsorption is 86% at pH 6.

5.2   Recommendations

In way to get more effective and success results, many improvements could be done from this research. One of that is to compare the rice husks with other adsorbents such as saw dust, maize corn cob and sugarcane bagasse to get which is the better adsorbent. Besides that, the researcher also could prolong the time, use more dosage of adsorbent and increase pH to get the actual equilibrium concentration. Despite of using synthetic waste water that prepared in laboratory, researcher could use waste water from industry. The other improvement could be make is using other chemical to treat rice husks and make the comparison.

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APPENDIX A

CALCULATION OF LEAD STANDARD SOLUTION

The lead standard solution that was get from lab that has concentration of 1000 mg/L was diluted to 100 mg/L in 250 mL ultrapure water

M_1V_1 $\quad\quad = M_2V_2$

$1000V_1$ $\quad\quad = 100(250)$

V_1 $\quad\quad = 25$ mL

25 mL of 1000 mg/L lead standard solution were added to water to get total 250 mL new solution that has concentrate 100mg/L using volumetric flask.

From, 100 mg/L, the solution was diluted again to lower concentration

M_1V_1 $\quad\quad = M_2V_2$

$100V_1$ $\quad\quad = 25(25)$

V_1 $\quad\quad = 6.25$ mL

M_2 (mg/L)	V_1 (mL)
25	6.25
12.5	3.125
6.25	1.563
3.125	0.781
1.5625	0.39
0	25

APPENDIX B

CALCULATION OF RESULT FROM AAS ANALYSIS

From this equation, we can calculate the percentage of adsorbent

For the example, using C_o is 400 mg/L, the percentage of contact time at 5 min is:

% Adsorption $= \dfrac{C_o - C_e}{C_o}$ *x 100%*

$\qquad = \dfrac{400 - 138.8}{400}$ x 100%

$\qquad = 65.3\%$

Contact Time (min)	Equilibrium concentration, C_o (mg/L)	Lead Adsorption (%)
5	138.8	65.3
15	137.9	65.525
30	127.9	68.025
50	124.75	68.8125
70	116.1	70.975

Adsorbent Dosage (g)	Equilibrium Concentration, C_o (mg/L)	Lead Adsorption (%)
0.5	151.85	62.0375
1.0	139.9	65.025
1.5	106.2	73.45
2.0	89.4	77.65
3.0	79.25	80.1875

pH of solution	Equilibrium Concentration, Ce (mg/L)	Lead Adsorption (%)
2	196.4	50.9
3	143.9	64.025
4	157.25	60.6875
5	90.4	77.4
6	54.4	86.4

APPENDIX C1

RAW DATA FROM AAS ANALYSIS - CONTACT TIME

Table of Each Element   11/23/2011 3:15 PM

Analysis Mode   : Flame/Manual
Analysis Name   : Standard Analysis
Comment   : BKF3771
Description   : biosorption of lead using rice husks

Meas. Date   : 11/23/2011 3:15 PM
Element : Pb   STD Unit   :   UNK Unit   :

Sample ID	Sample Name	Conc.	RSD(%)	ABS	REF
STD1		0.00	0.00	0.0796	0.0004
STD2		1.56	0.00	0.0953	0.0018
STD3		3.13	0.00	0.1137	0.0018
STD4		6.25	0.00	0.1515	0.0026
STD5		12.50	0.00	0.2116	0.0105
STD6		25.00	0.00	0.3190	0.0231

Coefficient   : K3=--
                 K2=--
                 K1=9.592118E-003
                 K0=8.434297E-002
Corr.Coef.   : 0.9979

Sample ID	Sample Name	Conc.	RSD(%)	ABS	REF
UNK-001	5 mnt	138.80	0.00	0.3506	0.0240
UNK-002	15 mnt	137.90	0.00	0.3489	0.0206
UNK-003	30 mnt	127.90	0.00	0.3297	0.0209
UNK-004	50 mnt	124.75	0.00	0.3237	0.0195
UNK-005	70 mnt	116.10	0.00	0.3071	0.0131

APPENDIX C2

RAW DATA FROM AAS ANALYSIS – ADSORBENT DOSAGE
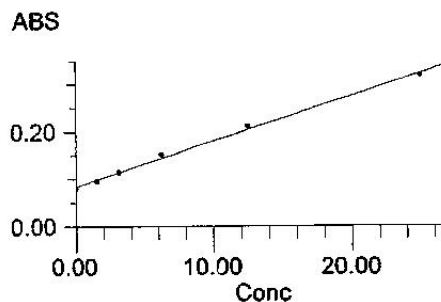
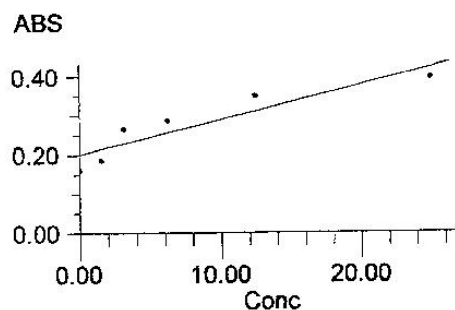Table of Each Element   11/22/2011 8:41 PM

Analysis Mode : Flame/Manual
Analysis Name : Standard Analysis
Comment   : BKF3771
Description   : biosorption of lead using rice husks

Meas. Date   : 11/22/2011 8:41 PM
Element : Pb   STD Unit   :   UNK Unit   :

Sample ID	Sample Name	Conc.	RSD(%)	ABS	REF
STD1		0.00	0.00	0.1594	-0.0001
STD2		1.56	0.00	0.1854	-0.0023
STD3		3.13	0.00	0.2643	0.0016
STD4		6.25	0.00	0.2857	0.0018
STD5		12.50	0.00	0.3494	0.0146
STD6		25.00	0.00	0.3938	0.0140

Coefficient : K3=--
       K2=--
       K1=8.812562E-003
       K0=2.018533E-001
Corr.Coef.   : 0.9117

Sample ID	Sample Name	Conc.	RSD(%)	ABS	REF
UNK-001	0.5g	151.85	0.00	0.4695	0.0139
UNK-002	1.0g	139.90	0.00	0.4484	0.0209
UNK-003	1.5g	106.20	0.00	0.3890	0.0078
UNK-004	2.0g	89.40	0.00	0.3594	0.0032
UNK-005	3.0g	79.25	0.00	0.3415	0.0028

APPENDIX C3

RAW DATA FROM AAS ANALYSIS – pH

Table of Each Element   11/22/2011 6:04 PM

Analysis Mode   : Flame/Manual
Analysis Name   : Standard Analysis
Comment   : BKF3771
Description   : biosorption of Pb using rice husks

Meas. Date   : 11/22/2011 6:04 PM
Element : Pb   STD Unit   :   UNK Unit   :

Sample ID	Sample Name	Conc.	RSD(%)	ABS	REF
STD1		0.00	0.00	0.2645	-0.0071
STD2		1.56	0.00	0.2832	-0.0293
STD3		3.13	0.00	0.3291	-0.0482
STD4		6.25	0.00	0.3544	-0.0475
STD5		12.50	0.00	0.4226	-0.0532
STD6		25.00	0.00	0.4825	-0.0510

Coefficient   : K3=--
                 K2=--
                 K1=8.573191E-003
                 K0=2.868358E-001
Corr.Coef.   : 0.9651
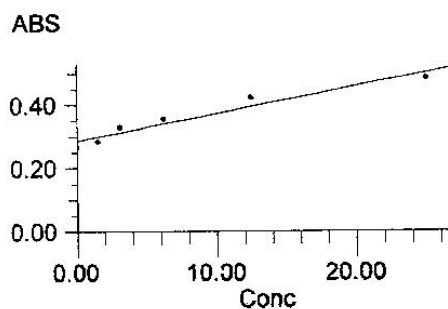
Sample ID	Sample Name	Conc.	RSD(%)	ABS	REF
UNK-001	ph 2	196.40	0.00	0.6236	-0.0472
UNK-002	ph 3	143.90	0.00	0.5336	-0.0651
UNK-003	ph 4	157.25	0.00	0.5565	-0.0712
UNK-004	ph 5	90.40	0.00	0.4418	-0.0801
UNK-005	ph 6	54.40	0.00	0.3801	-0.0894