BIOSORPTION OF COPPER USING RICE HUSK

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BORANG PENGESAHAN STATUS TESIS

JUDUL : BIOSORPTION OF COPPER USING RICE HUSK

SESI PENGAJIAN : 2011/2012

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BIOSORPTION OF COPPER USING RICE HUSK

TUAN NOR IMANI BINTI TUAN YUSOF

Thesis submitted in fulfillment of the requirements
for the award of the degree of
Bachelor of Chemical Engineering

Faculty of Chemical & Natural Resources Engineering
UNIVERSITI MALAYSIA PAHANG

JANUARY 2012

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

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ACKNOWLEDGEMENTS

I am grateful and would like to express my sincere gratitude to my supervisors, Mr. Mohd Najib Razali and Madam Siti Kholijah Abdul Mudalip, whose continuous encouragement, guidance and support me during done my undergraduate research project and completing this thesis. My sincere thanks go to all technical officers and staffs in laboratory of Faculty of Chemical and Natural Resources Engineering for the co-operation and kindest help.

Also, I owe my deepest gratitude to my friends and others coursemates who always beside me and help me a lot. Last but not least, special thanks to my beloved family especially my parents, Tuan Yusof Bin Tuan Hussin and Mariani Binti Ismail, for continuous support, advice and motivation me throughout my life.

Lastly, I offer my regards and blessings to all of those who supported me in any respect during the completion of this thesis.

ABSTRACT

Excessive release of heavy metals into the environment is becoming the important part to be considered. Some of heavy metals widely discharged as ions into wastewater are cadmium, copper, lead, zinc, mercury, and iron. Copper is a common substance that occurs naturally in the environment and spreads through the environment due naturally phenomena and some activities such as mining, metal production and phosphate fertilizer production. Thus, the elimination of copper is very important because copper is a trace element that is dangerous for human health. The objective of this thesis is to investigate the effectiveness of rice husk as adsorbent for the removal of copper ions from synthetic wastewater. This study was apply the adsorption process in copper solution. Investigation was carried out by studying the effect of initial solution pH, dosage amount of adsorbent and duration time. Effect of different pH value were study using pH value of 2 to 6, while dosage amount of rice husk is between 0.5 to 5.0 g/L and duration time is 10 to 90 minutes. The results of removal copper ion were determined using refractometer where the refractive index of each sample is checked. Then, the concentration is determined using the standard curve. It was found that, the removal of copper ions increased as dosage amount of rice husk increase. However, the percentage of removal decreased with the increasing of adsorbent dosage at value 3.0 g and above. Also, the adsorption of copper ions increases with increasing the pH value. At pH value 6, the percentage of removal is decrease because the solution started precipitate. For the effect of duration time, the result obtained show that the removal of copper is increase as the duration time is increase. The experimental data were analyzed to determine the maximum adsorption capacity of each parameter for copper ions removal. It shows that the maximum adsorption capacity for pH, adsorbent dosage and duration time parameter is 75%, 82.5% and 75% respectively.

ABSTRAK

Pembebasan unsur logam berat yang semakin meluas ke dalam persekitaran harus diberi perhatian yang serius. Logam berat seperti kadmium, kuprum, plumbum, zink, merkuri dan besi ini dibebaskan dalam bentuk ion menerusi sisa-sisa pembuangan industri. Kuprum adalah salah satu unsur logam berat yang banyak ditemui dalam persekitaran yang disebabkan oleh aktiviti seperti perlombongan, pembuatan logam dan penghasilan baja kimia. Oleh itu, penyingkiran logam kuprum dari persekitaran amat penting kerana ia dapat membahayakan kesihatan manusia. Objektif utama tesis ini ialah untuk menyiasat keberkesanan sekam padi sebagai agen penyerapan ion-ion kuprum yang terdapat dalam sisa air dan pembuangan. Kajian dilakukan dengan menggunakan larutan kuprum untuk mengkaji perubahan kepekatan untuk setiap pH, kuantiti sekam padi yang digunakan dan perbezaan tempoh masa. Untuk analisis ke atas perubahan pH, nilai-nilai pH yang digunakan ialah 2 hingga 6 manakala untuk kuantiti sekam padi, jumlah yang digunakan ialah antara 0.5 gram hingga 5 gram dan untuk tempoh masa ialah antara 10 minit hingga 90 minit. Hasil eksperimen yang diperolehi akan dianalisis dengan menggunakan refractometer dimana indek refrektif akan ditentukan. Kemudian, kepekatan setiap sampel akan ditentukan berdasarkan graf yang diperolehi. Berdasarkan keputusan yang diperolehi, didapati penyingkiran ion kuprum akan bertambah apabila jumlah sekam padi yang digunakan bertambah. Walau bagaimanapun, peratusan penyingkiran kembali berkurang apabila jumlah yang digunakan adalah 3 gram keatas. Penyingkiran ion daripada larutan kuprum juga meningkat apabila nilai pH yang digunakan meningkat. Pada nilai pH 6, peratusan kembali menurun kerana proses pemendapan berlaku pada larutan tersebut. Dan akhir sekali, untuk perubahan tempoh masa, semakin lama tempoh masa yang digunakan semakin meningkat peratus penyingkiran ion kuprum. Data yang diperolehi dianalisis untuk menentukan jumlah maksimum kadar penjerapan keatas unsur kuprum. Kadar penjerapan maksimum untuk perbezaan pH, jumlah sekam padi yang digunakan dan tempoh masa masing-masing ialah 75%, 82.5% dan 75%.

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CHAPTER 1

INTRODUCTION

1.1 Introduction

The presence of heavy metals in the environment is becoming the important part to be considered. Some of heavy metals widely discharged as ions into wastewater are containing cadmium, copper, lead, zinc, mercury, and iron. The industries that excessive release the heavy metals to environment includes chemical industries, electric and electronic, mining, constructions, urbanization process and many more. According to Demirbas (2008), heavy metal ions are reported as priority pollutant due to their mobility in natural water ecosystems. Also, heavy metals have high toxicity. Kehinde *et al.* (2009) state that heavy metals bioaccumulate in living organisms reaching levels that cause toxicological effects. So, industrial wastewaters contaminated with heavy metals are dangerous to the living things. The exposure of it can cause of diseases and affect the health. Thus, elimination of heavy metal from waste water is very important.

Copper metal is a widely used material. Copper can be found in many wastewater sources including printed circuit board manufacturing, electronics plating, plating, wire drawing, copper polishing, paint manufacturing, wood preservatives and printing operations. Unfortunately, copper is a persistent, bioaccumulative and toxic chemical that does not readily break down in the environment and is not easily metabolized. It may accumulate in the human or ecological food chain through consumption or uptake and may be hazardous to human health or the environment. The effects of consumption of high levels of copper may cause vomiting, diarrhea, stomach cramp and nausea. Also, the chronic effect may cause liver and kidney damage (Tumin *et al*, 2008).

There are several methods that suitable for elimination or removal of heavy metals from waste water including the copper. These methods include ion-exchange, adsorption, membrane separation and precipitation (Khan *et al*, 2004). However, among these methods, there have been found to be limited because of high capital and operational cost and precipitation generate large quantity of sludge (Kumar, 2006). Research done by Ahalya *et al*. (2003), also said that removal of heavy metals using reverse osmosis, ultrafiltration, ion exchange, chemical precipitation have disadvantages like incomplete metal removal, high reagent and energy requirements, generation of toxic sludge or other waste product that required careful disposal.

According to Kumar *et al*. (2010), in the past few years, adsorption has been shown to be an economically feasible alternative method for removing of metals from waste water. Compare to others method, adsorption become the cheapest method because adsorbent used is a by-product materials. Some of the advantages of using plants or agricultural wastes for waste water treatment include simple technique, requires little processing, good adsorption capacity, low cost and easy regeneration (Ngah and Hanafiah, 2008).

In the past few years, adsorption including biosorption derives from agricultural waste and microbes have appeared as emerging techniques that could provide alternative processes for conventional physical and chemical methods for removing toxic from wastewater. Hence, researchers have been made a lot of effort and modification on screening efficient biomass types, biosorption mechanism and their preparation.

The term of biosorption is used to describe the process that based on biological or biomass materials. According to Alluri *et al*. (2007), the biosorption process involves a solid phase that is sorbent or biosorbent; usually a biological material and a liquid phase as a solvent, normally water containing a dissolved species to be sorbed called sorbate which is a metal ion. The materials that used as adsorbent include bacteria, fungi, algae and agricultural by-products (Opeolu *et al*, 2010). Some of the agricultural materials used as adsorbent are sawdust, coconut shell, rice husk, soybean hulls, sugarcane husk and others.

Removal of heavy metal ions from the aqueous streams by agricultural waste materials is becomes an innovative and promising technology. Sud *et al.* (2008) said that the efficiency of the waste material depends upon the capacity, affinity, and specificity including physico-chemical nature of it. Also, due to inexpensive of biosorbent materials, high efficiency and other advantages, biosorption is becoming a potential alternative to the existing technologies for removal of heavy metals from waste water.

1.2 Problem Statement

Copper is a common substance that occur naturally in the environment and spreads through the environment due naturally phenomena and some activities. Examples of natural source that contribute to copper release are wind-blown dust, decaying vegetation, forest fires and sea sprays. The activities that release the copper to environment include mining, metal production, wood production and phosphate fertilizer production. Because copper is released both naturally and through human activities, it is very widespread in the environment.

The presence of copper in the environment give the bad effect on living things especially humans health. Long-term of exposure to copper can cause irritation of the nose, mouth and eyes and it causes headaches, vomiting, dizziness and diarrhoea. Thus, the elimination of copper is very important because copper is a trace element that is dangerous for human health. The adsorption of copper using adsorbent is one of the method to reduce this problem.

Paddy is one of most widely planted crop in Malaysia. During mailing of paddy, about 22% of the weight of paddy is received as husk. Thus, rice husk is become waste product that farmers struggle to dispose. Because of its large volume, it can cause the environmental pollution. Today, the uses of rice husk are continually growing. Many research had be done to investigate the advantage of rice husk in any field.

1.3 Objective

The purpose of this study is to investigate the effectiveness of rice husk as adsorbent for the removal of copper ions from wastewater.

1.4 Scope of Study

This research will be carry out by divided into two step. Firstly is preparation of raw material and followed by study the effect of parameters.

Preparation of raw material is done by treating the rice husk using citric acid. Modification of rice husk is done in order to increase the capacity of adsorption. Citric acid will help to bind with adsorption sites due to its functional group and hence can increase the percentage of removal.

Effect of parameters will be study by varying the pH value, dosage amount of adsorbent and duration time. Effect of different pH value will be study using pH value of 2 to 6, while dosage amount of rice husk is between 0.5 to 10 g/L and duration time is 10 to 90 minutes.

1.5 Rationale and Significance

The world's copper production is continually rising. This basically means that more and more copper ends up in the environment. Due to the disposal of copper-containing wastewater, rivers are contaminated with copper. Most copper compounds will settle and be bound to either water sediment or soil particles and usually water-soluble copper compounds occur in the environment after release through application in agriculture.

The rationale and significance of removing the copper ions from wastewater is to protect the human health. Excessive of exposure to copper will give the chronic effect to health. So, as the copper is harmful for us, it is important to remove it using adsorption process.

Besides for human health, it is helpful for industries that involve in mailing the paddy. This is because adsorption process can use the waste product of paddy as adsorbent. The significance for industry is they can reduce the cost of managing the waste product. Other than that, it can avoid from pollution of the environment. By using the waste product as an adsorbent, it can avoid from disposed to the environment.

CHAPTER 2

LITERATURE REVIEW

2.1 Adsorption

2.1.1 Background

Adsorption is a process in which molecules of gas, liquid or dissolved solids adhere to a surface. It used a solid to remove particles from a liquid or gas that passes across it. There are two types of adsorption that is physisorption and chemisorption.

Physisorption involve Van Der Waals and electrostatic forces while chemisorption involve chemical bonding. Physisorption is the most common form of adsorption. In the physisorption, the molecules are attracted by van der Waals forces, and attach themselves to the surface of the solid. The molecules are remain intact, and can be freed easily that the forces are small and short-range. While, chemisorption process is the molecules undergo a chemical bonding with the molecules of the solid, and this attraction may be stronger than the forces holding the solid together. If the molecules are removed, they may form different compounds (Willis, n.d.)

Adsorption technique is widely used method for the removal of organic and inorganic pollutants from wastewater streams. This is because adsorption is the simplest method and relatively cost-effective, thus it has been widely used (Asrari *et al*, 2010). The adsorption process need low cost and minimize in usage of chemicals sludge. It also has high efficiency in removal of ions concentration in heavy metals. Also, the operation of adsorption system is less maintenance and supervision required (Weng *et* *al*, 2007). There are many types of adsorption materials used as adsorbent such as activated carbon, waste materials include agriculture or industrial waste, inorganic or organic adsorbents and biosorbents.

2.1.2 Mechanism of Adsorption Process

The adsorption process involves a solid phase (sorbent or biosobent) and a liquid phase (solvent) containing a dissolved species to be sorbed (sorbate, a metal ion). Due to higher affinity of the sorbent for the sorbate species the latter is attracted and bound with the different mechanisms. The process continues till the equilibrium is established between the amounts of solid-bound sorbate species and its portion remaining in the solution.

While there is a preponderance of solute (sorbate) molecules in the solution, there are none in the sorbent particle to start with. This imbalance between the two environments creates a driving force for the solute species. The heavy metals adsorb on the surface of biomass thus, the biosorbent becomes enriched with metal ions in the sorbate (Alluri et al, 2007).

In adsorption processes, one or more component of a gas or liquid stream are adsorbed on the surface of a solid adsorbent and a separation is accomplished. While, in commercial processes, the adsorbent is usually in the form of small particles adsorb component from fluid. When the bed is almost saturated, the flow in this bed is stopped and the bed is regenerated thermally or by other method so that desorption occurs. The adsorbed material (adsorbate) is thereby recovered and the solid adsorbent is ready for another cycle of adsorption.

2.2 Adsorption Techniques

Many methods that are being used to remove heavy metal ions. The most common techniques that widely used in heavy metal treatment include biosorption, adsorption, ion exchange and chemical precipitation.

2.2.1 Biosorption

Biosorption of heavy metals from aqueous solutions is a relatively new process that has proven very promising in the removal of contaminants from aqueous effluents. Adsorbent materials derived from low-cost agricultural wastes can be used for the effective removal and recovery of heavy metal ions from waste water streams (Demirbas, 2008). Typical biosorbents can be derived from three sources as follows:

i) ion-living biomass such as bark, lignin, shrimp, krill, squid, crab shell and many more.
ii) algal biomass
iii) microbial biomass such as bacteria, fungi and yeast.

The major advantages of biosorption technology are its effectiveness in reducing the concentration of heavy metal ions to very low levels and the use of inexpensive biosorbent materials. Compared to others conventional treatment methods, the advantages of biosorption include low-cost in processing, high efficiency, minimization of chemical or biological sludge, regeneration of biosorbent, no additional nutrient requirement and possibility of metal recovery. The cost advantage of biosorption technology would guarantee a strong penetration of the large market of heavy metal polluting industries at nowdays.

2.2.2 Adsorption

Adsorption is now recognized as an effective and economic method for heavy metal wastewater treatment. The adsorption process offers flexibility in design and operation and in many cases will produce high-quality treated effluent. In addition, because adsorption is sometimes reversible, adsorbents can be regenerated by suitable desorption process (Fu and Wang, 2011).

For low concentrations of metal ions in wastewater, the adsorption process is recommended for their removal. The process of adsorption implies the presence of an adsorbent solid that binds molecules by physical attractive forces, ion exchange, and chemical binding. It is advisable that the adsorbent is available in large quantities, easily regenerable, and cheap (Demirbas, 2008).

Based on Naiya *et al*, (2009), among the other technologies, adsorption is a user-friendly technique for the removal of heavy metal. This process seems to be most versatile and effective method for removal of heavy metal if combined with appropriate regeneration steps. This solves the problem of sludge disposal and renders the system more viable, especially if low cost adsorbents are used.

According to Sud *et al*, (2008), another powerful technology is adsorption of heavy metals by activated carbon for treating domestic and industrial waste water. However the high cost of activated carbon and its loss during the regeneration restricts its application.

2.2.3 Ion Exchange

Ion exchange is a reversible chemical reaction wherein an ion (an atom or molecule that has lost or gained an electron) from solution is exchanged for a similarly charged ion attached to an immobile solid particle.

Ion-exchange processes have been widely used to remove heavy metals from waste water due to their many advantages, such as high treatment capacity, high removal efficiency and fast kinetics. In this process, metal ions from dilute solutions are exchanged with ions held by electrostatic forces on the exchange resin.

Ionic charge plays an important role in ion exchange process. The research done by Abo-Farha *et al* (2009), show the influence of ionic charge on the removal of heavy metals ions. Normally a weak base cation resin in the sodium form is effective for this treatment. But, anion resin can also be used if the copper is chelated with a soluble anion or the anion resin itself can be doped or spent with the desired anion to remove the copper. This method is useful in selectively removing copper in the presence of other metals

The solid ion exchange particles are either naturally occurring inorganic zeolites or synthetically produced organic resins. Either, synthetic or natural solid resin, ion-exchange resin has the specific ability to exchange its cations with the metals in the wastewater. The synthetic organic resins are the predominant type used today because their characteristics can be tailored to specific applications. Among the materials used in ion-exchange processes, synthetic resins are commonly preferred as they are effective to nearly remove the heavy metals from the solution (Fu and Wang, 2011).

2.2.4 Chemical Precipitation

Chemical precipitation is effective and by far the most widely used process in industry because it is relatively simple and inexpensive to operate. Inprecipitation processes, chemicals react with heavy metal ions to form insoluble precipitates. The forming precipitates can be separated from the water by sedimentation or filtration. And the treated water is then decanted and appropriately discharged or reused. The conventional chemical precipitation processes include hydroxide precipitation and sulfide precipitation. The others chemical precipitation is heavy metal chelating precipitation (Fu and Wang, 2011).

2.3 Rice Husk

2.3.1 Background

Rice husk is the outer covering of paddy and accounts for 20–25% of its weight. It is removed during rice milling and is used mainly as fuel generating CO_2 and other forms of pollution to the environment. In recent years, attention has been focused on the utilization of unmodified or modified rice husk as a sorbent for the removal of pollutants. Many researchers have done their research on the effectiveness of rice husk as an adsorbent. Unmodified rice husk has been evaluated for their ability to bind metal ions. Also, various modifications on rice husk have been reported in order to enhance sorption capacities for metal ions and other pollutants.

2.3.2 Production of Rice Husk

In Malaysia, paddy is the third most widely planted crop after palm oil and rubber. On average, paddy production in Malaysia is about 2 million tonnes yearly (Sarkawi and Aziz, 2003). During milling of paddy, about 78% of weight is received as rice, broken rice and bran. Rest 22% of the weight of paddy is received as husk. For every 1000 kgs of paddy milled, about 220 kgs (22 %) of husk is produced.

Table 2.1: Principal Statistics of Paddy and Rice by All Seasons in Malaysia

Year	Planted Area (Hectares)	Average Yield Hectareage (kg/hectares)	Paddy Production (Tonnes)	Rice Production (Tonnes)
2000	698 702	3064	2 140 904	1 381 662
2001	673 634	3110	2 094 995	1 351 461
2002	678 544	3238	2 197 351	1 415 117
2003	671 820	3360	2 257 037	1 453 137
2004	676 310	3434	2 291 353	1 467 052
2005	666 781	3471	2 314 378	1 490 015
2006	676 034	3236	2 187 519	1 407 220
2007	676 111	3514	2 375 604	1 530 971
2008	656 602	3584	2 353 032	1 516 470

Note: Peninsular Malaysia

Source: Department of Agriculture, Malaysia

2.3.3 Properties of Rice Husk

Rice husk has several characteristics that make it a potential adsorbent with binding sites capable to take up metals from aqueous solution. Rice husk is insoluble in water, has good chemical stability, has high mechanical strength, and possesses granular structure, making it a good adsorbent material for treating heavy metals from wastewater (Ngah & Hanafiah, 2007). This adsorbent also generally inexpensive and ready for use as it can be obtained locally.

In term of chemical composition, the rice predominantly contains cellulose (32-47%), hemicellulose (19-27%) and lignin (5-24%) (El-Sayed *et al*, 2010). Rice husk also contains lots of silica. Another characteristics of rice husk are:

- Rice husk is difficult to igninte and it does not burn easily with open flame unless air is blown through the husk. It is highly resistant to moisture penetration and fungal decomposition. Husk therefore makes a good insulation material.
- Rice husk has a high silica (SiO_2) contents which means that it decomposes slowly when brought back to the field. It also makes it a poor foder.
- Handling of rice husk is difficult because it is bulky and dusty. It has angle of repose is about 40-45° which means that it's flow ability, e.g. in feed hoppers is very poor.
- Rice husk has low bulk density of only 70-110 kg/m^3, 145 kg/m^3 when vibrated or 180kg/m^3 in form of brickets or pellets. It thus requires large volumes for storage and transport, which makes transport over long distances un-economical.
- Rice husk has a high average calorific value of an 3410 kcal/kg and therefore is a good, renewable energy source.
- Because of the high silica contents rice husk is very abrasive and wears conveying elements very quickly.
- Rice husk is not an easy fuel.

2.4 Heavy Metal

Heavy metals are chemical elements with a specific gravity that is at least 5 times the specific gravity of water. The specific gravity of water is 1 at 4°C (39°F). Some definition state that heavy metals are a group of element between copper and lead on the periodic table of the element-having atomic weight between 63.546 and 200.59. Example of heavy metal is copper, lead, cadmium, mercury, cobalt, zinc and others.

Heavy metals are dangerous because they tend to bioaccumulate. Bio-accumulation means an increase in the concentration of a chemical in a biological organism over time, compared to the chemical’s concentration in the enviroment. Compound accumulate in living things at any time as they are taken up and store fasted than they are broken down or excreted, (Lenntech (n.d.), retrieved on January 2012, from http://www.lenntech.com/processes/heavy/heavy-metals/heavy-metals.htm)

Heavy metals also become toxic when they are not metabolized by the body and accumulate in the soft tissues. Alluri *et al.* (2006), said that heavy metals even at low concentrations can cause toxicity to humans and other forms of life, and their effects is shown in Table 2.2 as below:

Table 2.2: Types of Heavy Metals and Their Effect on Human Health

Heavy Metals	Major Sources	Effect on Human Health
Arsenic	Pesticides, fungisides, metal smelters	Bronchitis, dermatities
Cadmium	Welding, electroplating, pesticide fertilizer, nuclear fission plant	Kidney damage, bronchitis, gastrointestinal disorder, bone marrow, cancer
Lead	Paint, pesticide, smoking, automobil emission, mining, burning of coil	Liver, kidney, gastrointestinal damage, metal retardation in children
Manganese	Welding, fuel addition, ferromanganese production	Inhalation or contact causes damage to central nervous system
Mercury	Pesticides, batteries, paper industry,	Damage to nervous system, protoplasm poisoning
Zinc	Refineries, brass manufacture, metal Plating, plumbing	Zinc fumes have corrosive effect on skin, cause damage to nervous membrane

Heavy metals may enter the human body through food, water, air, or absorption through the skin when they come in contact with humans in agriculture and in manufacturing, pharmaceutical, industrial, or residential settings. Industrial exposure accounts for a common route of exposure for adults while ingestion is the most common route of exposure in children. Alluri *et al.* (2006), on their research said that main sources of heavy metal contamination include urban industrial aerosols, solid wastes from animals, mining activities, industrials and agriculturals chemicals.

2.5 Copper

Copper is an essential nutrient, required by the body in very small amounts. Short periods of exposure can cause gastrointestinal disturbance, including nausea and vomiting. Use of water that exceeds the permissible level over many years could cause liver or kidney damage. Intentionally high intakes of copper can harm our health and even death. Copper is rarely found in source water, but copper mining and smelting operations and municipal incineration may be sources of contamination (Mohan and Sreelakshmi, 2007).

Copper is common in the environment. Most copper compounds found in air, water, sediment, soil, and rock are so strongly attached to dust and dirt or imbedded in minerals that they cannot easily affect our health. Copper found in hazardous waste sites is likely to be of this form. Some copper in the environment is less tightly bound to particles and may be taken up by plants and animals. Long-term exposure to copper dust can irritate nose, mouth, and eyes, and cause headaches, dizziness, nausea, and diarrhea. Tumin *et al.* (2008), also state that the chronic effects of consumption of high levels of copper are liver and kidney damage.

2.6 Refractometer

A refractometer measures the extent to which light is bent or refracted when it moves from air into a sample and is typically used to determine the index of refraction or also known as refractive index of a liquid sample.

The refractive index is a unitless number, between 1.3000 and 1.7000 for most compounds, and is normally determined to five digit precision. Since the index of refraction depends on both the temperature of the sample and the wavelength of light used, these are both indicated when reporting the refractive index.

The refractive index is commonly determined as part of the characterization of liquid samples, in much the same way that melting points are routinely obtained to characterize solid compounds. It is also commonly used to:

- Help identify or confirm the identity of a sample by comparing its refractive index to known values.
- Assess the purity of a sample by comparing its refractive index to the value for the pure substance.
- Determine the concentration of a solute in a solution by comparing the solution's refractive index to a standard curve.

A typical laboratory refractometer can determine the refractive index of a sample to a precision of ± 0.0002. However, small amounts of impurities can cause significant changes in the refractive index of a substance. Thus, a good rule of thumb within ± 0.002 of the literature value is a satisfactory match (Hanson, 2003).

Determining the concentration of a solute in a solution is probably the most popular use of refractometry. For example, refractometer-based methods have been developed for determining the percentage of sugar in fruits, juices, and syrups, the percentage of alcohol in beer or wine, the salinity of water, and the concentration of antifreeze in radiator fluid. Many industries use refractometer-based methods in quality control applications.

In most cases, the refractive index is linearly related to the percentage of dissolved solids in a solution. By comparing the value of the refractive index of a solution to that of a standard curve, the concentration of solute can be determined with good accuracy. However, the refractive index does not provide detailed information about a molecule's structure.

CHAPTER 3

METHODOLOGY

3.1 Chemical and Raw Material

Chemicals used in this study is $CuSO_4$ solution, citric acid solution, 0.1 M NaOH and 0.1 M HCl. Sodium hydroxide (NaOH) and hydrochloric acid solution is used to control the pH according to the value required. The grade for this entire chemical is standard grade. While, rice husk used as adsorbent in this study is obtained from the local paddy plants in Malaysia. Initially, rice husk will be sieved through sieve shaker to have the uniform size of adsorbent. Then, it will be washed with distilled water for several times to remove dust and particulate matter from the surface of material. After that, it will be dried in oven at 60ºC for 24 hours and preserved at room temperature.

3.2 Equipment

In this study, there are some important equipment that is used. The equipment is sieve shaker, pH meter, blender and refractometer. Sieve shaker will be used to sieve the rice husk to obtain the uniform size of rice husk. While, pH meter is used to check the pH value of the solution. Blender is used to blend the rice husk into small particles. Refractometer is used to determine the refractive index which is used to obtain concentration values of Cu(ii) solution.

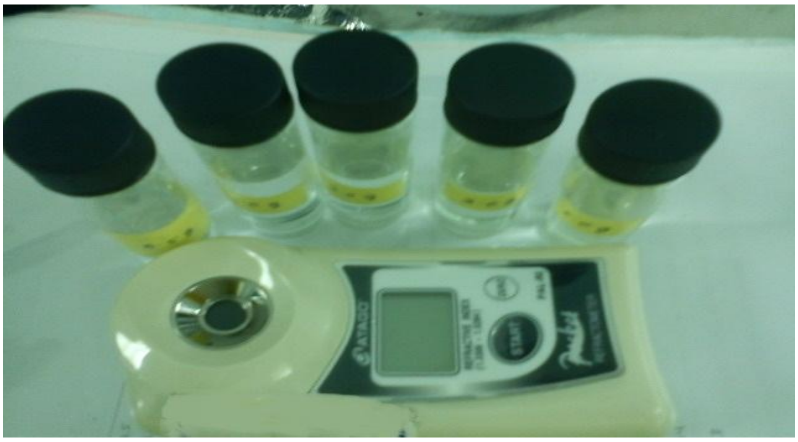

Figure 3.1: Refractometer

3.3 Experimental Procedure

3.3.1 Preparation of Raw Material

Initially, rice husk is washed using distilled water to remove dust and particulate matter from the surface of material. After that, it is dried in oven at 60ºC for 24 hours and preserved at room temperature. Then, rice husk is blended using blender into a small form.

3.3.2 Pretreatment of Rice Husk

In order to optimize the removal of metal ions, pretreatment of rice husk will be done. After washing using distilled water and dried, the rice husk is treated with citric acid and the solution is shaken for 2 hour. The purpose of shaken is to make sure that the solution is mixed well. Then, the sample is dried again at 60ºC overnight.

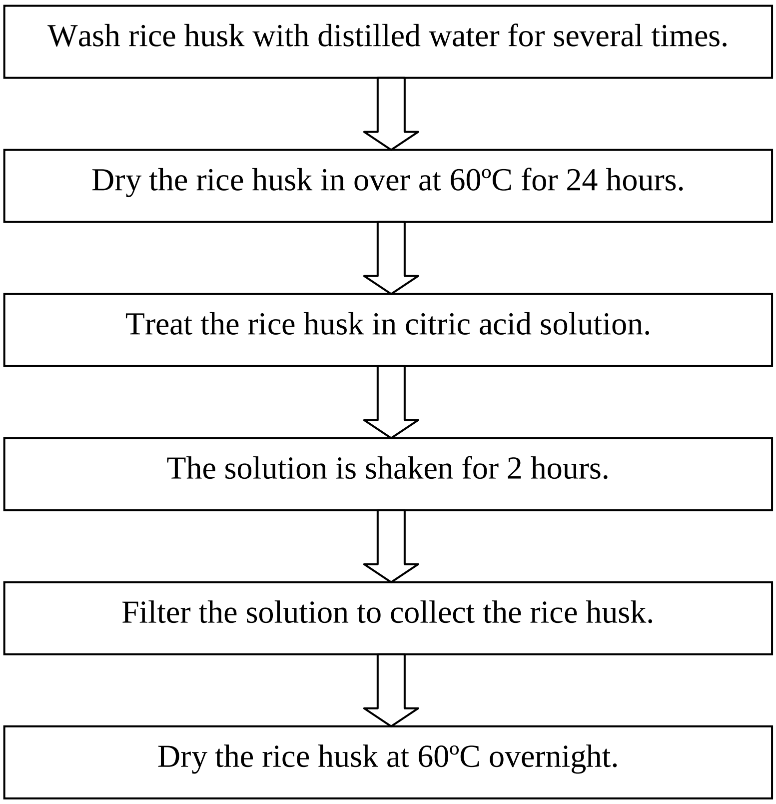

Figure 3.2: Preparation and Pretreatment of Raw Material

3.3.3 Effect of pH

100 ml of Cu(ll) solution is taken in a beaker. The pH of solution is adjusted by adding dilute solution of HCl or NaOH. The pH is varied from 2 to 6. The pH value is set for 2, 3, 4, 5, and 6. The initial concentration of Cu(ll) in this solution is set to be constant at 200 mg/L or 0.2 g/L. 50 ml of this solution is taken in a conical flask and will be treated with 2.0 g of adsorbent. Next, the solution is shaken for 1 hour. Then, the refractive index of Cu(ll) solution is determined using refractometer. The final concentration is determined using standard graft that has been plotted.

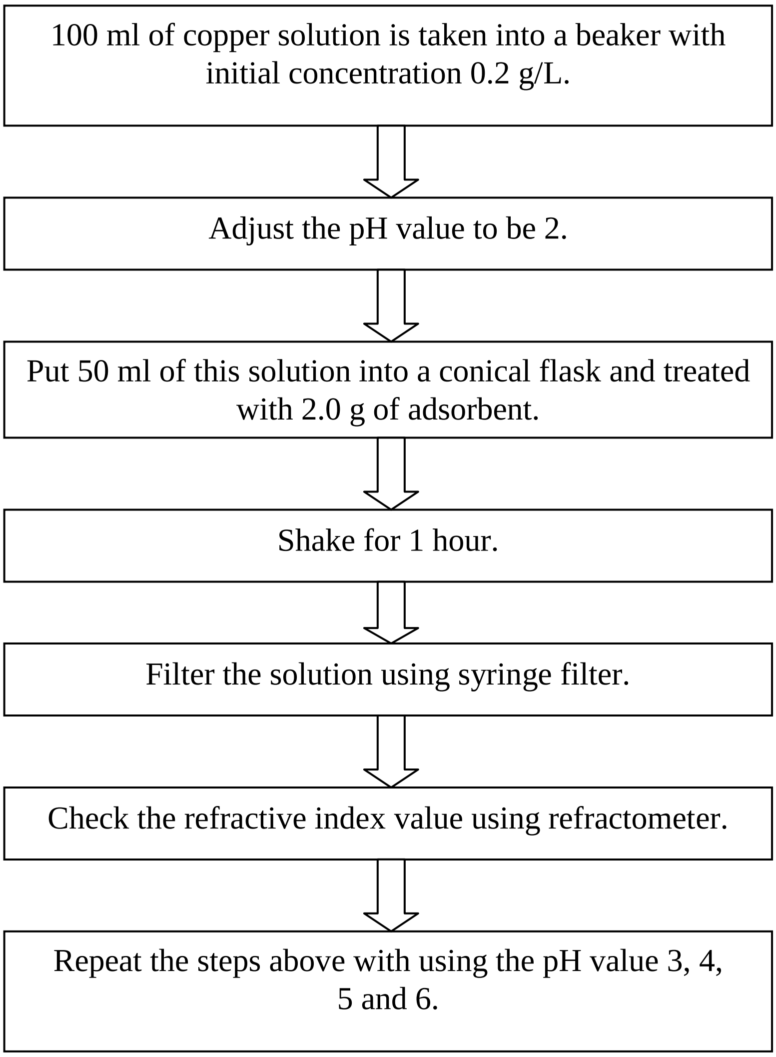

Figure 3.3: Preparation of Samples for Effect of pH

3.3.4 Effect of Adsorbent Dosage

The effect of the adsorbent dosage will be studied at room temperature (25ºC) by varying the sorbent amounts from 0.5 to 5.0 g. For this study, the amounts used are 0.5 g, 1.0 g, 2.0 g, 3.0 g and 5.0 g. The samples then are placed in conical flask and it will be shaken at 120 rpm for 1 h. For all these runs, the initial concentration of copper was fixed at 200 mg/L and pH is 5. Then, the refractive index of samples is determined using refractometer and final concentration is predicted from the graft.

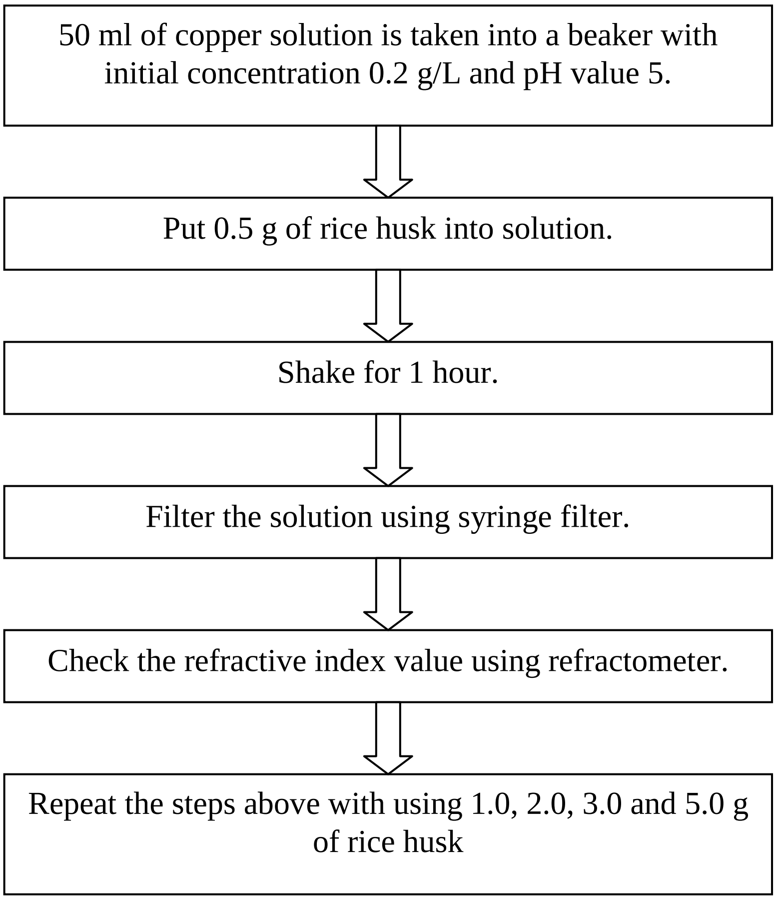

Figure 3.4: Preparation of Samples for Effect of Adsorbent Dosage

3.3.5 Effect of Duration Time

2.0 g of adsorbent is placed in a series of conical flask by adding 50 ml of solution with initial concentration of copper is fixed to at 200 mg/L or 0.2 g/L and pH value is 5. Then it is shaken in a shaker and at the predetermined intervals (10 to 90 minutes), the solution will be taken out. For this study, the duration time is fixed at 10 minutes, 30 minutes, 60 minutes, 80 minutes and 90 minutes. The concentration of samples is determined based on the graft refractive index versus concentration.

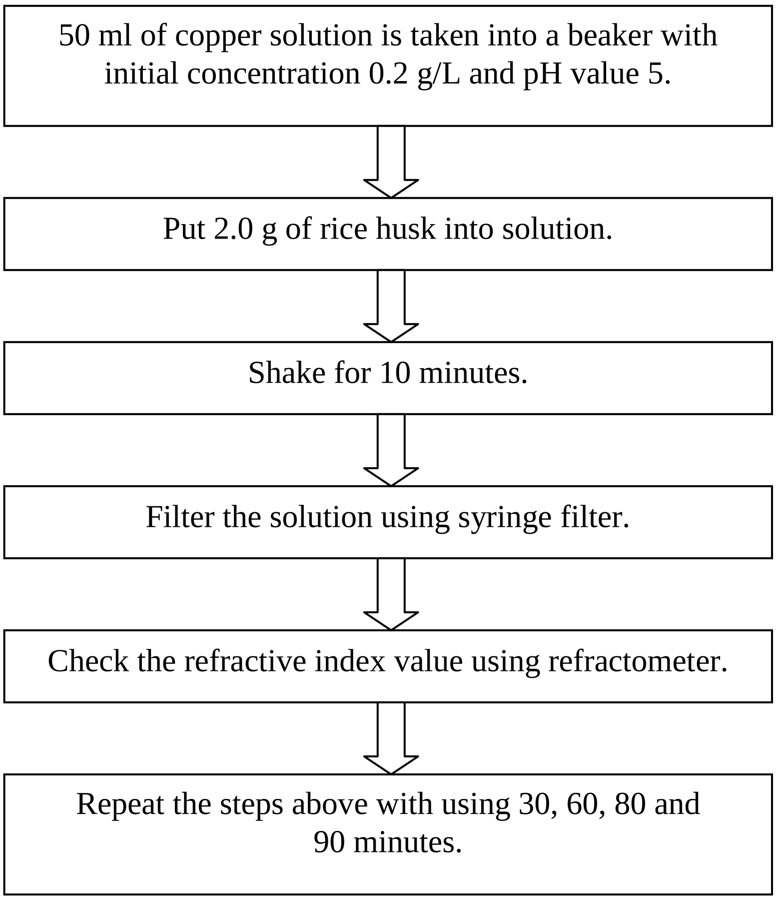

Figure 3.5: Preparation of Samples for Effect of Aduration Time

3.4 Analysis

All the samples are analyzed using refractometer. The refractive index is check for all samples. A standard curve is plotted for refractive index versus concentration which is the initial concentration of copper solution is varying. Then, from refractive index value of the sample, the final concentration is obtained from the standard curve.

The amount of metal ion adsorbed was calculated as in **Eq (3.1)**:

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

Where C_0 and Ce are the initial and equilibrium concentration of adsorbate, respectively.

CHAPTER 4

RESULT AND DISCUSSION

4.1 Background

This chapter is discussed about the result obtained from the experiment. For each of the parameter, the percentage of removal copper ions is calculated using equation 3.1. The percentage of removal copper ions is show in the graft. From the graft, the maximum values of removal copper ions can be determined.

4.2 Standard Curve

Standard curve is plotted for refractive index versus concentration in order to get the value of concentration for various pH, amount of dosage and duration time parameters. Standard curve is plotted using several of initial concentration starting from 0.025 g/L, 0.050 g/L, 0.100 g/L, 0.200 g/L and lastly 0.300 g/L. By using refractometer, refractive index value can be obtained. This standard curve is used to predict the concentration at certain parameters for the others. **Table 4.1** shows the values for refractive index according to initial concentrations while **Figure 4.1** in Appendix A shows the graft of refractive index versus concentration.

Table 4.1: Refractive Index for Standard Concentration

Concentration (g/L)	Refractive Index
0.025	1.3321
0.050	1.3323
0.100	1.3324
0.200	1.3333
0.300	1.3335

4.2 Effect of pH Parameter

Table 4.2 in Appendix B shows refractive index for pH parameter. By using the graft from **Figure 4.1** in Appendix A, the concentrations of copper solution at certain pH are show as in the **Table 4.3** in Appendix B. The percentage of removal copper ions from the solution is calculated using **Equation 3.1** and show in **Table 4.5**.

Table 4.4: Experiment Conditions on Effect of pH

Condition	Value
Initial concentration	0.2 g/L
Adsorbent dosage	2.0 g
Duration time	1 hour
Temperature	Room temperature

Table 4.5: Percentage of Removal Copper Ions at Various pH

pH	**Concentration (g/L)**	**Percentage of Removal Copper Ions (%)**
2	0.133	33.5
3	0.120	40.0
4	0.100	50.0
5	0.050	75.0
6	0.123	38.5

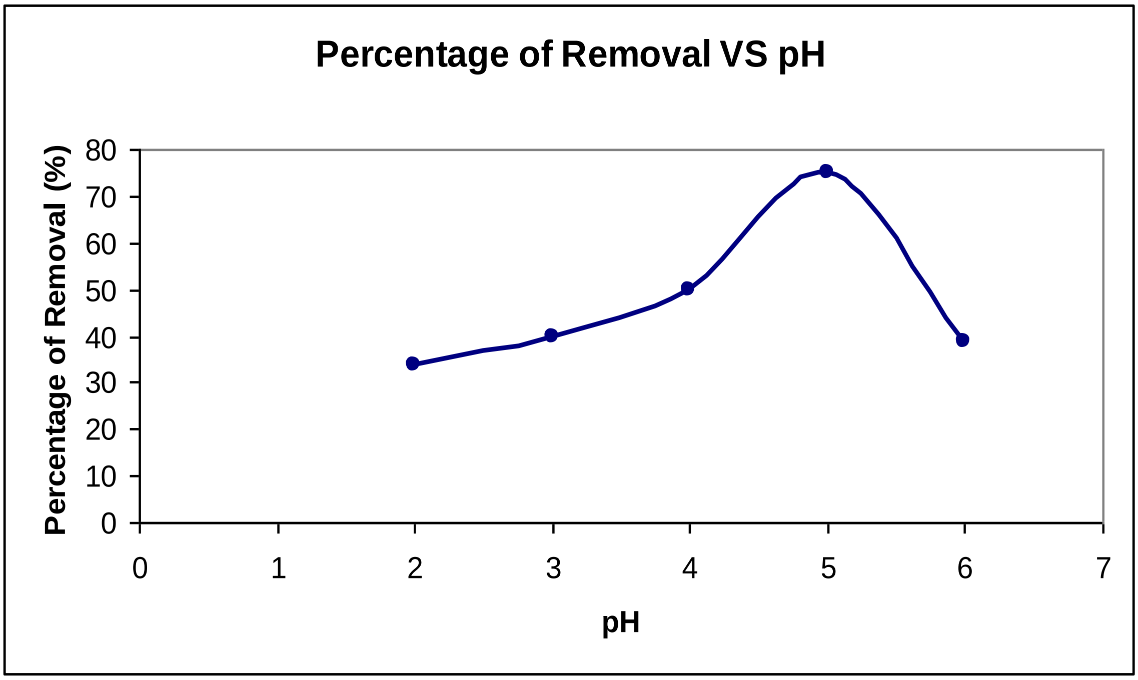

Figure 4.2: Graft of Percentage of Removal versus pH

The acidity of solution is one of the most important parameters that control the uptake of heavy metals from wastewaters and aqueous solutions. The percentage removals of copper ions from the aqueous solution are strongly affected by the pH solution as illustrated in **Figure 4.2**. The uptakes of copper are increases from 33.5% up to 75% when the pH increases from 2 to 5. After that, the percentage is decrease in pH 6. The decreasing in percentage means that the capacity of adsorption also decreases.

According to Tumin *et al*, (2008), the minimum adsorption observed at low pH that is pH 2 may be due to the fact that the higher concentration and higher mobility of H+ ions present favoured the preferential adsorption of hydrogen ions compared to Cu (II) ions. It can be said that at lower pH value, the surface of the adsorbent is surrounded by hydronium ions (H+), thereby preventing the metal ions from approaching the binding sites of the sorbent. In contrast, as the pH increases, more negatively charged surface becomes available thus facilitating greater copper removal.

However, at higher pH value that is 6, there is a decrease in the adsorption capacity. This is due to the occurrence of copper precipitation. Starting pH value 6 and above, the solution is precipitate when NaOH is added. According to Zhang (2011), with the pH value further increasing, the Cu(II) species existing in the solution predominantly would change from Cu(+2) to $Cu(OH)_2$ gradually, causing precipitation. The precipitation will disturb adsorption process. At pH 5, the removal of copper ions is at highest value. At this value, the solution is merely associated only with copper ions. Thus, the adsorption capacity is maximum. This is proved by Weng *et al.* (2007).

4.3 Effect of Adsorbent Dosage

Table 4.8: Experiment Conditions on Effect of Adsorbent Dosage

Condition	Value
Initial concentration	0.2 g/L
pH value	5
Duration time	1 hour
Temperature	Room temperature

Table 4.9: Percentage of Removal Copper Ions at Various Adsorbent Dosage

Adsorbent Dosage (g)	**Concentration (g/L)**	**Percentage of Removal Copper Ions (%)**
0.5	0.120	40.0
1.0	0.050	75.0
2.0	0.035	82.5
3.0	0.100	50.0
5.0	0.120	40.0

Table 4.6 in Appendix C shows the refractive index for adsorbent dosage while **Table 4.7** shows the concentration for various adsorbent dosages. By calculate the percentage using the removal equation, it is shows as in **Table 4.9**.

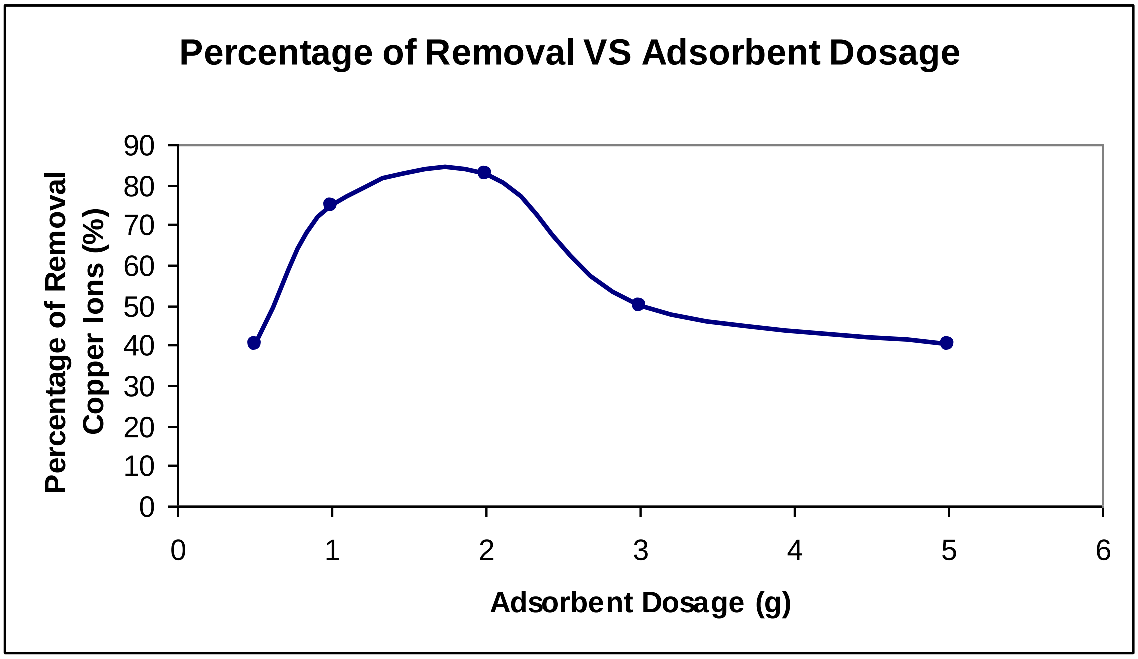

Figure 4.3: Graft Percentage of Removal versus Adsorbent Dosage

Amount of adsorbent dosage used is another important parameter which influent of capacity of removal copper ions from solution. Thus, varying the amount used gives effect to the percentage of removal. Based on **Figure 4.3**, it shows that increasing of adsorbent dosage will increase the percentage of removal copper ions from solution. The highest percentage of removal is 82.5% which is 2 grams of adsorbent used. Using amount of adsorbent 3g to 5g, the percentage are decreases.

At amount of 0.5 g to 2.0 g, the percent of removal copper increases. This is because the number of adsorption sites or surface area increases with increasing weight of adsorbent and hence results in a higher percent of metal removal (Atalay et al, 2010). However, the percentage of adsorption decreased with the increasing of adsorbent dosage at value 3.0 g and above. These results may due to the overlapping of the adsorption sites (Tumin *et al*, 2008). The adsorption sites are not fully exposed to the solution because of overcrowded of adsorbent particles in smaller area.

4.4 Effect of Duration Time

Refractive index values for various duration times are state in **Table 4.10** in Appendix D while the concentration is determined using standard curve in Appendix A. The values of concentration are shows in **Table 4.11** in Appendix D.

Table 4.12: Experiment Conditions on Effect of Duration Time

Condition	Value
Initial concentration	0.2 g/L
pH value	5
Adsorbent dosage	2.0 g
Temperature	Room temperature

Table 4.13: Percentage of Removal Copper Ions at Various Duration Time

Duration time (min)	**Concentration (g/L)**	**Percentage of Removal Copper Ions (%)**
10	0.133	33.5
30	0.123	38.5
60	0.120	40.0
80	0.100	50.0
90	0.050	75.0

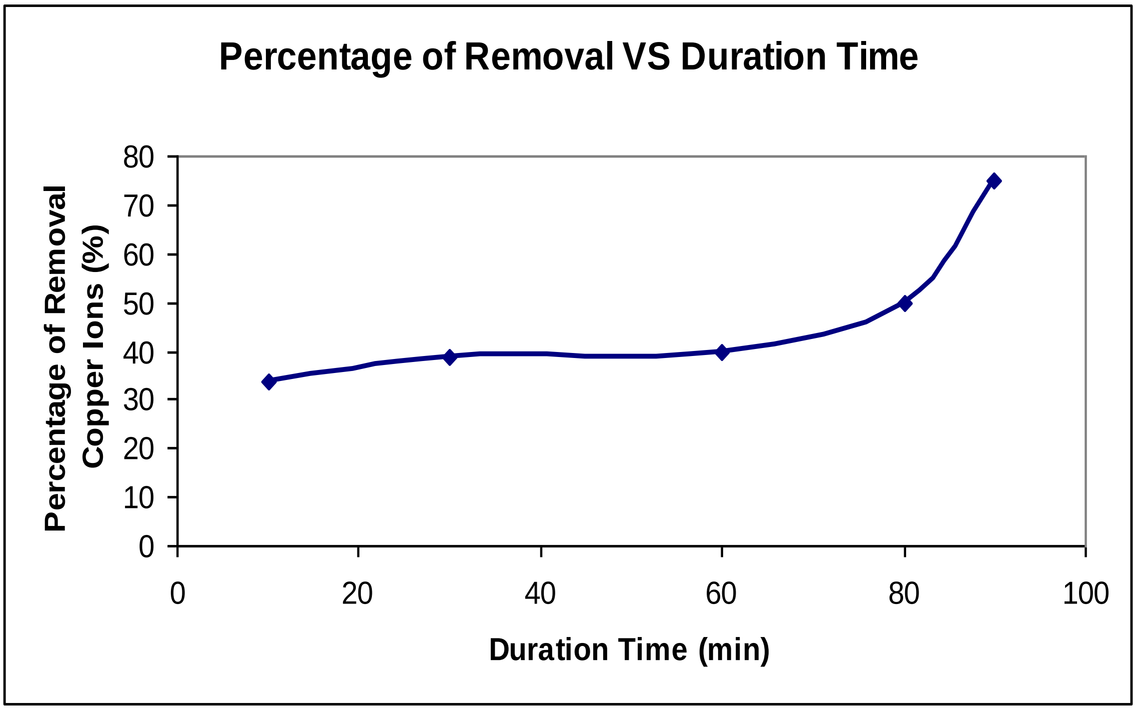

Figure 4.4: Graft Percentage of Removal versus Duration Time

For the effect of duration time, the result obtained show that the removal of copper is proportional to the duration time. The percentage of removal is increasing slowly. The highest percentage of removal is at duration time 90 minutes where it is 75%. This result is similar with the research done by Kumar *et al* (2010), where the adsorption is increasing with increasing contact time. However, this study also said that after a certain time the adsorption capacity is remain constant. This is because the reaction is reaching the equilibrium.

From the graft, it shows that the percentage adsorption rapidly increases. It is supposedly increase slowly and after that remain constant due to saturation of the adsorption sites. But for this study, there might be an experimental error thus affects the result.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

The objective of this study is to determine the effectiveness of rice husk as adsorbent for adsorption process in wastewater treatment. In this study, agricultural by-product that is rice husk has shown a positive result for heavy metal adsorption. It has a great potential for the elimination of heavy metals from wastewater. Thus, rice husk can be used as absorbent in order to reduce the cost during wastewater treatment.

From the study on biosorption of heavy metals using rice husk, it has found that pH value, adsorbent dosage and duration time are some of important parameters that effect the capacity of adsorption. For the effect of pH value, the result obtained show that the maximum capacity of removal copper ions is 75%. The result shown that increasing of pH value from 2 to 5 will increase the percentage of removal copper ions.

This finding of this study also show that increasing of adsorbent dosage will increase the percentage of removal copper ions from solution. The highest percentage of removal is 82.5% which is 2 grams of adsorbent used. Lastly, for the effect of duration time, the highest percentage of removal is at duration time 90 minutes where it is 75%. It shows that increasing of duration time will increase the percentage of removal copper ions.

5.2 Recommendations

This study can be improved by using others analysis method such as spectroscopic analysis like atomic absorption spectrometer (AAS), and Fourier transform infrared (FTIR). By using this analysis, the percentage of error can be reduced.

Other than that, more studies should be carried out to better understand the process of low-cost adsorption and to demonstrate the technology effectively. The comparison of more agricultural adsorbents such as sawdust, soybean hulls, sugarcane bagasse and others can be done to determine the effectiveness of that material as adsorbent. Also, more parameter like temperature and particle size can be study in order to determine the maximum capacity of removal heavy metal from solution.

It is suggested that comparison between modified and unmodified rice husk is done. Also, the study on chemically modified adsorbent using different chemical might improve the result. For example, comparison between hydrochloric acid, sodium hydroxide and tartaric acid treated rice husk.

Since this study also involves pretreatment of the raw material, so the modification of adsorbent surface might change the properties of adsorbent. Thus, it is recommended that for any work on chemically modified plant wastes, characterization studies involving surface area, pore size, porosity, and others should be carried out. All these properties might give effect to the result.

REFERENCES

Abo-Farha, S. A., Abdel-Aal, A. Y., Ashourb, I. A. and Garamon, S. E., (2009). Removal of some heavy metal cations by synthetic resin purelite C100. *J. Hazard.* 169, 190-194.

Ahalya, N., Ramachandra, T. V. and Kanamadi, R. D., (2003). Biosorption of heavy metal. *Research Journal of Chemistry and Environment*. 7(4). Retrieved March 15, 2011, from http://wgbis.ces.iisc.ernet.in/energy/water/paper/ biosorption/biosorption. htm

Alluri *et al*., (2007). Biosorption: An eco-friendly alternative for heavy metal removal. *Journal of Biotechnology*. 6 (25), 2924-2931.

Asrari, E., Tavallali, H., and Hagshienas, M., (2010). Removal of Zn(ll) and Pb(ll) ions using rice husk in food industrial wastewater. *J. Appl. Sci. Environ Manage.* 14 (4), 159-162.

Atalay, E., Gode, F. and Sharma, Y. C., (2010). Removal of selected toxic metals by a modified adsorbent. *Practice Periodical of Hazardous, Toxic, and Radioactive Waste Management*. 14 (2).

Demirbas, A., (2008). Heavy metal adsorption onto agro-based waste material: A review. *Journal of Hazardous Materials.* 157, 220-229.

El-Sayed, G. O., Dessouki, H. A., and Ibrahim, S.S., (2010). Biosorption of Ni (ll) and Cd (ll) ions from aqueous solutions onto rice straw. *Chemical Sciences Journal.* 9.

Fu, F. and Wang, Q. (2011). Removal of heavy metal ions from wastewaters: A review. *Journal of Environmental Management.* 92, 407-418.

Hanson, J. (2003). Refractometry. *Chemistry Lab Techniques.* Retrieved on January 11, 2012 from http://www2.ups.edu/faculty/hanson/labtechniques/refractometry/intro.htm.

Kehinde, O. O., Oluwatoyin, T. A. and Aderonke, O. O, (2009). Comparative analysis of the efficiencies of two low cost adsorbents in the removal of Cr(VI) and Ni(II) from aqueous solution. *Journal of Environmental Science and Technology*. 3(11), 360-369.

Khan, N. A., Ibrahim, S. and Subramaniam, P., (2004). Elimination of heavy metals from wastewater using agricultural waste as adsorbents. *Malaysian Journal of Science.* 23, 43-51

Kumar, P. S., Ramakrishnan, K., Kirupha, S. D. and Sivanesan, S., (2010). Thermodynamic and kinetic studies of cadmium adsorption from aqueous solution onto rice husk. *Brazilian Journal of Chemical Engineering.* 27(2), 347-355.

Kumar, U., (2006). Agricultural products and by-products as a low cost adsorbent for heavy metal removal from water and wastewater: A review. *Scientific Research and Essay*. 1(2), 33-37.

Lenntech (n.d.). *Heavy metal*. Retrieved January 11, 2012, from http: http://www.lenntech.com/processes/heavy/heavy-metals/heavy-metals.htm.

Mohan, S. and Sreelakshmi, G., (2007). Fixed bed column study for heavy metal removal using phosphate treated rice husk. *Journal of Hazardous Materials*. 153, 75-82.

Naiya, T. K., Bhattacharya, A. K., Mandal, S. and Das, S. K., (2009). The sorption of lead(ii) ions on rice husk ash. *Journal of Hazardous Materials*. 163, 1254-1264.

Ngah, W. S. W. and Hanafiah, M. A. K. M., (2008). Removal of heavy metal ions from wastewater by chemically modified plant wastes as adsorbents: A review. *Bioresources Technology*. 99, 3935-3948.

Opeolu, B. O., Bamgbose, O., Arowolo, T. A. and Adetunji, M. T., (2010). Utilization of biomaterials as adsorbent for heavy metal' removal from aqueous matrices. *Scientific Research and Essay*. 5(14), 1780-1787.

Sarkawi, S. S. and Aziz, Y., (2003). Ground rice husk as filler in rubber compounding. *Jurnal Teknologi*. 39, 135-148.

Sud, D., Mahajan, G. and Kaur, M. P., (2008). Agricultural waste material as potential adsorbent for sequestering heavy metal ions from aqueous solution. *Bioresource Technology*. 99(14), 6017-6027.

Tumin, N. D., Chuah, A. L., Zawani, Z. and Rashid. S. A., (2008). Adsorption of copper from aqueous solution elais guineensis kernel activated carbon. *Journal of Engineering Science and Technology*. 3(2), 180-189.

Weng, C. H., Tsai, C. Z., Chu, S. H., and Sharma, Y. C., (2007). Adsorption characteristics of Copper (ll) onto spent activated clay. *Separation and Purification Technology*. 54, 187-197.

Willis, B. (n.d.). *Adsorption.* Retrieved February 17, 2011, from http:// www. worsleyschool.net/science/files/adsorption/page.html

Zhang *et al.* (2011). Removal of Cu(II) from aqueous solution using the rice husk carbons prepared by the physical activation process. *Biomass and Bienergy*. 35, 464-472.

APPENDIX A

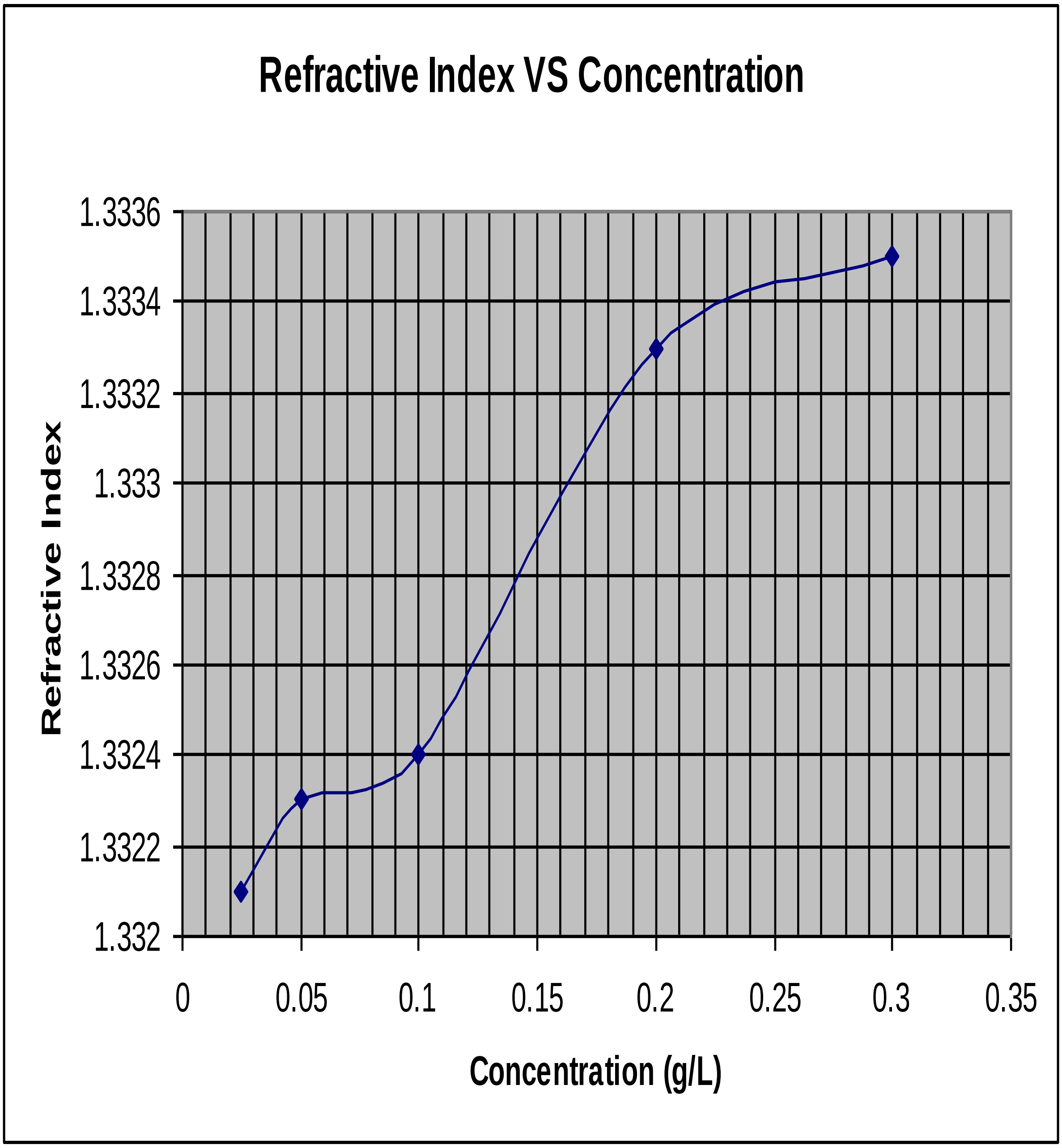

Figure 4.1: Graft Refractive Index versus Concentration

APPENDIX B

Table 4.2: Refractive Index for pH Parameter

pH	Refractive Index
2	1.3327
3	1.3325
4	1.3324
5	1.3323
6	1.3326

Table 4.3: Concentration of Copper Solution at Various pH

pH	Concentration (g/L)
2	0.133
3	0.120
4	0.100
5	0.050
6	0.123

APPENDIX C

Table 4.6: Refractive Index for Adsorbent Dosage

Adsorbent Dosage (g)	Refractive Index
0.5	1.3325
1.0	1.3323
2.0	1.3322
3.0	1.3324
5.0	1.3325

Table 4.7: Concentration of Copper Solution at Various Adsorbent Dosages

Adsorbent Dosage (g)	Concentration (g/L)
0.5	0.120
1.0	0.050
2.0	0.035
3.0	0.100
5.0	0.120

APPENDIX D

Table 4.10: Refractive Index for Duration Times

Duration time (min)	Refractive Index
10	1.3327
30	1.3326
60	1.3325
80	1.3324
90	1.3323

Table 4.11: Concentration of Copper Solution at Various Duration Time

Duration time (min)	Concentration (g/L)
10	0.133
30	0.123
60	0.120
80	0.100
90	0.050