## Production of Activated Carbon from Rice Husks and its Adsorption Characteristic for Pb<sup>2+</sup> ion.

By

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#### FINAL PROJECT REPORT

Submitted to the Chemical Engineering Programme in Partial Fulfillment of the Requirements for the Degree

Bachelor of Engineering (Hons)

(Chemical Engineering)

Universiti Teknologi Petronas Bandar Seri Iskandar 31750 Tronoh Perak Darul Ridzuan

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## CERTIFICATION OF APPROVAL

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Bachelor of Engineering (Hons)

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July 2005

## **CERTIFICATION OF ORIGINALITY**

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

Khuzaimah Mohd Nasir

#### **ABSTRACT**

The potential of the rice husks as the activated carbon was studied using Pb2+ ions as the heavy metal treated. The studies focused on the thermodynamic properties of the activated carbon form using rice husks as the raw material, where the favorability of the adsorbent towards adsorption process was determined. Two types of sample were used, base activated carbon and acidic activated carbon. It was determined that the base activated carbon has a higher adsorption capacity but the process was determined as unfavorable according to the Freundlich isotherm. As for the acidic activated carbon, the Langmuir isotherm fits the process better than Freundlich isotherm. Thermodynamic properties were determined using the Langmuir constant, showed that the process is spontaneous and endothermic in nature. In addition, the effect of the initial rice husks particle sizes, carbonization temperature and duration, and initial concentration with the effect of agitation time and temperature towards the adsorption behavior are studied. Particle size of 250  $\mu$ m, was determined to gave the highest adsorption capacity while 700 °C was determined to be the best carbonization temperature. Duration for the carbonization process and the shaking motion for the adsorption process also affect the adsorption capacity.

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## LIST OF ABBREVIATIONS

b<sub>1</sub>,b<sub>2</sub>,b<sub>3</sub> Langmuir constant at 27,35 and 45 °C, respectively

Q0 langmuir adsorption capacity

Qe amount of adsorbate adsorbed at equilibrium (mg/g)

C<sub>0</sub> initial concentration of the adsorbate; Pb<sup>2+</sup> (mg/L)

Ce final concentration of the adsorbate at equilibrium (mg/L)

n Freundlich constant (dimensionless)

KF Freundlich constant

b

 $\Delta G^0$  Gibb's free energy (kJ/mol)

 $\Delta H^0$  enthalpy change of the process (kJ/mol)

 $\Delta S^0$  entropy of adsorption (J/mol K)

Langmuir constant

r separation factor

R gas constant

# CHAPTER 1 INTRODUCTION

## 1.1 Background Study

Recently, as the health, safety and environment aspect are taken seriously by the global people, the issue on the disposal of any industrial waste that lead to the environmental problem have become a big concern to most people. Most of the industrial waste are toxic in nature contains heavy metals such as Pb, Cr, Cd, and Ag. Lead is ubiquitous in the environment and is a hazardous material that can harm people. It could poison the kidneys system, reproductive system, liver and brain, and central nervous system. It comes into the water from various sources. The major contributor comes from the processing industry such as plating, paint and dyes, and lead batteries [11].

Several methods are used in the wastewater treatment from the heavy material such as coagulation, reverse osmosis, ion exchange and adsorption. Adsorption is considered as the effective method based on its efficiency of removal from dilute solution, economic and handling. The most widely use adsorbent nowadays is activated carbon. There are three main usage of activated carbon in water treatment process. The original role is as "polishing agent", to remove species that adversely affect taste and odor of the water. It is also use in the treatment of water for the industrial purposes where the species that can cause corrosion, form deposits and fouling in the plant equipment such as heat exchanger are removed. And lastly, the activated carbon has been widely use in the treatment of waste waters that been derived from a broad range of manufacturing plants before been discharge into the environment [4].

As the commercial activated carbon is quite expensive, several studies were done in converting environmental waste to an activated carbon. A number of studies on converting the rice husk to activated carbon have been reported. As Malaysia is rich with paddy, a thorough study in converting the rice husk to activated carbon will give a lot of advantage to the country.

In order to use the rice husk as the activated carbon sources, its adsorption characteristic need to be determine. This is to make sure that the activated carbon produced is efficient in removing the heavy metal poisoned.

#### 1.2 Problem Statement

In wastewater treatment, the adsorption process is effective in removal of heavy metals at trace level. Conventional waste treatment methods like coagulation, chemical oxidation have not been successful because these methods are stable to light, oxidizing agents, while adsorption has come out as the cheapest, most profitable and most efficient one. A lot of studies have been done in using the environmental waste as a potential adsorbent in removing heavy metals, including studies on converting rice husks to activated carbon as the potential adsorbent. As Malaysia is rich with paddy, a thorough study in converting the rice husk to activated carbon will give a lot of advantage to the country.

## 1.3 Objectives of Studies

There are several objectives that should be accomplished by this study which are:

- 1. To produce the activated carbon from the rice husks according to the given preparation standard.
- 2. To study the effect of carbonization time towards the adsorption capacities.
- 3. To study the effect of activated carbon size towards the adsorption capacities.
- 4. To study the effect of carbonization temperature towards the adsorption capacities.
- 5. To study the adsorption rate of the produced activated carbon at different adsorption temperatures.
- 6. To identify the isotherm model for the adsorption.
- 7. To obtain the values of thermodynamic parameters for the adsorption process.
- 8. To determine whether the rice husks can produce a good activated carbon to be commercialized later.

## 1.4 Scope of Work

This study is a continuity study from the previous student. The previous study had already determined the best parameters in producing the activated carbon with the highest efficiency in adsorbing Pb<sup>2+</sup>. Because of time limitation, the activated carbon would be produced based on the parameters obtained and this study would focus more on the adsorption studies. The effect of temperature towards the adsorption efficiency, the adsorption thermodynamics parameters and the adsorption isotherm model will be determined. The study need to come out with the analysis whether the activated carbon form from the rice husks is favorable to the adsorption isotherm.

During the sample preparation, some parameters were changed to obtain the best activated carbon. As the sample varies, a few experiments are added in the research. The effect of contact time, initial lead concentration, the particle size of adsorbent, carbonization temperature and duration will be studied.

## CHAPTER 2 LITERATURE REVIEW / THEORY

## 2.1 Adsorption

The use of solids for removing substances from either gaseous of liquid solution has been widely used since older time. It involves the preferential partitioning of substances from the gaseous or liquid phase; adsorbate onto the solid surface; adsorbent. There are four things contributing to the effectiveness of adsorption process to happens; the surface interaction, adsorbate-solvent properties, system properties and adsorbent properties [5].

## 2.1.1 Surface interaction

Adsorptions happen as the result of the bonding of the adsorbate molecules, ions, or individual atoms with the adsorbent surface due to week intermolecular and electromagnetic force that held the adsorbate at the adsorbent outer layer. There are four principle for adsorption; exchange, physical, chemistry and specific adsorption.

Exchange adsorption, also called ion exchange involves electrostatic attachment of the adsorbent's ions onto the adsorbent surface, with subsequent displacement of these species by other ionic adsorbates of greater electrostatic affinity [5].

Physical adsorption happens due to Van der Walls forces between the adsorbate and the adsorbent surface. Meanwhile, for chemical adsorption, the adsorption happens when there is reaction between the adsorbate and the adsorbent; resulting in a change in the chemical form of the adsorbate. The results from the chemical adsorption are usually stronger than that derived from the physical intermolecular forces.

As for the specific adsorption, adsorptions happen due to the attachment of adsorbate molecules at functional group on adsorbent surfaces. But this reaction does not result in transformation of adsorbate. The net dispersion, electrostatic, chemisorptive and functional group interactions broadly define the affinity of an adsorbent for a specific adsorbate [5].

Thus, in determine a good adsorption process, the adsorbent are characterized by the surface properties; polarity and the surface area, and the physical size and the form of the adsorbent particles [5]. System parameter like pH and also temperature could also influence the adsorption capacity.

## 2.1.2 Adsorbate-Solvent properties

Adsorbate molecular size can affect the adsorption rates if the process is controlled by intraparticle diffusive mass transport within porous adsorbent, where smaller molecules size will result in faster process. But if higher energies or driving forces for the adsorption process is supplied, the larger molecules may adsorb more rapidly than the smaller one.

Beside molecular size, the surface chemistry of the adsorbent; activated carbon may also influence on the adsorption of certain compound. For adsorption of polar and ionic compound, the adsorption capacity is dependent more on the carbon surface chemistry. Several types of the adsorbent functional groups like hydroxyl, carboxyl, nitro, nitrile, carbonyl,sulfonate and amine tend to produce fairly high polarities in compounds [7]. It has been found out that the presence of acidic surface oxides, whose concentration can be increased by oxygen adsorption or chemical treatment, leads to a decrease in adsorption capacity but increase the base adsorption capacity.

[5]

#### 2.1.3 System properties

Temperature and pH of the aqueous solution for the adsorption process thus influence the adsorption capacity. pH for example, governs the degree of protolysis or "ionization" of the compounds. Neutral species like phenol tend to adsorb more from the aqueous phase than do their corresponding ionic forms, phenolate ions. [5]

## 2.1.4 Adsorbent properties

Adsorption is a surface phenomenon and practical commercial adsorbent are therefore characterized by large surface area, which is comprised of internal surfaces bounding the extensive pores and capillaries of highly porous solids. Further discussion on the characteristic of the adsorbent that enhance the adsorption process will be discussed in the manufacturing of the activated carbon part, below. [5]

#### 2.2 Lead in the environment

Lead has been introduced into natural water from a variety of sources like battery industry, lead smelting, ceramic glass industries, and paint and dyes industry. The permissible limit of lead in drinking water is  $0.05 \, \text{mg/L}$ . The presence of excess lead in drinking water can cause disease such as anemia, encephalopathy and hepatisis. Lead ions have an affinity for ligands containing thiol and phospathic group. They inhibit the biosynthesis of heme, causing damage both to kidney and liver; same behaviour as calcium. But lead can remain immobilized for years and therefore it is difficult to detect the metabolic disorder it causes. [12]

## 2.3 Manufacturing of the Activated Carbon

Activated carbon is formed by the carbonization and activation of carbonaceous (organic) material. These carbons are prepared in order to exhibit a highly ramified porous structure and an extensive surface area (typically about 1000 m<sup>2</sup>/g) [1].

Activated carbon consists of aromatics sheets and strips, with gaps of variable molecular dimensions between them, which called as the micropores. During the activation, the spaces between the graphitelike crystallites become cleared of various carbonaceous compounds and disorganized carbon, where the meso and macroporosity is developed. High ramified porous structure will result in a very large adsorption capacity [7].

Commercial activated carbon is usually made from woods or coal. Studies have been done in producing activated carbon from organic material where the environmental waste like the coconut shells, de-oiled soya, and dates pits come in handy. Recently, studies on producing the activated carbon using the rice husks are being done.

Manufacturing of activated carbon consists of two stages; activation and carbonization of the carbonaceous raw material at temperature below 1000 °C in the absence of oxygen. Thus all carbonaceous material can be converted into activated carbon, although the product quality would not be the same; depending on the properties of the raw material and the activation agent and process conditions [1].

During carbonization, most of the non carbon elements such as Oxygen and Hydrogen are eliminated as volatile gaseous products by the pryrolytic decomposition of the raw material, leaving the residual carbon atoms group which would bound together to form condensed aromatics ring system with a certain degree of planar structure. The mutual arrangement of these aromatics sheet is irregular and therefore leaves free interstices between them which may become filled with the tarry matter or the products of decomposition or partially blocked by the disorganized carbon. These interstices give rise to pores, which make the active carbons excellent adsorbents [1].

After carbonization, the treated carbonaceous will undergo an activation process using gases, vapors or activating agent. Activation is done to enhance the volume and enhance the diameters of the pores which were created during the carbonization period, and create new porosity. It removes the disorganized carbon, exposing the aromatics sheets to the action of activating agents and leads to the development of the microporous structure. Besides widening the existing pores, it also form large size pores by complete burnouts of the walls between the adjacent pores. This results in an increase in the transitional pores and microporosity, whereas the volume of the micropores decreases. Thus the extend of burnoff of the carbon material is a measure of the degree of activation [8].

According to Dubinin and zaverina, a microporous active carbon is produced when the degree of burnoff is less than 50 % and a microporous active carbon form when the degree is greater than 75 %. When the degree of burnoff is between 50 to 75%, the products is said to have both macro and miroporous structures. But the final pore structure of the activated carbon will still be determined by the properties of the raw material use [1].

Although it is known that the activation process will enhance the pores of the active carbon, but the exact mechanism in doing it is still not completely understood. There is also various methods use for activating the carbonaceous material. As in this study, the activation process is done by mixing the carbonaceous material with NaOH solution, there are also other method done in other studies. For example, research done by the researcher from Department of Chemistry, Jilin University, Changchun 130023, China. The active carbons were prepared by sealed dry distillation and activation from rice husk. First, the rice husk was washed and dried. Secondly, the dried rice husk was carbonized at 350–500 °C in the presence of Nitrogen. Later, the carbonized product was heated in the presence of a substantial weight of potassium hydroxide or sodium hydroxide at 350–400 °C for 0.3–1.0 hr to dehydrate the combination thereafter the temperature was raised to 650–850 °C for 1 hr to activate the combination. Finally, the activated product was ground, washed with water and dried at 120 °C to form the porous carbon and readied for adsorption test [11].

## 2.4 Effect of carbonization temperature on activated carbon

Carbonization involves thermal decomposition of the carbon material, eliminating non carbon species and producing a fixed carbon mass and rudimentary pore structure. The process is usually carried out in a vacuum furnace at temperature below 1000°C. There are several parameters that affect the result of the carbonization process:

- 1) rate of heating
- 2) final heat treatment temperature
- 3) soaking time at the final temperature
- 4) nature and physical properties of the raw material.

Low heating rate during carbonization results in lower volatilization and higher char yield because of increase dehydration and better stabilization of the polymeric components. However the char microporosity was found to be independent of the precursor composition and carbonizing heating rate. The basic microstructure was formed by 500 °C, although some of these pores were blocked by the carbonization products and could be available only when high treatment temperature were given.

When the chars were prepared at temperature lower than the activation temperature, they underwent further pyrolytic decomposition during activation, resulting in weight loss independent of the activating gas. The oxidative reactivity of the activating agent gas dependent largely on the heating rate below 500 °C, duration of exposure to temperature near 900 °C during carbonization, and the nature of oxidizing atmosphere. Thus the low-temperature chars gasify at a much faster rate in the initial stages of the activation process [1].

The carbonization involves two important stages that determine the properties of the final product. The first stage is the softening period, during which the temperature control has an important bearing on the type of char obtained. After the softening period, the chars begin to harden and shrink. The shrinkage of the char also plays a role in the development of porosity in the char. In the case of soft coal, the temperature rise during the softening stage should be very slow so that the gas can escape through the pores in the granules without a collapse or deformation. However in the case of wood, lignin, coconut, and petroleum coke the softening stage does not

produce any particular problems but the low rate of heating can results in denser and harder chars. However low rate of heating can promote shrinkage, which reduce the char pore volumes [1].

## 2.5 Effect of structures and pore size distribution

The performance of the activated carbon as the adsorbent relates in large measure to their intraparticle properties. Surface area and the distribution of area with respect to the pore size generally are the primary determinants of the adsorption capacity. The nature of the intraparticle surface area markedly affects the types of adsorption interactions that will be operative for an adsorbent, and it is a major distinguishing factor between the activated carbon and other synthesis adsorbent.

Commercial activated carbon typically have total surface are in between 450-1500 m<sup>2</sup>/g measured by the nitrogen adsorption technique. However the actual surface area available for adsorption is dependent on the specific nature of the adsorbate and can be considered less than the total. The pore volumes of activated carbon range from 0.5 to 1.5 cc/g. It is however only that fraction of the pore volume contained in pores larger than about 10Å which determine the effective capacity of carbons for liquid phase applications. The effective capacity thus depends on the distribution of molecular size to be adsorbed. [5]

#### 2.6 Effect of surface chemistry

The surface chemistry of the activated carbon is also important in determining the adsorption capacity of the adsorbent. The chemical properties of the surface of the raw material used, the type of activation process, and the condition employed in the activation process all contributing towards the adsorbent surface chemistry.

Activated carbon surfaces consist of two different types, basal plane areas and heterogeneous edges of carbon plane to which carbon-oxygen functional group formed by oxidation in the manufacturing duration process are attached. At basal plane, the large uniform nonpolar surfaces support the solvophobic and physical

adsorptions activities. While the heterogeneous edges of carbon plane, the halogenation, hydrogenation and oxidation process are allowed to happen. These group, provide the ability for the electrostatic, hydrogen bonding, functional group, and chemisorption adsorbent-adsorbate interaction which generally exceed the the physical adsorption and greatly extend the spectrum and degree of adsorbability of adsorbates on the activated carbon. This group enhances the adsorption efficiency at very low adsorbate concentrations in the solution phase [7]

#### 2.7 Characterization of rice husks

Characteristic of the raw material is the important factor in producing a good activated carbon. It includes the pore structure, particle size, total surface area and void space between particles. The composition of the raw material is also important as it will determine the hardness and selectivity of the adsorbent. Studies done by Rahman, Ismail and Osman [13] indicate the composition of rice husks as follows:

Table 1: Composition of organic constituent in the activated rice husks compared to the raw rice husks.

Raw rice husks	Activated rice husks		
16.1	74.0		
35.5	22.8		
22.3	3.1		
13.6	0.2		
12.5	0		
100	100.1		
	16.1 35.5 22.3 13.6 12.5		

The table shows that the activation has increase the amount of silica. This is due to the reduction in overall mass after digestion. After activation, the sample consists of finely degraded cellulose-silica skeleton that consists 74 % silica and 26 % cellulosic material. The Scanning Electron Micrograph indicates that the activated rice husks size decrease with activation time. At the same time, the porosity of the rice husks also increase with increasing of carbonization duration. This is caused by the thermal decomposition of cellulosic materials during carbonization process [8].

Figures below show the structure of activated carbon produced from coconut shell as an example of activated carbon pores structure.

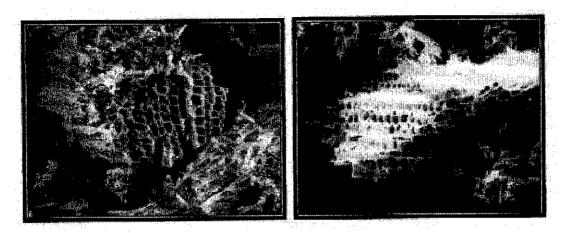


Figure 1 : Close up image of pores by Scanning Electron Microscope

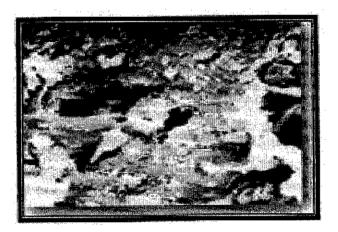


Figure 2 : Pores after carbonization process

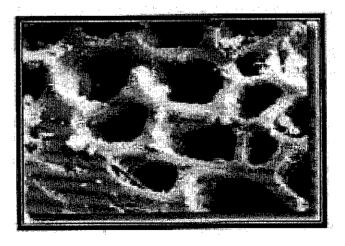


Figure 3 : Pores after activation process

## 2.8 Equilibrium Isotherm for the Adsorbents

The adsorption of a substance from one phase to the surface of another system leads to a thermodynamically defined distribution of that substance between the phases when the system reach equilibrium; when no further adsorption occurs. At this stage, the amount of substances adsorbed per unit weight of adsorbent, Qe, is express as a function of the residual equilibrium concentration, Ce of substance remaining in the solution phase. This relationship is called adsorption isotherm model, defined the functional equilibrium distribution of adsorption with concentration of adsorbate at constant temperature. Commonly, the adsorption capacity will increase as the concentration increase, but not in direct proportional order.

Isotherm is very important in predictive modeling procedures for analysis and design of adsorption system. It is also use for theoretical evaluation and interpretation of thermodynamics parameters, such as heat of adsorption. Several equilibrium models have been developed to describe the adsorption isotherm relationship where in this study Freunlich and Langmuir isotherm are studied.

## 2.8.1 Freundlich isotherm

$$Qe = KCe^{(n)}$$

Rearrange the equation to linear form;

$$Log Qe = Log K_F + (n) Log Ce$$

Where  $K_F$  is the indicator of adsorption capacity, while 1/n is the indicative of the energy or intensity of the reaction (Weber, 1972).

## 2.8.2 Langmuir isotherm

$$Q_e = Q_0 C / (K_L + C)$$

Rearrange the equation to linear form;

$$1/Qe = K_I/Q_0(1/C) + 1/Q_0$$

Where Qe is the amount of solute adsorbed per unit weight of adsorbent,

Q is the solid phase concentration corresponding to complete coverage of available sites, or the limiting adsorption capacity and C is the residual liquid phase concentration at equilibrium.

# CHAPTER 3 PROJECT METHODOLOGY

## 3.1 Adsorbent preparation

Two types of activated carbon sample were manufactured; based activated carbon and acidic activated carbon. The earlier stages of the productions were the same and only differ in the last method.

First, the rice husks were washed with distilled water to remove any unwanted impurities attached to it before been dried in the oven at 110 °C for 24 hours. Later, the rice husks were grinded and sieved to be classified to four different sizes; 1 mm, 500  $\mu$ m, 250  $\mu$ m and less than 250  $\mu$ m. After being classified, the rice husks were carbonized in the furnace at two different temperatures with different time duration; 500 °C, and 700 °C for 0,  $\frac{1}{2}$  and 1 hours. But because of the difficulty in getting the activated rice husk at 700 °C, the carbonization duration for this temperature were done at 0 hour only.

After being carbonized, the rice husks were activated using 0.1 M Sodium Hydroxide solution as the activating agent; for 24 hours on a platform shaker. Further treatment, for an acidic to neutral activated carbon, the samples was neutralized with Nitric Acid. As for base activated carbon, after being activated, the samples were straightly dried in an oven for 3 hours at 120 °C before been used for the adsorption studies.

## 3.2 Adsorbate preparation

0.8475 gram of Lead Nitrate, Pb(NO<sub>3</sub>)<sub>2</sub> was weighted in a clean dried beaker and was dissolved in 1 L of distilled water to produce 500 mg/L lead concentration solution. (Refer appendix 1 for the sample calculation) For the adsorption studies, five other different concentrations of Lead (II) Nitrate solutions were produced, 20 mg/L, 40 mg/L, 60 mg/L, 80 mg/L and 100 mg/L. For the calibration curve needed for the AAS assessment, three different solution concentrations were prepared as the standard solution; 4 ppm, 8 pm and 16 ppm.

## 3.3 Apparatus

In this project, the equipments used to perform the studies area as follows:

- Oven to remove moisture (pretreatment)
- Grinder to grind the sample into smaller size
- Sieve to classify the sample into three different size groups.
- Furnace for the carbonization of the sample.
- Shaker to ensure the sample surface area are being activated uniformly.
- AAS for the adsorption studies.

Common glassware such as Erlenmeyer flask, beaker, crucible and lid, Desiccators, Petri dish and stirring rod will be used during the studies period.

## 3.4 Batch adsorption experiments

# 3.4.1 Effect of agitation time and adsorption temperature on the capacity of the adsorbent for heavy metal adsorption.

Adsorption experiment to determine the time taken for the adsorption process to reach equilibrium at certain process temperature was conducted as follow: 0.15 gram of activated carbon was suspended in a 150 ml of lead solution containing 40 mg/L of lead for both base activated carbon and neutral to acidic activated carbon sample. The adsorption temperature were varies at 35 °C, 40 °C and 45 °C using a water bath shaker as the reaction platform. The reaction time was conducted for 3 hours and 5 minutes where sample were taken after 5, 15, 35, 55, 80, 115, 145 and 185 minutes.

#### 3.4.2 Effect of particle size

Adsorption experiment to determine the effect of adsorbent size towards adsorption capacity was conducted as follow: 0.1 gram of activated carbon from various sizes; 1 mm, 500  $\mu$ m, 250  $\mu$ m, and <250  $\mu$ m were suspended in a 100 ml of lead solution containing 20 mg/L and 40 mg/L of lead. The adsorption process was done on a platform shaker machine with the rpm of 120 for a period of 2 hours.

## 3.4.3 Effect of carbonization temperature and duration

The effect of carbonization temperature and duration was studied using a 0.1 gram of activated carbon from different carbonization duration and temperature; 700 °C with 0 hour duration, 500 °C with 1 hour duration and 500 °C with 0 hour duration. The activated carbon were suspended in a 100 ml of lead solution containing 20 mg/L, 40 mg/L and 80 mg/L lead concentration. The adsorption process was done on a platform shaker machine with the rpm of 120 for a period of 2 hours.

## 3.4.4 Effect of temperature on the adsorption rate

The adsorption isotherms were studied at different process temperature, 27 °C, 35 °C and 45 °C. Experiment was done using 0.1 g of activated carbon which were suspended in 100 ml of lead solution from 20 mg/L to 100 mg/L of lead concentration. Samples were put in the water bath shaker at 120 rpm for a period of 2 hours. The adsorption isotherm for two different type of activated carbon was studied, base carbon and neutral to acidic carbon. Langmuir and Freundlich isotherm model were constructed from the experiment results.

## 3.4.5 Effect of shaking motion on the adsorption rate

The maximum adsorption capacities of the same type of sample used in the experiments done were compared. As the experiments were done on difference type of shakers, different shaking motions were observed. The effects of the motions were studied.

#### 3.4.6 Surface characterization of the activated carbon

The functional groups of the activated carbon from rice husks were determined using Fourier Transform Infrared test (FTIR). The results were compared with the commercial activated carbon functional groups.

#### 3.5 Adsorption isotherm

## 3.5.1 Development of adsorption isotherm model

Using the values obtained from the above experiments, an adsorption isotherm would be developed. The student will determined the best isotherm model; using both Freundlich and Langmuir equation.

## 3.5.2 Identify thermodynamic parameters for the adsorption process

As to study the effect of temperature towards the adsorption rate, Langmuir equation will be used;  $1/Q_e = [1/bQ_0] \ 1/C_e + 1/Q_0$ 

Where  $Q_e$  is the amount of lead adsorbed per unit weight of the adsorbent (mg/g),  $C_e$  is the equilibrium concentration (mg/L),  $Q_0$  is the maximum adsorption capacity) and b is the is the energy of adsorption capacity which can be calculated from the regression analysis [8]

For the thermodynamics parameters calculation, the equations below would be used:

- 1. Gibbs free energy,  $\Delta G^0 = -RT \ln b$
- 2. Enthalpy,  $\Delta H^0 = -R [T_2T_1/(T_2-T_1)] ln[b_2/b_1]$
- 3. Entrophy,  $\Delta S^0 = [\Delta H^0 \Delta G^0]/T$

## 3.5.3 Identify the favorability of the adsorption process

To detect whether the adsorption process is favorable or not, the favorability is determine using the separation factor, r calculation;

$$r = 1/[1+bC_0]$$

where b is the Langmuir constant and C<sub>0</sub> is the initial concentration.

# CHAPTER 4 RESULTS AND DISCUSSION

## 4.1 Preparation of Activated Carbon from Rice Husks

The samples of activated carbon were prepared at different carbonization parameters and different sample finishing. As the rice husks were characterized according to their sizes; 1 mm, 500  $\mu$ m, 250  $\mu$ m and less than 250  $\mu$ m, the carbonization temperature and duration were also varied; 700 °C with 0 hour duration, 500 °C with 1 hour duration and 500°C with 0 hour duration. For each different parameter, the sample is then divided into two type of sample, acidic to neutral activated carbon and base activated carbon; where the sample is differentiate after the activation process with 0.1 M NaOH. Table 2 below shows the type of sample produced for this study.

Table 2 : Types of activated carbon produced with various parameters

Carbonization temperature	Duration	Type of samples (μm)							
(°C)	(Hr)	acidic					ba	ise	
		1000	500	250	<250	1000	500	250	<250
700	0		√			<b>√</b>			
500	1			$\sqrt{}$	√	V			
500	0	√							

Several initial attempts in making the activated carbon were failed where almost all of the rice husks which were carbonized at 500°C turned into ashes (Refer Figure 4). It should be noted that the required equipment for the carbonization process is the vacuum furnace, but because of the unavailability, an electric furnace was used for this study. From the discussion made with the supervisor, it was found out that the type of the crucible used was the main contributor for the failure. The crucibles used

either have no cover or have holes at the bottom, which allow the rice husks to have direct contact with oxygen. Therefore, instead of being carbonized, the rice husks were burned inside the furnace. Later, other type of crucibles with the cover was used for carbonization process, where good results were produced.

(Refer Figure 5)

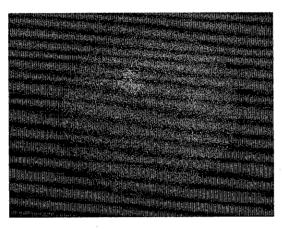


Figure 4 : Rice husks turned into ashes for initial carbonization attempt at 500 °C

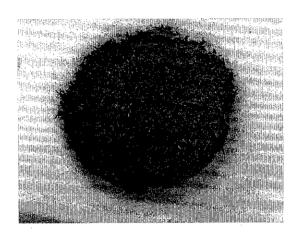


Figure 5 : Carbonized rice husks at temperature 500 °C

Through out the samples preparation process, it was observed that after the carbonization process, the weight of the rice husks had decreased from 6 g to 2.5 g. This was due to removal of the moisture content and other unwanted volatile component inside the rice husks, leaving most of the carbon chain in it. Later, the samples were activated by the activating agent; 0.1 M NaOH solution for 24 hours. It was observed that when the activating agent was contact in the samples, most of the ashes evaporate to the atmosphere. Later, the samples were weighed again and it was

found that the weight left is only around 1.5 g. Reducing in weight may be cause of the ashes evaporation, samples dilution in the NaOH solution, and samples losses while removing the dried samples from the filter paper.

# 4.2 Effect of agitation time and adsorption temperature on the capacity of the adsorbent for heavy metal adsorption.

The main objective of this research is to develop the isotherm model for the adsorption process at different process temperature. Therefore the time taken for the system to reach equilibrium was studied in this experiment. With the same lead solution concentration, 40 mg/L and the same amount of adsorbent per amount of lead solution, the time taken for each different process temperature to reach equilibrium state were determined.

For acidic activated carbon sample, it were observed that the adsorption capacity for system at 45 °C gave the highest value, followed by process temperature at 40 °C while adsorption at 35 °C gave the lowest adsorption capacity. The maximum adsorption capacity for the system is 167.87 mg lead per gram of activated carbon.

As for the base activated carbon, the same pattern were obtained where adsorption at temperature 45 °C, gave the highest adsorption capacity, followed by adsorption at 40 °C, then 35 °C. In terms of the maximum adsorption capacity between both samples, the adsorption capacity of base activated carbon is slightly more than acidic carbon; 171.73 mg/g compared to 167.87 mg lead per gram of activated carbon. But in this experiment, the focused would be the time taken for the system to reach equilibrium. It was observed that the time required for base activated carbon to reach equilibrium is much more shorter compared to the acidic activated carbon; 40 minutes versus more than 60 minutes for acidic carbon.

The equilibrium time determined in this experiment was later being used for the isotherm model experiment and thermodynamic calculations.

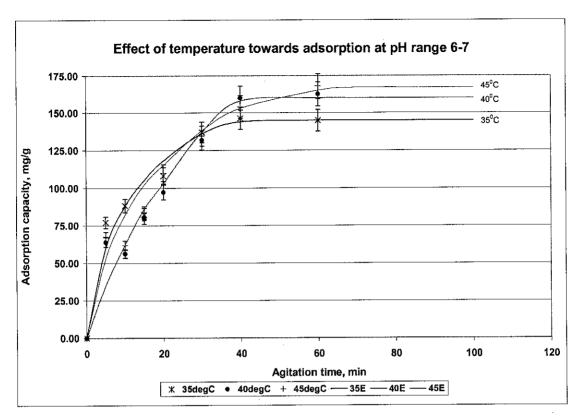


Figure 6: Adsorption capacity for acidic activated carbon at different process temperature.

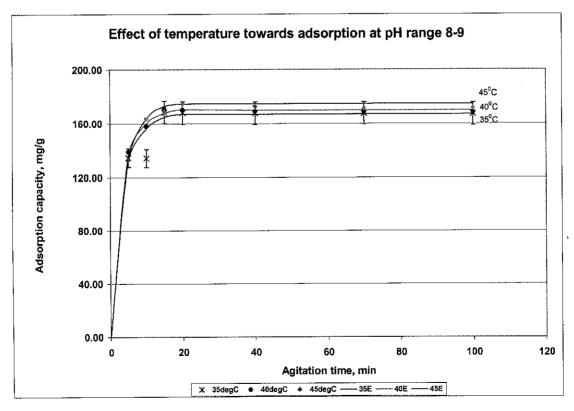


Figure 7 : Adsorption capacity for base activated carbon at different process temperature.

## 4.3 Effect of temperature on the adsorption rate (Adsorption isotherm)

As the determination of the thermodynamic properties for the adsorption process is the purpose of this study, the isotherm models were built based on three different adsorption temperature; 27 °C, 35 °C and 45 °C using two types of samples, acidic activated carbon (1 mm, 700 °C with 0 hour) and base activated carbon (1 mm, 500 °C, 1 hour)

Figure 8 and figure 9 below show the adsorption capacity for both type of activated carbon sample at different lead concentration; 20 mg/L, 40 mg/L, 60 mg/L, 80 mg/L and 100 mg/L. The results showed that the adsorption capacity for the base activated carbon is much more higher compared to the acidic activated carbon. For base activated carbon, the maximum adsorption capacities at all adsorption temperature are in the range of 430 mg/g to 470 mg lead /g activated carbon. But for acidic activated carbon, the maximum adsorption capacities are around 220 mg/g to 230 mg lead /g activated carbon.

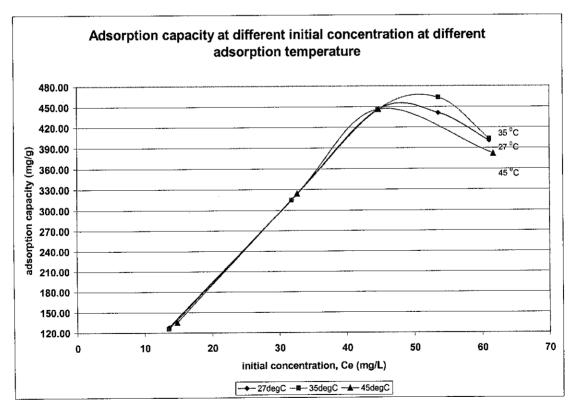


Figure 8 : Adsorption capacity at different initial concentration and adsorption temperature for base activated carbon.

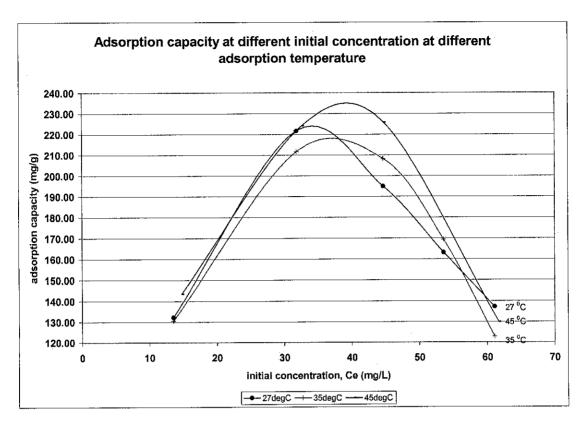


Figure 9 : Adsorption capacity at different initial concentration and adsorption temperature for acidic activated carbon.

From the results of the final lead concentration at equilibrium time, and the amount of lead adsorbed per g activated carbon at equilibrium, Langmuir and Freundlich isotherm model were built. Refer figure 10 and 11 for the Langmuir and Freundlich isotherm model for acidic activated carbon. For the acidic activated carbon, the Langmuir isotherms fits best with all adsorption data at difference temperatures have an R square value almost equal to 1. While for the base activated carbon, the Freundlich isotherm model fits best. But the slope of the model indicate a negative value, thus the adsorption by the base activated carbon is unfavorable. Refer figure 12 for Freundlich model of base activated carbon.

#### 4.3.1 Langmuir isotherm

$$Q_e = Q_0 C / (K_L + C)$$

Where  $K_L$  and  $Q_0 = Langmuir constant,$ 

 $Q_e$  = amount of lead adsorbed on the adsorbent (mg/g)

C = final concentration of lead solution at equilibrium (mg/L)

Rearranging the equation to the linear form;

$$1/Qe = K_L/Q_0(1/C) + 1/Q_0$$

#### 4.3.2 Freundlich isotherm

$$Oe = K_F Ce^{(n)}$$

Where  $K_F$  and n = Freundlich constant

 $Q_e$  = amount of lead adsorbed on the adsorbent (mg/g)

C = final concentration of lead solution at equilibrium (mg/L)

Rearranging the equation to the linear form;

$$Log Qe = Log K_F + (n) Log Ce$$

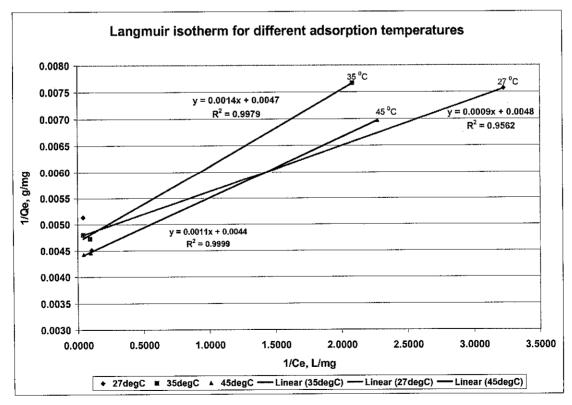


Figure 10: Langmuir isotherm for adsorption process at different temperatures.

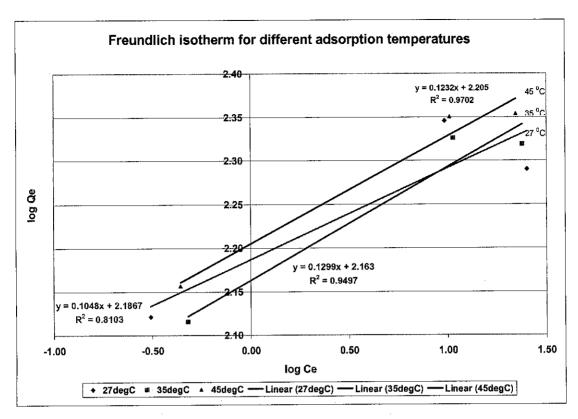


Figure 11: Freundlich isotherm for adsorption process at different temperatures for acidic activated carbon.

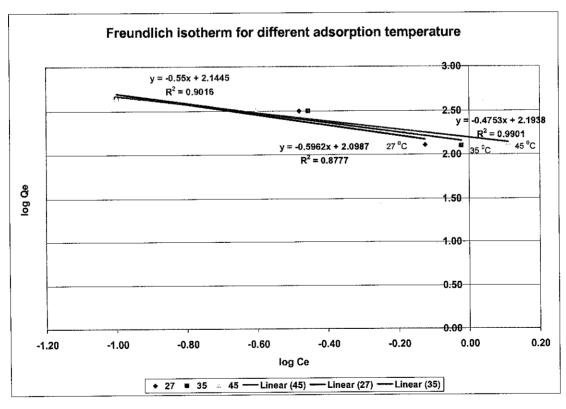


Figure 12 : Freundlich isotherm for adsorption process at different temperatures for base activated carbon.

The constant value for both Langmuir and Freundlich isotherm model were tabulated in the table below. As Langmuir isotherm fits better for the acidic activated carbon graph, the constant values were used in the thermodynamic calculation.

Table 3 : Values of Langmuir constant ( $Q_0$  and  $K_L$ ) and Freundlich constant ( $K_F$  and n) at different temperature

Temperature ( <sup>0</sup> C)	Langmui	r constant	Freundlich constant		
remperature (C)	Q <sub>0</sub> (mg/g)	K <sub>L</sub> (mg/L)	Kf (mg/g)	n (L/mg)	
27	208.333	0.1875	1.1105	0.1048	
35	212,766	0.2979	8.7303	0.1299	
45	227.273	0.2500	9.0703	0.1232	

The favorability of the adsorption process are detected by the calculation of the separation factor, r which is calculated using equation, [12]

$$r = 1/[1+bC_0]$$

where b equal to  $(1/K_L)$  and  $C_0$  is the initial concentration. The results are tabulated in Table 3. All r values, calculated per equation were found less than 1. Positive values of r, which are less than 1, confirm the favourability of the adsorption isotherm. It may be noted that on the basis of different r values, the diagnos criterion about the nature of isotherm involved is as follows:

r > 1, = unfavorable isotherm

r = 1, = linear isotherm

0 < r < 1, = favorable isotherm

r = 0, = irreversible isotherm

Table 4 : r value for different initial concentration at different temperatures.

r								
Temperature( <sup>0</sup> C)	10ppm	20ppm	40ppm	60ppm	80ppm	100ppm		
27	0.018	0.009	0.005	0.003	0.002	0.002		
35	0.029	0.015	0.007	0.005	0.004	0.003		
45	0.024	0.012	0.006	0.004	0.003	0.002		

Using the Langmuir constant, the thermodynamic properties for the adsorption process was calculated using the equation below;

- 1. Gibbs free energy,  $\Delta G^0 = -RT \ln b$
- 2. Enthalpy,  $\Delta H^0 = -R [T_2T_1/(T_2-T_1)] \ln[b_2/b_1]$
- 3. Entrophy,  $\Delta S^0 = [\Delta H^0 \Delta G^0]/T$

Where b,  $b_1$ ,  $b_2$  are the Langmuir constant at temperature 27 °C, 35 °C and 45 °C respectively. The negative values of  $\Delta G^0$  obtained confirm the feasibility and spontaneous of the adsorption process at each temperature. It was also observed that the value of  $\Delta G^0$  decrease with positive values of enthalpy change ( $\Delta H^0$ ) suggest the endothermic nature of the process, while positive  $\Delta S^0$  value reflect the affinity of adsorbent material towards the Pb<sup>2+</sup> ions. Table 4 shows the thermodynamic properties of the system

Table 5: Values of thermodynamics parameters for the lead-activated carbon adsorption process.

Properties	Value
ΔG <sup>0</sup> @ 27 °C	- 13.309 kJ/mol
ΔG <sup>0</sup> @ 35 °C	- 8.601 kJ/mol
ΔG <sup>0</sup> @ 45 °C	- 10.580 kJ/mol
ΔH <sup>0</sup> @ 35 °C	44.493 kJ/mol
ΔH <sup>0</sup> @ 45 °C	12.689 kJ/mol
ΔS <sup>0</sup> @ 35 °C	172.30 J/mol.K
ΔS <sup>0</sup> @ 45 °C	73.14 J/mol.K

#### 4.4 Effect of carbonization temperature and carbonization duration

In order to evaluate the best carbonization temperature and duration needed for the best activated carbon production, sample prepared were varied in terms of different carbonization temperature with the same duration (700 °C, 0 hour and 500 °C, 0 hour) and the same carbonization temperature but different duration (500 °C, 1 hour and 500 °C, 0 hour) Figure 13 below shows the result obtained from the experiment.

It can obviously be seen that sample prepared at 700 °C, gave the highest adsorption capacity, varies from 140 mg/g up to 467 mg lead /gram of activated carbon followed by sample prepared at 500 °C, 1 hour. The difference of adsorption capacity between both sample prepared at 500 °C is quite small but it thus shown that the carbonization duration also affect the activated carbon adsorption capacity where the capacity for activated carbon produced in 1 hour duration gave a slightly higher value than 0 hour sample carbonization duration.

The results indicate that at higher carbonization temperature, good activated carbon with larger adsorption capacity will be produced. From literature, temperature 700°C to 900°C is the best temperature in producing good activated carbon. [4] At this temperature, the specific surface area is considered the largest with its micropore structures are well developed. The total pore volume (micro, meso and macroporores) also been said to increase with increasing in carbonization temperature. However, from previous study, at temperature more than 700°C, the structure of the activated carbon produced start to collapse due to intense heat which result in extinction of micropores [1]. This is due to the thermal degradation of the activated carbon produced at this temperature which will induce reduction of the specific surface area thus decrease the adsorption capacity.

In terms of the duration for the carbonization process, from the results shown, it can be conclude that longer duration would enhance the volume of the contact surface area for the adsorption process. The result also shows that different carbonization temperature gave a different amount of the optimum adsorption capacity. For sample 700 °C, the adsorption capacity increase as the lead concentration increase but for sample 500 °C, the optimum adsorption capacity was at 32 mg/L of lead concentration for 0.1 gram of activated carbon used.

In lower concentration, the adsorbate could occupy the active sites on the carbon surface sufficiently. But with the increase in adsorbate concentration, the number of active adsorption sites is not enough to accommodate adsorbate ions. In addition, the limit of pore size dimension and the electrostatic repulsion among the adsorbate ions results in the decrease of adsorption percentage. From this result, it can be conclude that higher carbonization temperature will results in enhancing the surface area and the pores volume of the activated carbon which increase the adsorption capacity of the adsorbent.

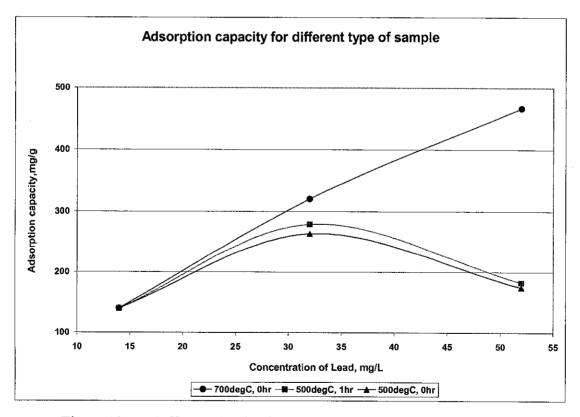


Figure 13 : Effect carbonization temperature and duration

#### 4.5 Effect of particle size

The activated carbon were classified according to the size of 1 mm,  $500 \mu m$ ,  $250 \mu m$ , and  $<250 \mu m$  which is actually the size of the rice husks before undergo any treatment to become activated carbon. When the rice husks undergo the carbonization and activation process, all four sizes characterized become a powdered activated carbon, with no difference in sized from their outer look. As the adsorption capacity is dependent on the volume and distribution of the pores, the result of this experiment could provide information on the total surface area of the activated carbon.

From the results of this experiment, 250  $\mu$ m gave the highest adsorption capacity; 136 mg/g to 477 mg lead / gram of activated carbon, followed by <250  $\mu$ m; 131 mg/g to 395.42 mg/g. The third highest is the 1 mm, with the adsorption capacity varies from 134 to 309 mg/g and lastly 500  $\mu$ m; 135 to 293 mg/g.

From the figure below, it was observed that for the initial size of rice husks at 250  $\mu$ m and <250  $\mu$ m, both samples have higher adsorption capacity compared to the others sizes. This were shown by the results, where at higher lead concentration (above 40 mg/L) only activated carbon from initial rice husks size at 250  $\mu$ m and <250  $\mu$ m can still adsorb lead at maximum capacities. For the other two sizes, the adsorption capability started to decrease at higher lead concentration.

This results shows that the total volume of the active site and its distribution (micro, meso and macroporous pores) does not determine by the initial size of the raw material. Instead, it is affected by the carbonization and activation process which they had undergone. Thus the actual pore size volume and distribution can be determined by analyzing each of the samples using BET surface analyzer.

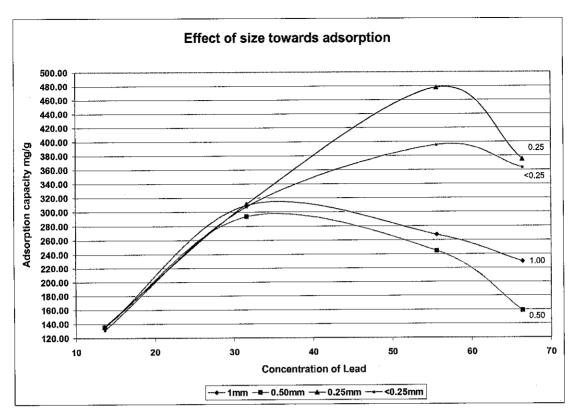


Figure 14 : Effect of particle size towards the adsorption capacities.

#### 4.6 Effect of shaking motion towards the adsorption capacity

Based on several types of experiment done previously, there had been some difference on the adsorption capacity of a same type of sample which was used in the experiment. For example, acidic activated carbon sample (1mm, 700 °C, 0 hour duration) was used for experiment to find the effect of carbonization temperature and duration, and also for the effect of temperature. Both experiment, using the same amount of adsorbent, 0.1 g activated carbon immersed in 100 mL of 20 to 80 mg/L lead concentration, gave different value of adsorption capacity.

For carbonization experiment, the equilibrium adsorption capacity is around 133 to 225 mg lead per g activated carbon. While for carbonization temperature and duration experiment, the adsorption capacity was determined to be in range of 135 to 483 mg lead per g activated carbon. The maximum adsorption capacities differ for about 250 mg/g. Taking the changes cause by differences of adsorption temperature were negligible compared to this differences, the different type of rotation while doing the experiment was determined to be the main reason for this finding. For the effect of

temperature, the experiment was done in a water bath shaker while for the effect of carbonization temperature and duration, a platform shaker was used. The type of rotation produced by both shakers was not the same, even though the rotation was set to be 120 rpm for both equipments. Figures below show the types of shaking motion for each shaker.

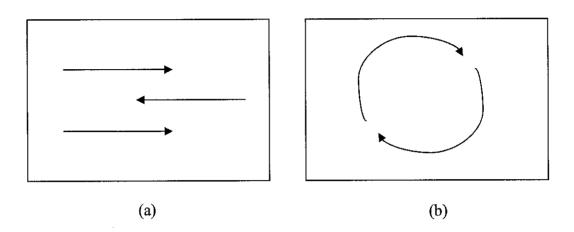


Figure 15 : Shaking motion pattern for (a) water bath shaker (b) platform shaker

Refer to Appendix G for the picture of both types of shaker.

#### 4.7 Comparison with published data

There have been many studies done using agricultural waste such as coconut shell, wheat straw, and palm oil shell to produce activated carbon. As for comparison with the published research, the adsorption capacity of the activated carbon studied in this research is compare with the coconut shell activated carbon at the same amount of activated carbon (0.1 g adsorbent in 100ml lead solution) suspended in lead solution concentration range from 10 mg/L to 50 mg/L.

From this study, it was found that the rice husks activated carbon lead uptake capacity range from 131 to 310 mg/g. Meanwhile, from studies done by M Sekar, the coconut shell is able to adsorb lead at maximum of less than 45 mg lead /gram of activated carbon [11]. As conclusion, the activated carbon from rice husks has a good adsorption capacity for lead ions compared to coconut shell activated carbon.

#### 4.8 FTIR Analysis

There are three basic processes by which the molecules can adsorb the radiation which are rotation, vibration and stretching. The intensity of the spectrum is directly proportional to the atomic masses and inversely proportional to chemicals bonds. The position of peaks depends on the molecular structure and bonding between the atoms. Stretching and vibration of many functional groups (C-H, C=O and ect.) are typically found in the region from 1600 <sup>cm-1</sup> to 4000 <sup>cm-1</sup>. [6]

In this study, the FTIR is used for qualitative identification of molecular components on the commercial activated carbon and the activated carbon produce from the rice husks. The FTIR spectrum of both activated carbons is shown in Figure 16. The spectrum contains several peaks associate with the functional group in both sample. Type of functional group found on both sample were compared.

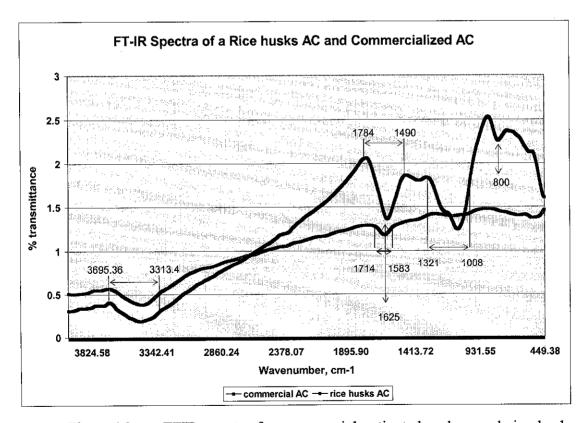


Figure 16: FTIR spectra for commercial activated carbon and rice husks activated carbon.

Figure above represent the FTIR spectrum of the commercial activated carbon and the rice husks activated carbon. Both samples indicate the same functional group in the region of 3313.4 to 3695.36 cm-1, representing hydroxyl group (O-H) and amino group (-NH) and 1583 to 1714 cm-1, representing the carboxyl group and stretching of C=C, C=O and C=N on the sample surface. From the comparison, there are two additional functional group determined on the surface of the rice husks activated carbon which are in the region of 1008 to 1321 cm-1 and around 800 cm-1. The additional region indicate the C-O and C-N vibration on the surface and the aromatic region of benzene ring and C=C bending vibration. [6]

## CHAPTER 5 CONCLUSION AND RECOMMENDATION

Rice husks are found to be a good raw material for production of activated carbon. Studies is done on various of parameters like the carbonization temperature and duration, the size of raw material, the adsorption temperature and the different type of sample; acidic activated carbon and base activated carbon. It is revealed that the base activated carbon has higher adsorption capacity and need shorter time to reached equilibrium than the other sample but the process is unfavorable according to their isotherm model.

The carbonization temperature and duration thus have an effect towards the adsorption capacity where production of activated carbon at 700 °C gave the highest adsorption capacity. This may be due to formation of micropores during the carbonization period. For the initial sizes of the rice husks effect, it does not really affect the adsorption capacity, as the development of the pore size is affected by the carbonization and activation treatment of each sample.

For further studies, it is recommended to study the effect of pH towards the adsorbent adsorption capacity using both type of activated sample produced to look at the effect of base activated carbon in different pH solution. As for the adsorbent adsorption capacity studies, to look at the effect of the pores size, BET surface analysis or Scanning Electron Microscopy; SEM test is encourage to be done by the next student. If possible, as an addition to the batch experiment, a continuous adsorption experiment is encouraged to be done.

In terms of commercializing the rice husks activated carbon, a comparison with the current activated carbon used in the industry should be done on similar experimental scale, based on the adsorption capacity of both activated carbons. From the data gained, basic economic justification can be done to support the fact.

In overall, considering the high adsorption capacities of the activated carbon, their utilization as a source of material for the activated carbon is expected to provoke a significant economical benefit.

#### REFERENCES

- 1. Roop Chand Bansal, Jean Baptiste Donnet, and Fritz Stoeckli, 1988, *Active Carbon*, Marcel Dekker Inc, USA.
- 2. Christie John Geankoplis, *Transport Processes and Separation Process Principles*, Fourth Edition, Prentice Hall, New Jersey.
- 3. J D Seader, Ernest J Henley, *Separation Process Principles*, John Wiley and Sons, 1998, United States of America.
- 4. LJUBISA R RADOVIC, Chemistry and Physics of Carbon; A series of advances, Marcel Dekker Inc, New York.
- 5. Frank L Slejko, Adsorption Technology, A step by step approach to process evaluation and application, Marcel Dekker Inc, New York.
- 6. W J Criddle and G P Ellis, Spectral and Chemical Characterization of organic compound, 3<sup>rd</sup> edition, John Wiley & Sons.
- 7. Mattson, James S, Activated carbon; Surface Chemistry and adsorption from solution, Marcel Dekker Inc, New York.
- 8. Norhaslinda Nasuha, Production of Activated Carbon from Rice Husks and its Adsorption Characteristic for Pb<sup>2+</sup> ion, Final year research project, 2004, UTP, Malaysia.
- 9. Alok Mittal, Lisha Krishnan, VK Gupta, 2004, Removal and recovery of malachite green from wastewater using an agricultural waste material, deoiled soya, journal < <a href="https://www.sciendirect.com">www.sciendirect.com</a>>
- 10. Archana Agrawal, K.K Sahu, B.D Pandey, 2004, Systematic studies on adsorption of lead on sea nodule residues, journal < www.sciendirect.com >

### **APPENDICES**

# APPENDIX A CHEMICAL SAFETY DATA SHEET FOR LEAD (II) NITRATE

### APPENDIX B PROCESS METHODOLOGY

#### **Pretreatment**

· Drying · Grinding · Sieving

#### Carbonization

- Two different temperature; 500 °C and 700 °C
- Two different duration; 0 hr and 1 hr

#### **Chemical Activation**

- Activating agent: 0.1 M NaOH
- Method: Shake with NaOH for 24 hr.
- Neutralized with HNO<sub>3</sub> / do not neutralized

#### **Adsorption Test**

- Effect of carbonization temperature and duration
- Effect of sample size
- Effect of different adsorption temperature
- Effect of different sample condition; base or acidic

Develop adsorption isotherm model

**Determine the Thermodynamics Properties** 

# APPENDIX C RESULTS OF ADSORPTION CAPACITIES FOR DIFFERENCES ADSORPTION TEMPERATURES

Temp	127 degC 10,4 vg₁am	The state of the s	enderigen gestellt betreet gestellt betreet gestellt. Name of the state of the stat	ing saka aktor mengan mengal Maja maja maja seman pengan Maja mengan
	le fy je	<b>du</b> Tan	.500degC,/lhr; pH(8-	9)
2.17538888613 <b>4</b>	ACCOMMENDED TO SECURITION OF S	final conc,	adsorbed mg/g ,	<b>%</b>
		Ce	Qe Qe	removal
initial conc	13.5	0.75	127.80	94.46
	31.8	0.33	314.90	98.96
	44.67	0.10	445.70	99.78
	53.6	9.49	441.00	82.29
	61.1	21.02	400.60	65.59
Temp	35 degC			May Joseph .
AC loading	0.1 gram	enter de la companya de la companya La companya de la co		
Samp	le type	de dimm	,500deg <b>C-1hmpH</b> (8	Company of the Compan
		final conc	adsorbed mg/g, Qe	% removal
initial conc	13.5	0.95	125.80	92.98
	31.8	0.35	314.70	98.90
	44.67	0.1	445.70	99.78
	53.6	7.26	463.30	86.45
	61.1	20.73	403.50	66.06
Temp	45 degC	Landard Company		
AC loading				
samp	enter PAS CARRES	1mm	, 500degC,1hr, pH(8-	9)
		final conc,		% removal
	44.0	Ce	adsorbed mg/g, Qe 135.00	91.28
initial conc	14.8	1.29 0.25	324.00	99.23
	32.7 44.72	0.25	446.20	99.23
	61.70	23.51	381.90	61.90
	01.70	20.01	301.80	01.50

Temp 27 degG	Para a Large Consideration of the Consideration of	Prijeka karanja kapata kapata ya ketang Prijeka karanja kapata kapata kapata kapata kapata kapata kapata kapat Kapata kapata kapat Kapata kapata kapat	er en
sample type		,700degC,0hr, pH(6-	7)
[10] [1] [1] [1] [1] [1] [1] [1] [1] [1] [1	final conc,		0/
	Ce ,	adsorbed mg/g, Qe	removal
initial conc 13.5	0.31	132.20	97.71
31.8	9.65	221.70	69.67
44.67	25.18	194.90	43.63
53.6	37.28	163.10	30.43
61.1	47.36	137.20	22.46
Temp 35 degC	The state of the s	Para Bahana Aga Aga Aga Aga Aga Aga Aga Aga Aga Ag	Maries of the party of the second of the sec
AC loading 0.1 gram			
was a sample type was	A THE PERSON	,700degC,0hr#pH(6#	76)从静中以上。
	final conc.	adsorbed mg/g, Qe	%/************************************
initial conc 13.5	0.48	130.50	96.45
31.8	10.65	211.70	66.53
44.67	23.84	208.30	46.63
53.6	36.66	169.30	31.59
61.1	48.80	122.80	20.10
Temp 45 degC			) 1
AC loading 0.1 gram			
sample type	The second property of	.700dea(C.0hf., pH(6-	<b>7)</b> , wie en
	final cone ;		
1	Company of the second s	adapthod mala Oc	romovol
initial ages 44.0	Ce	adsorbed mg/g, Qe	removal
initial conc 14.8	0.44	143.50	97.03
initial conc 14.8 32.7 44.72			

### APPENDIX D

# RESULTS OF ADSORPTION CAPACITIES FOR DIFFERENCES INITIAL RICE HUSKS SIZES

oncentration	1	20ppm was and a	1 1,11	40ppm	de erholik se	- 80ppm		100ppm
Cloading	Prop. <b>0</b> , <b>1</b> ,		0.1	g	0.1 ************************************			
size (mm)	coric left *** (mg/L)**	amount adsorbed (mg/g)	conc left (mg/L)	amount adsorbed (mg/g)	conc left (mg/L)	"famountadsorbed * """" (mg/g)		udajnioumijajesoriga Santajnio (DISO)
1.00	0.120	134.90	0.680	309.40	26.844	267.46	38.146	229.3
0.50	0.070	135.40	2.280	293.40	29.138	244.52	45.232	158.4
0.25	0.000	136.10	0.530	310.90	5.840	477.50	23.583	374.9
<0.25	0.510	131.00	0.890	307.30	14.048	395.42	24.767	363.1

#### **APPENDIX E**

# RESULTS OF ADSORPTION CAPACITIES FOR DIFFERENCES CARBONIZATION TEMPERATURE AND DURATION

AC type:		700degC, 0hr		500degC, 1hr		m - 1 - 1588,51	500degC; Ohr		
					700 . THE			Part for the state of the state	
	final	mg lead/g	•	final	mg lead/g	ka Power	final-	mgleadge in the spirite and the	
initial conc	conc	AC	%removal	conc	AC	%removal	Concession	AC %remove	
13.5	0	135	100.00	. на <b>0</b> 7	135.00	100.00	a installer and a 10 s	14-44-48-1185 AV 400.0	
31.8	0	318	100.00	4.11	276.90	87.08	5.68	261.2	
53.6	5.3	483	90.11	33.76	198.40	37.01	34,54	190.6 35.5	

## APPENDIX F SAMPLE CALCULATIONS

#### 1) Adsorption Capacity (mg/g);

capacity = (Initial lead concentration - Final lead concentration)

Amount of adsorbent used

#### 2) Thermodynamic properties;

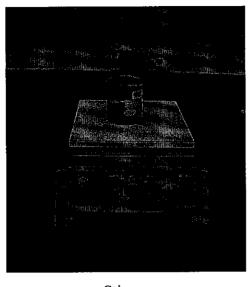
- Gibbs free energy,  $\Delta G^0 = -RT \ln b$
- Enthalpy,  $\Delta H^0 = -R [T_2T_1/(T_2-T_1)] \ln[b_2/b_1]$
- Entrophy,  $\Delta S^0 = [\Delta H^0 \Delta G^0]/T$

R constant Temp K 8.314 273.15

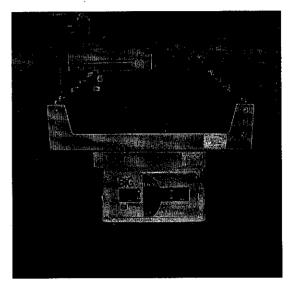
	Temp (degC)	J/(mol)	kJ/mol
	Gibbs Free	Energy, deltaG	
	27	-13309.051	-13.309
(-RTInb)	35	-8600.8627	-8.601
,	45	-10580.396	-10.580
· · · · · · · · · · · · · · · · · · ·	Entha	lpy, delta H	
(-R(T2T1)/(T2- T1)ln(b2/b1)			
. , .	35	44493.31	44.493
	45	12688.80	12.689
······································	Eı	nthropy	
(delta H - delta G)/T			
,	35	172.30	0.1722998
	45	73.14	0.0731391

### APPENDIX G

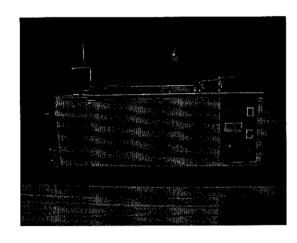
### PICTURES OF EQUIPMENTS USED

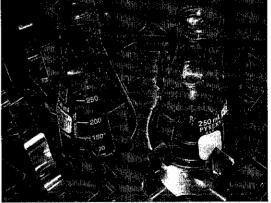


Stirrer

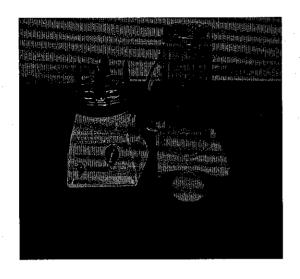


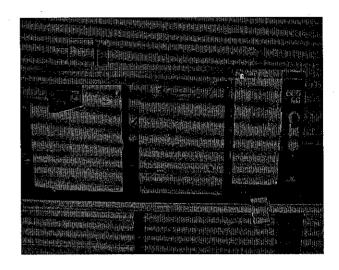
Platform shaker





Water bath shaker and its inner part





Laboratory blender

Water deionizer



Atomic Absorption Spectrometer (AAS)