Faculty of Resources Science and Technology

Preparation of Heavy Metal Adsorbent from Microwave Pyrolytic Char of Sago Wastes

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DECLARATION

I hereby declare that no portion of the work referred in this final year project thesis has been submitted in support of an application for another degree or qualification to this or any other university or institution of higher learning.

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(CALIDYA ANAK IDEM @ ININ)

Date:

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LIST OF ABBREVIATION

˚C	Degree Celcius
%	Percent
MHz	Mega Hertz
N_2	Nitrogen gas
pH	A measurement of the acidity/alkalinity of solution [p stands for "potenz" (this means the potential to be) and H stands for Hydrogen
K	Kelvin
FTIR	Fourier transform infrared spectroscopy
SEM	Scanning electron microscope
W	Watt
SWAC	Sago waste activated carbon
CAC	Commercial activated carbon
$W_{.cr}$	Weight of crucible
$W_{.s}$	Weight of sample
$W_{.ds}$	Weight of dry sample

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Preparation of Heavy Metal Adsorbent from Microwave Pyrolytic Char of Sago Wastes

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ABSTRACT

Preparation of activated carbons from sago wastes were investigated in this study. The raw material of sago wastes was first pyrolysed in a pyrolysis reactor in inert condition for a total of 3 minutes. The samples was subjected with N_2 gas for 30 minutes to get an inert environment inside the quartz reactor before exposing the samples to microwave action for at least 3 minutes. The char sample was added with 50 % H_2SO_4 and 50% Na_2SO_4 for activation. The adsorption rate has been studied under several parameters like adsorbent dosage, initial concentration, pH and agitation time with three types of heavy metals, which include Lead, Pb(II), Copper, Cu(II) and Chromium, Cr(II). The adsorption parameters influenced on the adsorption rate were analyzed using Langmuir and Freundlich isotherm. The characteristics of the sago waste activated carbon were also investigated by studying the moisture content, ash content, volatile matter content, fixed carbon, surface morphology (SEM) and functional groups (FT-IR). Batch Adsorption test showed that the adsorptions of Pb(II), Cu(II) and Cr(II) metal ion differ for each parameter. According to the evaluation using Langmuir equation, the monolayer adsorption capacity obtained were 0.4464 mg/g, 0.0371 mg/g and 3.5714 mg/g for Pb(II), Cu(II) and Cr(II) respectively.

Key words: Adsorption, sago waste, heavy metals, pyrolysis, adsorption capacity

ABSTRAK

Penyediaan karbon teraktif dari sisa sagu telah disiasatdalam kajian ini. Bahan mentah yanbg digunakan ialah ahan-bahan buangan dari sagu telah dipyrolysed di dalam reaktor pirolisis dengan keadaan lengai selama 33 minit. Sampel kemudiannya didedahkan dengan gas N_2 untuk 30 minit untuk mendapat persekitaran lengai di dalam reaktor kuarza sebelum mendedahkannya dengan tindakan gelombang mikro sekurang-kurangnya untuk 3 minit. Sampel arang telah ditambah dengan 50 % H_2SO_4 dan 50% Na_2SO_4 untuk pengaktifan. Kadar penyerapan telah dikaji di bawah beberapa parameter seperti dos bahan penyerap, konsentrasi awal, pH dan masa pengocakan dengan tiga jenis logam berat, yang termasuk Lead, Pb(II), Copper, Cu(II) dan Chromium, Cr(II). Pengaruh parameter penyerapan terhadap kadar penyerapan telah dianalisis menggunakan isoterma Langmuir dan Freundlich. Ciri-ciri karbon teraktif sagu juga telah disiasat dengan mengkaji kandungan lembapan, kandungan abu, kandungan jirim meruap, karbon tetap,morfologi permukaan (SEM) dan kumpulan-kumpulan fungsian (FT-IR). Ujian penyerapan menunjukkan yang penyerapan ion logam Pb(II), Cu(II) dan Cr(II) berlainan untuk setiap parameter. Menurut penilaian menggunakan persamaan Langmui , keupayaan serapan mronolayer yang diperolehi ialah 0.4464 mg / g, 0.0371 mg / g dan 3.5714 mg / g untuk Pb(II), Cu(II) dan Cr(II) masing-masing.

Kata Kunci: Penyerapan, sisa sagu, logam berat, pirolisis, keupayaan penyerapan

CHAPTER 1

INTRODUCTION

1.1   Research Background

The development and urbanization of many places all over the world have been one factor that causes the increase of industrial activities. Heavy metal exists in various types of water body in our environment as the unwanted products or as the deposits from the industrial activities such as metal planting, mining operations, tanneries, alloy industries, storage batteries industries and so on (Kadirvelu *et al.*, 2001; Khan *et al.*, 2004). Heavy metal had been contaminating the water body and causes toxicity to many life that depends on it, including human as the ions do not degrade into harmless end products (Wahi *et al.*, 2009).

With the increasing of industrial activity, the problem of removing pollutants from water is becoming more important (Rengaraj *et al.*, 2004). There has been a great deal of research into finding cost-effective methods for the removal of contaminants from wastewater (Abdel-Ghani *et al.*, 2007). All metals including the essential metal micronutrient are toxic to aquatic life and human if being exposed to a sufficiently high level of contaminants (Ilhan *et al.*, 2004).

Previous study of treatment processes for heavy metal removal from wastewater or polluted water include precipitation, membrane filtration, ion exchange, adsorption and co-precipitation. From all these studies, adsorption had been revealed as the highly effective technique (Chand *et al.*, 1994; Khan *et al.*, 2004). The other techniques, apart from being

economically expensive have disadvantages like incomplete metal removal, high reagent and energy requirements, and generation of toxic sludge or other waste products that require disposal (Kushwaha *et al.,* 2008). Adsorption has been thought to be efficient and economically feasible as a wastewater treatment operation and several adsorbents can be used to remove metal ions, including activated carbons, alumina, silica, bentonite and peat (Rengaraj *et al.,* 2004).

Natural materials that are available in large quantities and include certain waste from agricultural operations have the potential to be used as low cost adsorbents as they represent unused resources, widely available and are environmentally friendly (Abdel-Ghani *et al.,* 2007). Activated carbon has been used as the material for the adsorption process and proved to work well with many types of heavy metal. Agricultural waste by-products like oil-palm shell, sago, rice husk and coconut husk (Khan *et al.,* 2004) are used to produce chars which later will be activated to become activated carbon.

In this study, a material which is abundant in Malaysia: sago waste is chosen. The waste are a very versatile natured chemical species as they contain a variety of organic and inorganic compounds like cellulose, hemicelluloses, pectins and lignin which present in the cell wall that contain hydroxyl, carboxylic, carbonyl, amino and nitro groups and act as the most important adsorption sites (Quek *et al.*, 1998).

Microwave-Induced Pyrolysis is the best process to produce activated carbon. Chars from the pyrolysis can be activated to form activated carbon by using several activating solvents so that it can be effective for the metal adsorption (Guo & Lua, 1998). Research found that most of a lot of newly-developed diseases ar from the deposition of heavy metal

into the human body by food consuming especially marine-based foods. The water bodies are polluted with excess deposition of heavy metals, reducing the valuable water sources. Commercial activated carbon is well-known adsorbent for the removal of heavy metals from water, but it is very expensive. Agricultural wastes which are a type of pollutants can be use to form activated carbon. Microwave-Induced Pyrolysis is the best process to produce activated carbon. Microwave pyrolysis of biomass will yield carbonaceous residue (char) as by-product (Miura *et al*., 2004), which can be activated for better adsorption.

1.2   Problem Statement

Research found that most of the newly-developed diseases are from the deposition of heavy metal into the human body by food consuming especially marine-based foods. The water bodies are polluted with excess deposition of heavy metals, reducing the valuable water sources. The disposal of agricultural wastes also is a problem faced by many since it is excessive and not much uses can be obtained by it. Adsorption is known as one of the most proficient methods for the removal of heavy metals from wastewater. Activated carbon is the most extensively used adsorbent appropriate to its exceptional adsorption capability for heavy metals. However, the use of the methods is often restricted due to the expensive preparation cost. It is important that these problems are addressed since it can help to save our readily tattered environment.

1.3   Objectives

1. To prepare activated carbon from sago waste via microwave pyrolysis followed by chemical activation.

2. To analyze the characteristics of the activated carbon produced via microwave pyrolysis.

3. To conduct an adsorption study on selected heavy metals (Cr, Cu, Pb).

CHAPTER 2

LITERATURE REVIEW

2.1   Heavy Metal

2.1.1   Chromium (Cr(II))

Chromium can be found in several types of forms which include metallic chromium (Cr^0), trivalent chromium (Cr^{+3}) and hexavalent chromium (Cr^{+6}) (Water Quality Association, 2005). Metallic elemental chromium occurs naturally in the environment where it is formed from chrome bearing rock or earth. Metallic chromium is used to make steel and metal alloys. Trivalent chromium on the other hand, occurs naturally in the environment like in rocks and soil. It could also be found in fruits, vegetables and meat. Hexavalent chromium does not come about in nature but it is created from some chemical processes and is thought as toxic (Water Quality Association, 2005).

Chromium can be considered as dominance pollutants because of their high toxicity even at low concentrations (Krim, Nacer & Bilango, 2006). Chromium is extremely soluble in water and can be adsorbed easily by living organisms. Severe health problem can occur once it mounts up in living organisms if the concentration value is greater than the permissible value (Babel & Opiso, 2007).

Over the years, many technologies and techniques for the removal of chromium in aqueous solutions have been developed. The most noteworthy of these techniques include filtration, chemical precipitation, ion exchange by resin, reverse osmosis, and membrane

systems (Babel & Opiso, 2007). The main disadvantages that come from these technologies include high reagent and energy requirement, imperfect removal, high operational cost and generation of toxic sludge (Babel & Opiso, 2007). In recent years, adsorption has been revealed to be an alternative method for removing dissolved metal ions from water. Widespread research using adsorbents which include diverse kinds of soils, wastes and clay materials has been carried out in some experiments, in order to minimize the cost (Babel & Opiso, 2007).

The U.S Enviromental Protection Agency (EPA) has established a maximum contaminate level (MCL) and the MCLG for total chromium of 0.1 ppm (100 ppb) in drinking water. Water from tap, normally has an average value of 0.4 to 8 ppb while air has an average value of 0.1 ppb, which is consider safe. Soil on the other hand, has an average chromium value of 400 ppm (Water Quality Association, 2005).

2.1.2 Copper (Cu(II))

Copper is the principle element for many important of alloys (Maheswari *et al*., 2008). Industrial applications include alloy industries, paper and pulp, petroleum refining industries and so on. (Maheswari *et al*., 2008) Copper polluted the water environment through wastewater from coal burning industries, copper wire mills, fungicides and insecticides (Maheswari *et al*., 2008). High concentration of copper can cause neuron toxicity from the deposition in the lenticular nucleus of the brain and liver. Other than that, congestion of nasal mucous membrane and pharynx, ulceration of nasal septum and metal

fume fever could also become an effect from high concentration in human body (Sharma *et al.*, 1996).

Copper can be found in surface water since the element and its compounds are ubiquitous in our environment (Rengaraj *et al.,* 2004). Copper is a metal that occurs naturally throughout the environment like the soil, rocks, water and air (Keith *et al.,* 2006). So that is why plants and animals absorbed some copper from eating, drinking and breathing.

In recent years, this metal pollutants are being discharged in excess into the environment (Lazaridis *et al.*, 2004) and although copper is not as toxic as hexavelent chromium or arsenic, it can be potentially serious to the human body if high levels are present in drinking water (Keith *et al.*, 2006). Acid mine drainage and mining wastes that bears dissolved copper are being discharged significantly, and these include discharged from fertilizer industry, plating baths, paints and pigments, storm water and municipal run off (Rengaraj *et al.*, 2004). Excessive doses intake of copper ion by human body could lead to severe mucosal irritation and corrosion, hepatic and renal damage, capillary damage, and central nervous system irritation followed by depression (Rengaraj *et al.*, 2004).

Conventional treatment of waste water containing copper includes chemical precipitation, solvent extraction, evaporation and so on. But because of operational demerits and the high cost of treatment this method are not the choice for adsorption (Maheswari *et al.*, 2008).

The maximum permissible limit for copper in water according to the World Health Organization standard is 15.0 mg/dm^3 while the maximum admissible concentration is 0.05 mg/dm^3 (Bala *et al.*, 2008). The maximum recommended concentrations of Cu^{2+} in drinking water set by both WHO and USPHS is 1.0 mg/dm3 (Rengaraj *et al.*, 2004).

2.1.3 Lead (Pb(II))

Lead can be found naturally in the earth's crust and in ores such as galena or lead (II) sulphide (Win *et al*., 2003). In excess, lead is a heavy metal with high toxicity (Okoye *et al*., 2010) even at low concentration. Lead is among the heavy metals that are most common pollutant found in industrial effluent (Ghazy *et al*., 2008). Lead is used in mining, battery manufacturing, smelting, refining, electrical wiring, home demolition and construction, ceramic glazing, painting and making of stained glass (Ghazy *et al*., 2008), photographic materials, matches and explosives (Qaiser *et al*., 2007).

Due to its mobility and great toxicity, the increasing amount of lead is a huge problem to both surface water and underground water (Ghazy *et al*., 2008). Research on lead by environmental and medical scientist has become dominant for a topic due to two obvious reasons: (i) lead has no known biological use, and (ii) lead is toxic to most living things (Badmus *et al.*, 2007).

If releases into the water environment, lead can bio accumulate and enter the food chain. High concentration of lead ion in human bodies are known to cause mental retardation, reduces haemoglobin production necessary for oxygen transport, damages the body nervous system, interferes with normal cellular metabolism, reduces the I.Q level in

children (Qaiser *et al*., 2007) and also have the tendency to damage kidneys and reproductive system, particularly in children (Ghazy *et al*., 2008).

Conventional method for treatments includes ion exchange, lime and soda ash precipitation, oxidation, reduction and many more. These methods however, are economically hostile, complicated and are used only in special cases of waste water treatment (Qaiser *et al*., 2007).

The maximum permissible limit for lead in water according to the World Health Organization standard is 0.10 mg/dm^3 while the maximum admissible concentration is 0.05 mg/dm^3 (Bala *et al.,* 2008). The United States, Environmental Protection Agency (EPA) requires the amount of lead ion in drinking water is to not exceed 0.015 mg/L (Ghazy *et al*., 2008).

2.2   Sago Wastes

An estimation of approximately 60 million tonnes of sago starch, extracted from sago palms is produced annualy in South East Asia (Petrus *et al*., 2009). The factories for the processing of sago are mainly built near the river side where waste from sago part is likely to be thrown into rivers, a practice which contributed to water pollution. Research have been done to make use of this sago waste including as substrate for cultivation of edible mushrooms, animal feed, backbone of fertilizers (extraction of humic acid from mature compost), production of enzymes and as an absorbent (Petrus *et al*., 2009). The residues are composed of celluloses and lignins, which both are a waste and a pollutant.

Their chemical composition suggests that they could have some potential as a biosorbent (Quek *et al.,* 1998).

2.3   Activated Carbon

Activated carbon is a solid, permeable from the presence of pores and carbonaceous matter prepared by carbonizing and activating an organic substance (Food and Agriculture Organization of the United Nations, 2011). The raw materials could comprise of sawdust, peat, lignite, coal, cellulose residues, coconut shells, petroleum coke, palm oil waste, sago waste and wood waste, which is carbonized and activated at high temperature. The carbonaceous matter is treated with a chemical activating agent such as phosphoric acid or zinc chloride. The mixture then are carbonized at a high temperature, followed by removal of the chemical activating agent by washing them with a lot of water (Food and Agriculture Organization of the United Nations, 2011).

Activated carbons is also a group of well-established, universal and versatile adsorption intermediate for substances like heavy metal, which become bonded to the carbon, and are tightly held when being adsorb. The better contact of the surface area samples and the faster the rate of adsorption depend on the particle sizes of an activated carbon (Alaya *et al.,* 2000). Removal of heavy metal pollutants from wastewater by using adsorbent from activated carbon has proved to be effective, due to its good adsorption properties which depend on its well developed porous structure and large active surface area (Okoye *et al.,* 2010)

There are two types of activation of activated carbon which is physical and chemical activation (Alaya *et al.,* 2000). The chemical activation that will be used in this research is about mixing with chemical such as acids like phosphoric acid and sulphuric acid or bases like potassium hydroxide, sodium hydroxide or salts like zinc chloride. Chemical activation give several advantages since it is carried out at lower temperatures and therefore resulted in the development of a better porous structure.

A wide range of commercial sorbents including chelating resins and commercial activated carbon are available for metal sorption, but the cost is considered as expensive (Qaiser *et al.,* 2007). Another types of activated carbon has been studied by many scientists; include pillared clay, cassava waste, banana pith, peanut skins, Medicago sativa (Alfalfa) and spagnum moss peat (Horsfall *et al*., 2005). These types of activated carbon are cheaper since they are abundant in the nature.

2.4   Microwave Pyrolysis

Microwave pyrolysis is one way that are being applied to convert biomass into higher value products such as oils, gases and charcoal (Moen *et al*., 2009). Among the benefits reported about microwave processing of materials are increased process yield, environmental compatibility, saving in process time and low requirements for space and capital equipment (Moen *et al*., 2009).

Pyrolysis is an efficient and sustainable procedure of conversion of one substance into other types of substances by means of generating energy in the form of heat with the aid of the catalyst in the absence of air or oxygen which is also known as in inert condition,

where only nitrogens are being supplied. This process is simple, pollution free, have less waste and effective compared with other processes.

The pyrolysis processes have diverse stages that are reached at certain times depending on the mass of the samples and catalysts. Time is a good pointer of how the catalysts influence the heating rate and the pyrolysis speed, since the mass does not change much between the tested samples (Moen *et al*., 2009). The first stage is when the first condensation of liquids starts. The water is condensed, followed by lighter orange/brown pyrolysis volatiles. The water and these volatiles together form so-called water phase (Moen *et al*., 2009). The second stage is when the condensation of darker pyrolysis volatiles starts. Most of the heavy oils and burnable gases are produced in this stage (Moen *et al*., 2009).

Microwave pyrolysis works with the use of microwave oven. Microwave oven heat up substances using "dielectric heating" where polar molecules such as water are caused to vibrate and revolve as they try to line up themselves to the shifting incoming microwave radiation frequencies (Thostenson & Chou, 1999). Microwave pyrolysis should work well with organic substances that contain many polar molecules like the agricultural biomass, although it require an excessive amount of time and energy, to heat the material (Thostenson & Chou, 1999).

2.5   Adsorption

Adsorption is a method that took place when a gas or liquid solute mount up on the surface of a solid or a liquid called adsorbent, structuring a molecular or atomic film called adsorbate (Uhriková, 2006).

Adsorption is known as an effective purification and separation technique that are used in industry especially in water and wastewater treatments (Shaker, 2007). It has been found to be one of the most efficient and economic process for the removal of heavy metal ions from aqueous solution (Eddy & Odoemelam, 2009). In recent years, considerable awareness has been dedicated to the study of using biomaterials or biomass for removal of heavy metal ions from solution by adsorption method (Shaker, 2007).

Ion exchange, reverse osmosis, chemical precipitation, membrane filtration evaporation and adsorption are the most widely used methods for removing heavy metals from wastewater (Kongsuwan *et al.*, 2006). Most of these technologies however have some disadvantages like requirements for expensive equipment and monitoring system, incomplete metal removal, high reagent or energy requirements and generation of toxic sludge or other waste products that require disposal (Karthika *et al.,* 2010).

But among the various treatment technologies, adsorption is commonly used as an proficient process which has a wide purpose in the removal of metal ions from wastewater (Karthika *et al.,* 2010) since it was shown to be economically favorable compared with ion exchange or electrodialysis, technically easy compared with precipitation or reverse osmosis, and improved the efficiency of metallurgical removal particularly at low concentration level (Kongsuwan *et al.,* 2006). The most generally used sorbent is activated carbon (Karthika *et al.,* 2010).

Constant search are being done for alternative low-cost adsorbents to top the high cost and associated problems of adsorption of metal ion (Karthika *et al.,* 2010). These low-

cost sorbents include industrial or agricultural waste products such as straw and nut shells, lignin, sawdust and bark (Karthika *et al.,* 2010) and in this study sago waste.

2.6   Heavy Metal Adsorption by Activated Carbon

In recent years, the study of removal of heavy metal ions from solution by adsorption using agricultural materials have been applied (Abdel-Ghani *et al.*, 2007). Activated carbon is getting well-known as an effective adsorbent for the treatment of heavy metals (Wahi *et al*., 2010). Many studies on heavy metal removal like lead (Wahi *et al*, 2009, Karthika *et al*., 2010; Badmus *et al.,* 2007), copper (Maheswari *et al*., 2008; Wahi *et al*., 2009,) and chromium (Babel & Opiso, 2007; Arivoli *et al*., 2008) have been done and proved to be favourable but greatly depends on several parameters like the dosage, pH, agitation time and initial concentration.