PREPARATION OF LEAD, COPPER AND MERCURY ADSORBENT FROM PALM OIL WASTE: EMPTY FRUIT BUNCHES (EFB)

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This project is submitted in partial fulfillment of the requirements for the degree of Bachelor of Science with Honours (Resource Chemistry)

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Universiti Malaysia Sarawak
(2008)

DECLARATION

No portion of the work referred to in this dissertation has been submitted in support of an application for another degree of quantification of this or any university or institution of higher learning.

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ACKNOWLEDGEMENTS

I would like to express my heartiest appreciation and gratefulness to my supervisor, Mdm. Rafeah bt Wahi and my co-supervisor, Dr. Zainab bt Ngaini, for their advice, guidance and constructive critisms throughout this project. Beside that, I would like to take this opportunity to express my gratitude to my beloved parents who give me all the moral support and financial support. I would also like to acknowledge the help extended by all postgraduate students in Physical Chemistry Laboratory, my close friends, course-mates and family members. Finally, I would like to thank all the staff of the Department of Chemistry and administration staff for their help and support.

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LIST OF ABBREVIATIONS

AAS	Atomic Absorption Spectroscopy
Å	Angstron
Cu	Copper
^0C	degree celcius
EFB	Empty fruit bunches
g/mol	gram per mol
HCl	Hydrochloric acid
Hg	Mercury
m^2	meter square
m^2/g	meter square per gram
mm	millimeter
mg/g	miligram per gram
mg /L	milligram per gram
NaOH	sodium hydroxide
Pb	lead
ppm	parts per million
R^2	correlation coefficient
µg	micro gram
%	percent

Preparation of lead, copper and mercury adsorbent form palm oil waste: Empty fruit bunches (EFB)

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2008

ABSTRACT

The ability of low-cost activated carbon prepared from empty fruit bunches (EFB), an abundant palm oil waste to remove lead, copper and mercury was investigated. Activated carbon was produced by using both chemical and physical activation process. The activated carbon was characterized based on its elemental analysis, proximate analysis, density and surface area. The activated carbon showed the adsorption capacity of 112.51 mg/g for lead, 55.49 mg/g for mercury and 5.36 mg/g for copper. The EFB activated carbon showed a good adsorption performance in removing lead and mercury and gave the percentage of removal up to 100% even at a lower adsorbent dosage of 0.2g. The activated carbon produced also showed higher capacity by removing up to 20ppm of lead and mercury ions. The adsorption isotherm study showed that Langmuir isotherm fitted the adsorption data for copper while the adsorption of lead and mercury was best described by the Fruendlich isotherm model.

Keywords: activated carbon, chemical activation, physical activation

ABSTRAK

Keupayaan karbon teraktif yang dihasikan dari tandan kelapa sawit untuk menjerap bahan-bahan logam seperti plumbum, merkuri dan kuprum dikaji dalam kajian ini. Karbon teraktif yang dihasilkan didapati dapat menjerap plumbum serta merkuri sehingga 100% walaupun dalam dos yang sedikit iaitu 0.2g. Selain itu, karbon teraktif yang dihasilkan juga dapat menjerap plumbum dan merkuri sehingga kepekatan 20mg/l. Karbon teraktif yang dihasilkan mempunyai kapasiti penjerapan 112.21 mg/g untuk plumbum, 55.49 mg/g untuk merkuri serta 5.36 mg/g untuk kuprum. Sifat-sifat karbon teraktif ini kemudiannya dikaji berdasarkan kandungan elemen, ketumpatan dan luas permukaannya. Proses penjerapan bagi logam kuprum didapati menepati model Langmuir manakala proses penjerapan bagi plumbum dan merkuri boleh diterangkan berdasarkan model Fruendlich.

Kata kunci: karbon teraktif, pengaktifan kimia, pengaktifan fizikal

CHAPTER ONE: INTRODUCTION

1.1 Background

In the world nowadays, industry is the sector that contributes a lot to the economical growth of a country. The development in each country is measured by how well developed its industry sector is. However, increase in industrial activities can cause many aquatic bodies receiving loads of heavy metals and organic chemical wastes that exceeding the water quality criteria for wastewater discharge designed to protect the environments, humans and animals (Iqbal and Saeed, 2006). Heavy metals refer to any metallic chemical element that has a relatively high density and is toxic or poisonous at low concentrations. These compounds cannot be degraded or destroyed. Heavy metals are released into the aqueous environment through a variety of sources such as metal smelters, effluents from plastics, textiles, microelectronics, wood preservatives producing industries, usage of fertilizer and pesticides (Bhatti et al., 2007). Pollution by metal ions has become a major issue throughout many countries because the contents of metal ions in potable waters and wastewaters often exceed the admissible sanitary standards (Lodeiro et al., 2006).

Heavy metals in our environment bring bad impacts to both living and non-living things. Heavy metals will polluted our environment and risk our health. Several health problems that can cause by exposure to heavy metals are intestinal irritation, effects on kidneys and gastrointestinal tract, damage to the nervous system and problem to our respiratory system. Conventional methods for the removing of heavy metals include chemical precipitation and ion exchange. However, these methods are inefficient or expensive especially when the concentration of the heavy metal ion is low, of the order of 1-100mg/L (Bhatti et al., 2007).

Therefore, the aim of this work was to study the efficiency of adsorbent prepared from palm oil waste which is in the formed of empty fruit bunches (EFB) prepared by both physical and chemical activation methods. Apart from that, this study also had the aim to investigate the adsorption capacity of EFB activated carbon in the removal of heavy metals such as copper, lead and mercury from aqueous solution. In this study, EFB was undergo two times of carbonization at higher temperature which were at 400 ^{0}C and also 700 ^{0}C. Both carbonizations were done under inert atmosphere. For chemical activation, 20% of sodium hydroxide solution was used as the activating agent.

EFB was used in this study because it contained high concentration of cellulosic fibre and also because this type of agricultural by-products is abundant since Malaysia is one of the largest producers of oil palm in the world (Ravigadevi et.al., 2003). Each year, the palm oil industry generates 14 million tones of waste including EFB (Randhawa, 2004). The abundance and availability of the EFB make them good sources of raw materials for activated carbons. EFB as agricultural by-products are renewable sources of raw materials for activated carbon production because the development of methods to reuse waste material is greatly desired (Ankur et al., 2001). Disposal of agricultural by-products is currently a major economic and ecological issue because these wastes usually are being burnt especially for fibrous residues or used for mulching. Due to that, the conversion of by-products to adsorbents such as activated carbon, represent a possible outlet (Malik et al., 2007).

Activated carbons are extensively used as efficient and versatile adsorbents for purification of water, air and many chemical and natural products (Malik et al., 2007). The adsorption process has an advantage over the other methods due to the excellent adsorption efficiency of activated carbon for organic compounds even from dilute solutions, but commercially available activated carbons are very expensive (Malik et al., 2007). Basically, activated carbon consists of carbon arranged in a quasi-graphitic form in a small particle size. Under an electrode, the structure of activated carbon looks a little like ribbons of paper which have been crumpled together, intermingled with wood chips. There are a great number of nooks and crannies and many areas where flat surfaces of graphite-like material run parallel to each other, separated by only a few nanometers or so. These microspores provide superb conditions for adsorption to occur, since adsorbing material can interact with many surfaces simultaneously. Because of that, activated carbon has been known as compound that has extraordinary large surface area and pore volume that gives it a unique adsorption capacity. A gram of activated carbon can have a surface area in excess of 500 m^2 with 1500 m^2 being achievable. That is why the usage of locally available waste materials to produce activated carbon is very much encouraged since it is very economical.

From the previous studies, it is clearly that agricultural waste materials can be produced into activated carbon and become a good adsorbent. For example, the study done by Rao et al. (2007) indicated that activated carbon prepared from *Ceiba pentandra* hulls could be used as an effective adsorbent material for the treatment of lead and zinc bearing aqueous wastewater. Another study on preparation of activated carbon from agricultural water materials also been done by Malik et al. (2007). In this study, groundnut shells based powdered activated carbon was found to be an effective adsorbent for the removal of malachite green dye from aqueous solutions and its adsorption capacity is quite comparable to the commercial powdered activated carbon

1.2 Objectives

Basically, there were three main objectives of this study.

a) to investigate the applicability of chemical activation by using NaOH in activated carbon production.

b) to characterize the adsorbent produced according to its proximate and ultimate properties and also its surface morphology

c) to determine adsorption capacity or adsorption efficiency of the activated carbon on the removal of lead, copper and mercury

CHAPTER TWO: LITERATURE REVIEW

2.1 Heavy Metals

Heavy metals are toxic pollutants released into the surface and ground water as a result of different activities such as industries, mining and agriculture (Hawari and Muligan, 2005). As trace elements, some heavy metals for example copper, selenium and zinc are essential to maintain the metabolism of human body. However, at higher concentration they may lead to poisoning.

Hoekman (2007) in his article on heavy metal toxicology said that heavy metals produce their toxicity by forming complexes or "ligands" with organic compounds. He also said that these modified biological molecules lose their ability to function properly and resulting in malfunction or death of the affected cells. The most common groups involved in ligand formation are oxygen, sulfur and nitrogen. When metals bind to these groups they may inactive important enzyme systems or affect protein structure.

Heavy metals are also said to be dangerous because they tend to bio-accumulate which means they undergo an increase in the concentration of a chemical in a biological over time, compared to the chemical's concentration in the environment. Compounds accumulate in living things any time they are taken up and stored faster than they are metabolized or excreted.

2.1.1 Copper

Copper is reddish colored, takes on a bright metallic luster, and is malleable, ductile, and a good conductor of heat and electricity (second only to silver in electrical conductivity). Copper is an essential substance to human life. But, in high doses it can cause anemia, liver and kidney damage, and stomach and intestinal irritation. The fumes and dust cause irritation of the upper respiratory tract. Inhalation of copper fume results in the irritation of the upper respiratory tract. Contact with copper fumes will also cause irritation of the eyes, nose and throat. Emission from road traffic is the largest source of copper emissions.

One way of removing copper from environment is by using plants and this method is called phytoextraction. This method used the principle that some plant species can take up heavy metals and concentrate them in their tissue. The plants can be harvested and the contaminated plant material disposed of safely. Sometimes soil amendments are added to the oil to increase the ability of the plants to take up the heavy metals. Examples of plants that may be used for phytoextraction include alfalfa, cabbage, tall fescue, juniper, and poplar trees.

2.1.2 Lead

Lead is one of the metals that have the most damaging effects on human health. Exposure to lead can result in a wide range of biological effects to human depending on the level and duration of exposure. High levels of exposure may result in toxic biochemical effects that in turn cause problems in synthesis of haemoglobin, effects on the kidneys, gastrointestinal tract, joints and reproductive system. Besides, high exposure to lead also can cause acute or chronic damage to the nervous system.

Because of size and charge similarities, lead can substitute for calcium and included in bone. Children are especially susceptible to lead because developing skeletal systems require high calcium levels. Lead that is stored in bone is not harmful, but if high levels of calcium are ingested later, the lead in the bone may be replaced by calcium and mobilized. Once free in the system, lead may cause nephrotoxicity, neurotoxicity, and hypertension.

Most lead concentrations that are found in the environment are the result of human activities. Due to the application of lead in gasoline and unnatural lead-cycle has consisted. In car engines lead is burned so that lead salts which are chlorines, bromines and oxides will originate.

One of the common methods used to remove lead is called stabilization. Generally this is done by stabilizing heavy metals by adding chemicals to the soil that cause the formation of minerals that contain the heavy metals in a form that is not easily absorbed by plants, animals, or people. This method is called in situ fixation or stabilization. This process does not disrupt the environment or generate hazardous wastes. Instead, the lead metal will combines with the added chemical to create a less toxic compound. The heavy metal remains in the soil, but in a form that is much less harmful.

2.1.3 Mercury

Mercury is a global pollutant with complex and unusual chemical and physical properties. The major natural source of mercury is the degassing of the Earth's crust, emissions from volcanoes and evaporation from natural water bodies. Besides, the sources of mercury presence in our environment also from the manufacture of chlorine in mercury cells, non-ferrous metal production and coal combustion. Mercury is highly toxic and can cause neurotoxicological disorders. Mercury can breaks down the barriers in the capillaries and resulting in edema throughout the body. A common effect of mercury is deterioration of alveolar bone in the jaw which also resulted in loosening teeth. There are also substantial liver and kidney toxicity because of mucosal degeneration.

Mercury poses a great risk to humans, especially in the form of methylmercury. When mercury enters water it is often transformed by microorganisms into the toxic methyl mercury form. Symptoms of acute poisoning are pharyngitis, gasteroenteritis, vomiting, nephritis, hepatitus, and circulatory collapse. Chronic poisoning is usually a result of industrial exposure or a diet consisting of contaminated fish (mercury is the only metal that will bioaccumulate).

Randall et al. (2004) reported that there are two general types of treatment technologies were evaluated for mercury that are stabilization or amalgamation and selenide combined with four disposal options which are hazardous waste landfill, hazardous waste monofill, engineered below-ground structure and mined cavity. Randall et al. (2004) also stated that there are three storage options for elemental mercury which are aboveground structure, hardened structure and mined cavity.

2.2 Adsorption

A process when a gas or liquid solute accumulates on the surface of a solid or more rarely, a liquid (adsorbent), forming a molecular or atomic film called the adsorbate is called adsorption. Adsorption is the most studied of property in activated carbon. Physical adsorption involves the attraction by electrical charge differences between the adsorbent and the adsorbate. Chemical adsorption is the product of a reaction between adsorbent and adsorbate. Adsorption is a consequence of surface energy. Tseng and Tseng (2005) reported that the adsorption capacity depends on physical and chemical characteristics of the adsorbent (carbon), physical and chemical characteristics of the adsorbate (reactant), concentration of the adsorbate in liquid solution, characteristics of the liquid phase (examples are pH and temperature) and also the amount of time the adsorbate is in contact with the adsorbent which means its residence time.

Nollet et al. (2003) observed that the adsorption rate increases with increasing temperature in the study about the removal of polychlorinated biphenyls from wastewater using fly ash. Adsorption process also changes dramatically with the change in pH (Iqbal and Saeed, 2007). That is why to undergo any study involving adsorption process, the data for all comparative studies must be obtained at the same pH values.

2.3 Adsorbent

An adsorbent is a substance, usually porous in nature and with a high surface area that can adsorb substances onto its surface by intermolecular forces. The adsorbents are used usually in the form of spherical pellets, rods, moldings or monoliths with hydrodynamic diameter between 0.5mm and 10mm (Rao et al., 2007). Adsorption capacity is the most important characteristic of an adsorbent (Knaebel, 2000). It refers to the amount of adsorbate taken up by adsorbent per unit mass (or volume) of the adsorbent. It depends on fluid phase concentration, temperature, and other initial condition of an adsorbent.

Basically, there are three types of adsorbent. The first one is activated carbon which based on organic materials. They are highly porous, amorphous solids which consisting with a graphite lattice. They are non-polar and cheap. They are also combustible. The second type of adsorbent is silica gel which based on inorganic materials. Silicas are generally clear or faintly tinted, and transparent or translucent. However, some silica gels are manufactured with alumina blended in (Knaebel, 2000). This yields the appearance of alumina, viz., opaque and white or tan. Silica gel is a chemically inert, nontoxic, polar and dimensionally stable (<400^0 C) with amorphous form of SiO_2. The third type of adsorbent is zeolites which are natural or synthetic aluminium silicates that form a regular crystal lattice and release water at high temperature. They are polar in nature. Non-polar zeolites are synthesized by dealumination of polar zeolites. They are used in non-polar organics removal. The micropores in zeolites are so small and uniform that they are commonly can distinguish almost identical sized molecules.

2.4 Activated carbon

Activated carbon is a crude material from graphite (Wan Nik et al., 2007). It is one of the most effective adsorbents and is commonly used for dye removal, owing mainly to its highly porous structure and high surface area (Garg et al., 2004; Tseng and Tseng, 2005). The specific mode of activated carbon is extremely complex since it has both chemical and physical effects on substance where it is used as a treatment agent. It activities can be separated into four groups which are adsorption, mechanical filtration, ion exchange and surface oxidation. Among these, adsorption is effective and economical (Rao et al., 2007).

There are two different processes for the preparation of activated carbon which are physical and chemical activation (Ahmadpour and Do, 1996). Physical activation involves carbonization of the carbonaceous precursor followed by activation of the resulting char in the presence of chemical agents of activating agents such as carbon dioxide or steam. Chemical activation on the other hand in involves carbonization of the precursor in the presence of activating agents. In physical activation, the elimination of large amount of internal carbon mass is necessary to obtain a well developed porous structure, whereas in chemical activation process, chemical agents used are dehydrating agents that influence pyrolytic decomposition and inhibit the formation of tar, thus enhancing yield of carbon (Rodriguez-Reinoso and Molina-Sabio, 1992). Chemical activation has more advantages (Lillo-Rodensas et al., 2003) over physical activation with respect to higher yield, more surface area and better development of porous structure in carbon. It also helps to develop oxygenated surface complexes on the surface of activated carbon (Malik et al., 2007).

Activated carbon consists mainly of carbon (87 -97%) and other elements such as hydrogen, oxygen, sulfur and nitrogen. Various compounds are also present either originating from the material or generated during its preparation. Activated carbon also can adsorb various substances both from gas and liquid phases. This ability justifies it as an adsorbent. The two main reasons why chemicals adsorb into activated carbon are because chemicals ‘dislike’ water and because chemicals have strong attraction to activated carbon (Wan Nik et al., 2006).

There are three main forms of activated carbon (Wan Nik et al., 2006). The first one is pellet activated carbon. This type is extruded and cylindrical shaped with diameter from 0.8 to 5mm. These are mainly used for gas phase application because of their low pressure drop, high mechanical strength and low dust content. The second type is powder activated carbon (PAC) which is pulverized carbon with a size predominantly less than 0.18mm. These are mainly used in liquid phase application and for flue gas treatment. The third type is granular activated carbon (GAC). GAC has irregular shaped particles sizes ranging from 0.2mm to 5mm. This type of activated carbon is used in both liquid and gas applications (Wan Nik et al., 2006).

Activated carbon can be characterized by using moisture and volatile matter content. These two analyses are important since the production of activated carbon involving heating at higher temperature.

The other method to study the properties of activated carbon is by using the ash content. Ash reduces the overall activity of activated carbon. It reduces the efficiency of reactivation. The metals can leach out of activated carbon resulting in discoloration.

The fixed carbon content is the carbon found in the sample that is left after volatile materials are driven off. Fixed carbon is used as an estimate of the amount of activated carbon that will be yielded from a sample of empty fruit bunches. Fixed carbon is determined by removing the mass of volatiles determined by the volatility test from the original mass of the sample.

Apparent density also been used for activated carbon characterization. Higher density provides greater volume activity and normally indicates better quality activated carbon.

Apart from that, particle size distribution is also been used to determine the properties of activated carbon. The more fine the size of an activated carbon, the better the access to the surface area and the faster the rate of adsorption kinetics.

There were a number of studies done on activated carbon previously. For example, Rao et al. (2007) observed that activated carbon could be prepared from *Ceiba petandra* hulls, an agricultural waste material. The maximum removal of lead and zinc using this activated carbon is 99.5% and 99.1% with 10g/l of sorbent was observed at 50mg/L sorbate concentration (Rao et al., 2007). Malik et al. (2007) also reported their study on activated carbon preparation from agricultural waste material. In this study, groundnut shell was used as the raw material to produced activated carbon. The result showed that groundnut shell activated carbon removed 94.5% of malachite green dye in 30 minutes equilibrium time while commercial activated carbon removed 96% of the dye in 15 minutes.

2.5 Palm oil waste

The Malaysian palm oil industry generates a substantial amount of residues. At the plantation, pruned fronds, felled trunks and fronds are the residues produced. Felled