Preparation and Characterization of Activated Carbon from Rubber Seed Shell via Chemical Activation Using Phosphoric Acid

By

Mohd Norshafizan Bin Abdullah

Dissertation submitted in partial fulfilment of the requirements for the
Bachelor of Engineering (Hons)
(Chemical Engineering)

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CERTIFICATION OF APPROVAL

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Chemical Engineering Programme
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(CHEMICAL ENGINEERING)

Approved by,

____

(Dr. Azry Bin Borhan)

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
May 2013

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.

MOHD NORSHAFIZAN BIN ABDULLAH

ABSTRACT

Activated carbons are widely used as adsorbents. This research presents on the preparation and characterization of activated carbon from rubber seed shell by chemical activation with impregnation of phosphoric acid, H_3PO_4 as the chemical activating agent. This project revolved on finding the most optimum parameters for preparation and characterization of activated carbon from rubber seed shell by manipulating different parameters like raw material size, impregnation ratio, activation temperature and activation time of the activation process. The potential of activated carbon produced in adsorption is evaluated by removing oil and grease from the waste water sample. The preparation of the activated carbon varies by two different sizes of 1mm and 500 µm, by using two impregnation ratio (1:1 and 1:2). The samples were set under nitrogen gas flow for various temperature of 400°C, 500°C and 600°C for carbonization process with two activation time (30 minutes and 90 minutes). The BET surface area of activated carbon corresponding to an impregnation ratio of 1:2 is found to be 8.2310m2g-1 with total pore volume of 0.07918 cm3 g-1 and average pore diameter 5.5418nm by using Micrometrics ASAP 2020, whilst the morphological structures were characterized by using Variable Pressure Field Emission Scanning Electron Spectroscopy (VPFESEM). The optimum condition for the preparation condition is at 500°C activation temperature in 90minutes.The adsorption behavior was described by Nitrogen adsorption-desorption reveal that the pore size widely distributed with the contribution of mesopores. It was found that 84 % of oil and grease successfully removed in the adsorption test. This proved that activated carbon prepared from rubber seed shell, an agricultural waste, can be effectively used as adsorbent for the removal of oil and grease from waste water sample.

ACKNOWLEDGMENTS

In the name of Allah the Most Gracious, the Most Merciful.

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ABBREVIATIONS AND NOMENCLATURES

BET	Brunauer-Emmet-Teller (BET)
BJH	Barret-Joyner-Halenda
C	Carbon
EDX	Energy Dispersive X-Ray
FESEM	Field Emission Scanning Electron Microscope
FYP	Final Year Project
H_3PO_4	Phosphoric acid
IR	Impregnation ratio
N_2	Nitrogen
O	Oxygen
Ppm	Part per million
STP	Standard temperature pressure

CHAPTER 1

INTRODUCTION

1.1 Background of the Study

In the latest statistics of rubber industry in Malaysia, the production of natural rubber in Malaysia recorded an increase of 9.6 per cent in 2010 as compared to 2009 to 939,241 tonnes. The total planted area on estates that was recorded in 2010 was 116,413 hectares comprise of oil palm (54.9%), rubber (42.8%),cocoa and other crops (2.3%).The biggest rubber planted area on estates in 2010 was Kedah & Perlis (23.4%), followed by Negeri Sembilan (19.3%), Kelantan & Terengganu (16.6%) and other states (Annual Rubber Statistics Dept.,2013). Chart 1 shows the percentage of annual rubber production statistics in Malaysia. This shows that rubber plantation is the second largest plantation after oil palm industry in Malaysia.

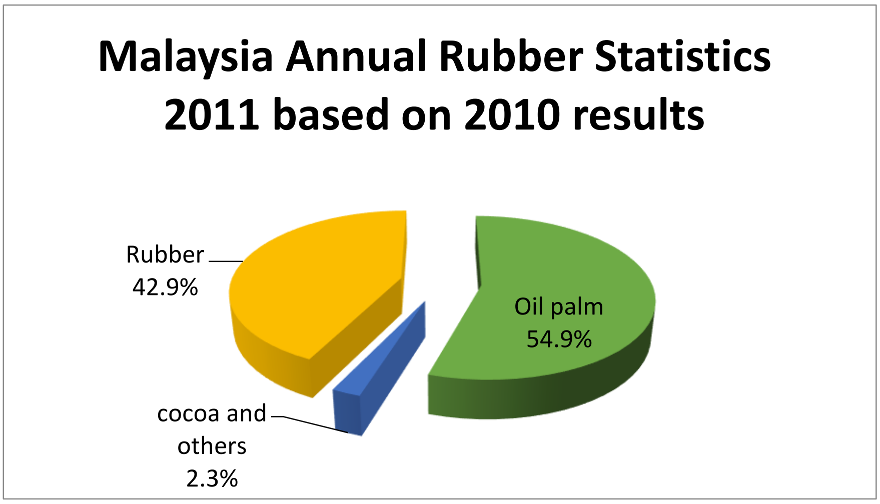


Figure 1.0: Annual rubber statistics in Malaysia 2011

According to the Association of Natural Rubber Producing Countries, Kuala Lumpur, Malaysia has an estimated acreage of 1,229,940 hectares of rubber plantation in 2007. Based on an estimated average of 1000 kg seeds per ha/ yr, the projected annual production of rubber seeds in Malaysia would be 1.2 million metric tons (Eka et.al, 2010). This rubber seed produced can be used in variety of practical such as fertilizers, protein concentrate supplement for animal (Babatunde, 1990), and also biodiesel. However, the using of the rubber seeds will always produce unutilized rubber seed shell. This unutilized rubber seed shell can be used as activated carbon (Azry, B & Ahmad, F. K., 2012).

Activated carbon, also called activated charcoal, activated coal, or carbo activatus, is a form of carbon processed to be riddled with small, low-volume pores that increase the surface area available for adsorption or chemical reactions (Activated carbon, 2012).In addition, activated carbon is one of the most important microporous adsorbents due to its tremendous adsorptive capacity, an affinity for variety of dissolved organics and ability to be custom-tailored to suit specific applications.(Man and Ridzuan, 2008).

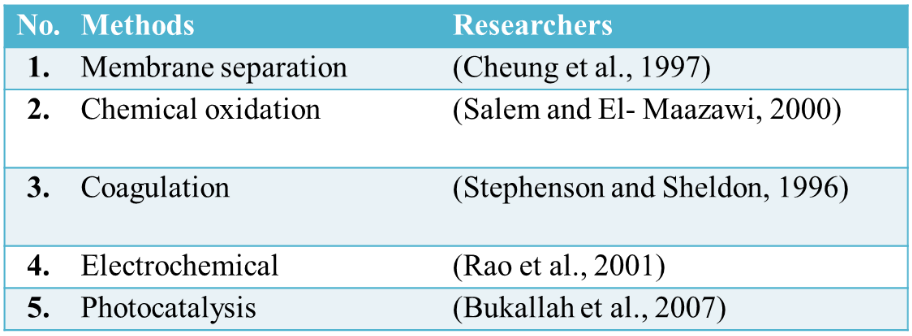
Historically, activated carbon is used for removal of odor, removal of color pigments and various catalytic functions. However, applications of activated carbon have increased significantly in the recent years with the advancement of activated carbon process capability. Activated carbon in its present efficient form is a relatively new comer in the field, particularly in its employment on a commercial scale for a number of purposes, for example; gas-phase application liquid-phase application, application as molecular sieving, application as shape-selective catalyst as well as catalyst support. Application of activated carbon for effluent treatment and pollution control can never be overemphasized to day. Therefore, this project is carried out in order to use this unutilized waste by producing activated carbon via chemical activation with phosphoric acid as chemical activating agent. This activated carbon will be very useful adsorbent in waste water treatment process.

1.2 Problem Statement

Nowadays, the using of rubber seeds to produce biodiesel are very popular among industries. Biodiesel has been produced from refined rubber-seed oil by trans-esterification processes. This production of biodiesel has generated large amount of solid wastes especially the rubber-seed shells. These solid wastes are left unutilized on the fields, causing significant environment and disposal problems (Wan Ngah and Hanafiah, 2008).Waste minimization programs were implemented in these industries in order to maximize the unutilized rubber seed shell and one of the cost effective way is to convert the rubber seed shell to activated carbon. One solution for this situation is the reuse of this waste to produce activated carbon which is one of the most widely used materials because of its low cost and its exceptional adsorption properties (Ioannidou, O. and A. Zabaniotou, 2007). Recently there are many research that prove the agricultural wastes like activated carbon prepared from agricultural waste can be a good adsorbent.

The use of activated carbon prepared from agricultural waste as adsorbent has proven to be effective in the removal of inorganic and organic pollutants from industrial waste water. Before this there are conventional methods used to remove inorganic pollutants from industrial wastewater. The conventional methods used are as below:

Table 1.0: Conventional methods used to remove inorganic pollutants from industrial wastewater



No.	Methods	Researchers
1.	Membrane separation	(Cheung et al., 1997)
2.	Chemical oxidation	(Salem and El- Maazawi, 2000)
3.	Coagulation	(Stephenson and Sheldon, 1996)
4.	Electrochemical	(Rao et al., 2001)
5.	Photocatalysis	(Bukallah et al., 2007)

However, these methods are generally expensive. Therefore this project is carried out in order to investigate the feasibility of using cheaper raw materials which is effective and economic. One of the cheap biomass available are rubber seed shell which is currently unutilized causing disposal problem due to the production of biodiesel from rubber seed oil. In addition, there are no study has been conducted by using rubber seed shell impregnated with phosphoric acid as chemical activating agent.

1.3 Objectives

The main objective of this project is to undergo the preparation of activated carbon from rubber seed shell with phosphoric acid, H_3PO_4 as the chemical activation agent. The discovery of the chemical activating agent effect on the development of activated carbon pore structure produced will be carried out. This project also intended to study the effect of operating parameters such as raw material sizes, impregnation ratio (IR), temperature and time of activation on the adsorption characteristic of activated carbon produced by N_2 adsorption-desorption isotherms. In order to assure the reliability of the activated carbon produced; this project also has to evaluate the potential of activated carbon produced by removing oil and grease from the waste water sample.

1.4 Scope of Study

The scope of study that will be implanted in this project is the finding of the most effective parameters for preparation and characterization of activated carbon. In addition, the project will also investigate the key parameter which affects the activated carbon which is the chemical activating agent (phosphoric acid) on the activated carbon during pretreatment activation. Laboratory tests on the chosen agricultural waste which is rubber seed shell will be performed starting from activation and carbonization process, characterization of the activated carbon produced and as well as the experimental to see the effectiveness of the activated carbon on the sample. In this laboratory test, the most effective parameters for preparation and characterization of activated carbon like size of raw materials, impregnation ratio, temperature and time of activation will be investigated. Data collection and yield distribution will be analyzed by using Brunauer-Emmet-Teller (BET) method and Barret-Joyner-Halenda (BJH) model (Azry, B & Ahmad, F. K., 2012). Adsorption isotherms such as Langmuir and Freundlich will also be covered theoretically throughout the project.

1.5 The Relevancy of the Project

The project is very relevant to the university and to the department as achieving the objectives stated earlier will allow the filtration of impurities from many petrochemical or plants. The activated carbon that is produced are also from the agricultural waste. By converting the low cost agricultural waste to be an adsorbent would be the major contribution that the university can made to the industries not only to the petrochemical industries but also to the whole industries in the world.

1.6 Feasibility of the Project within the Scope and Time Frame

The project of the preparation and characterization of activated carbon from rubber seed shell via chemical activation using phosphoric acid is very challenging project as it requires skill in conducting laboratory experiment. However, the project is able to be conducted with the help from supervisors and other laboratory staffs. This project is feasible to be executed by the author as it falls under the author's scope of study.

In fact, the main concern of this project is to find the most effective parameters to produced activated carbon as adsorbent. An organized Gantt chart is made in order to plan the project's activities (refer to methodology part) and make sure that the project is on track. By referring to the Gantt chart, it can be prove that this project is feasible to be conducted. Thus, the project is very practicable to be assigned by author's supervisor.

CHAPTER 2

LITERATURE REVIEW

2.1 Activated Carbon

Activated carbon, also called activated charcoal, activated coal, or carbo activatus, is a form of carbon processed to be riddled with small, low-volume pores that increase the surface area available for adsorption or chemical reactions (Activated carbon, 2012).Activated charcoal, known as an excellent adsorbent, is well known for its wide applications. Its main use today is in the treatment of solutions (or effluents) for the removal of noxious constituents or colouring matters by sorption. Recovery of solvents from gases, removal of colouring matters from aqueous and other solutions as well as removal of odour and the more recent use of active carbons in ionic change process, are only a few of the examples where the unit operation of adsorption has been employed.

Activated carbon is an extremely versatile material with high porosity and surface area. It has become one of the technically important and most widely used adsorbents because of high adsorptive capacity. Nevertheless, its application fields are restricted due to high cost .The use of low cost wastes and agricultural by- products to produce activated carbon has been shown to provide economic solution (M. Shrestha Rajeshwar et al., 2012).

Activated carbon in its present efficient form is a relatively new comer in the field, particularly in its employment on a commercial scale for a number of purposes, for example, gas-phase application, liquid-phase application , application as molecular sieving, application as shape-selective catalyst as well as catalyst support (L. R. Radovic and F. Rodriguez-Reinoso,1996).

Adsorption capacity of activated carbon depends on the magnitude of the internal surface, the distribution of pore size and shape. The surface chemistry of activated carbon can be modified by a number of ways (Sing, S.K, 1989). Surface chemistry of activated carbon refers to chemically bonded elements of activated carbon which can originate in the starting material or incorporate during activation or subsequent chemical treatment.

Raw materials for the activated carbon productions are usually apricot stones, peach stones, peanut shell, and lapsi seed stones (M. Shrestha Rajeshwar et al., 2012) which are some examples of low cost accessible raw materials for the production of activated carbons.

For this project, activated carbon will be prepared by chemical activation and carbonization of rubber seed shell and the process of combustion and activation was performed in presence of air or nitrogen.

2.2 Activation of Activated Carbon

The preparation of activated carbons can be carried out by one of the following two processes which are Physical activation and Chemical activation. In physical activation, the process of carbonization and activation are done separately. Carbonization process eliminates non carbon elements. Activation or oxidation is carried out by exposing the carbonized material to oxidizing gases like carbon dioxide, or steam at high temperature. While for the chemical activation, the process of carbonization and activation is done in a single step. The raw material is impregnated with certain chemicals at specific ratios before carbonization. The chemical is typically an acid, strong base, or a salt (phosphoric acid, potassium hydroxides, sodium hydroxide, zinc chloride, etc.) (M. Shrestha Rajeshwar et al., 2012).

Then, the impregnated raw material is carbonized at lower temperatures. In this research, the proposed activation method is the chemical activation method. Chemical activation is preferred over physical activation because it requires lower temperatures and shorter time for activating the material (Yanhui Li et al.,2010) .The final result is depending on the raw material used, activating agent and the condition or parameters used in the activation process. In order to identify what is the best raw material and activating agent as well as the optimum parameters of the activation process, the study is need to produce a good adsorbent.

The most widely used of activating agent in industry nowadays is the Phosphoric Acid, H_3PO_4, Potassium Hydroxide, KOH and also Zinc Chloride, $ZnCl_2$. The common feature of these activating agents is that they are dehydrating agents which influence the pyrolytic decomposition and inhibit the formation of tar. They also decrease the formation of acetic acid, methanol and enhance the yield of carbon (Roop Chand B et.al, 1988). In this research, the activating agent that will be used is phosphoric acid. Phosphoric acid produces better modification than other acids to the botanic structure by penetrating, swelling and breaking the bonds of lignocelluloses materials (Girgis B.S., El-Hendawy, 2002).

Chemical activation is usually carried out at temperature between 400 and 600 °C. There is an optimum temperature which is different for different types of raw materials. The optimum activation temperature for a particular raw material must be studied for further discovery. The optimum activation conditions were found at temperature of 500°C and at activation time of 180 min for activated carbon from rubber seed shell by chemical activation impregnated with potassium hydroxide, KOH. (Azry, B & Ahmad, F. K., 2012).

Below are the preparation conditions and results of previous works done by previous researchers on the chemical activation using phosphoric acid:

Table 2.0: Previous work done by researcher

No.	Researchers	Activation	Material	Research Findings
1.	(V. Go´mez-Serranoa et al., 2005)	Chemical activation	Chestnut wood	The microporous structure is more heterogeneous for the 1:3 concentration at **400 °C** and for the 1:1 and 1:2 concentrations at **600 °C** activation temperature.
2.	(W.C. Lim et al., 2010)	Chemical activation	Palm shells	Low activation temperature (425 ◦C), activation time (30 min), impregnation ratio (IR) of phosphoric acid from 0.5 to 3.Widely distributed with the contribution of micropores around 50%.
3.	(N.V. Sych et al., 2012)	Chemical activation	Corncob	Phosphoric acid/carbon ratio 1:1, under which a surface area of 1432m2/g and a carbon yield of 48% could be reached. Activation temperature **600°C**.
4.	(L. Qing-Song et al., 2010)	Chemical activation	Bamboo	Phosphoric acid/carbon ratio 1:1, under which a surface area of 1432m2/g and a carbon yield of 48% could be reached. Activation temperature **600°C**.
5.	(M. Shrestha Rajeshwar et al., 2012)	Chemical activation	Lapsi seed stone	Surface area of 1322 m^2/g. Use IR 1:1 at **400°C** activation temperature.

2.3 Activated Carbon Pore Structure

According to (TIGG Corporation, 2012), the activated carbon structure may be of various shapes, the term "pore," implying a cylindrical opening, is widely used. A description of the minute distances between walls of these pores, normally expressed as a function of the total surface area or total pore volume presented by pores of various "diameters," is the pore structure curve. Thus no pore within the activated carbon is likely to have precisely the average shape, but the granular activated carbon overall will often perform as if all its surface area were in pores of that shape.

The smallest diameter pores make up the micropore structure, and are the highest adsorption energy sites. Microporosity is helpful in adsorbing lower molecular weight, lower boiling point organic vapors, as well as in removing trace organics in water to non-detectable levels. Larger pore openings make up the macroporosity, which is useful in adsorbing very large molecules and aggregates of molecules, such as "color bodies" in raw sugar solutions. Another important function of the macropore structure is in assisting diffusion of fluids to adsorption sites in the interior of the carbon particle.

According to (IUPAC,1994):

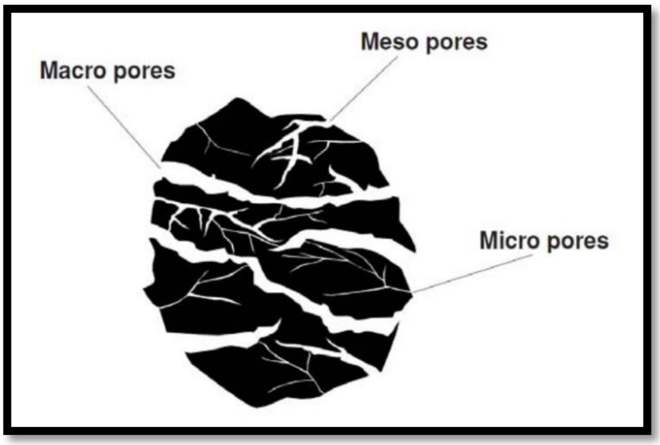


Figure 2.0: Pore structure of activated carbon

- Micropores : pore diameter < 2 nm
- Mesopores   : pore diameter 2-50 nm
- Macropores : pore diameter > 50 nm

2.4 Adsorption

Adsorption is a process by which liquid or gaseous molecules are concentrated on a solid surface, in this case activated carbon. This is different from absorption, where molecules are taken up by a liquid or gas (Chemviron carbon, 2013).

The reason that activated carbon is such an effective adsorbent material is due to its large number of cavernous pores. These provide a large surface area relative to the size of the actual carbon particle and its visible exterior surface. An approximate ratio is 1 gram = 1000 m^2 of surface area (Steve Kvech and Erika Tull, 1997).

The separation process includes the removal of organic compounds from water or organic solutions, colored impurities from organics, and various fermentation products from fermentor effluents are occurred in liquid phase adsorption. In other hand, for the gas phase adsorption, the separation includes the removal of water from hydrocarbon gases, sulfur compounds from natural gas, solvent from air and other gases, and odors from air (Geankoplis, 2003).

Many adsorbents have been developed for a wide range of separations. According to (Geankoplis,2003).Typically, the adsorbents are in the form of small pellets, powder, or granules ranging from about 0.1 mm to 12 mm in size. Activated carbon adsorption proceeds through 3 basic steps:

1. Substances adsorb to the exterior of the carbon granules
2. Substances move into the carbon pores
3. Substances adsorb to the interior walls of the carbon

The most important factors affecting adsorption process are surface area of adsorbent. Surface area and porosity are the important characteristics that is capable in determining the effectiveness of activated carbon produced. Larger sizes imply a greater adsorption capacity. Smaller particle sizes reduce internal diffusion and mass transfer limitation to the penetration of the adsorbate inside the adsorbent. For this reason, it is important to determine and control it accurately. In this project, BET method or Brunauer-Emmet-Teller method will be utilized in achieving the target.

The determination of specific surface area by means of BET theory is based upon the phenomenon of physical adsorption of gases on the external and internal surfaces of a porous material. Activated carbon, which surrounded by and in equilibrium with N_2 gas in which has a certain temperature, T, and relative vapour pressure, p/po, adsorbs physically a certain amount of N_2 gas.

While the porosity of activated carbon, name it mesopores or micropores can be determined by using a method called the Barret-Joyner-Halenda (BJH) method. BJH method is a method where can be applied to all porous solid whose structure includes large density of pores and hence a large surface area per unit of volume. A large volume of small pores contributes more surface area than the same volume of larger pores. The characterization of activated carbon in this project will be based on the volume of mesopores and micropores in the production of activated carbon.

The actual adsorption occurs almost only in the micropores. The macropores will determine the accessibility of the adsorbent, while the mesopores influence the transport of the adsorbate from the gas phase to the micropores. An adsorbent with a high activation degree, and therefore a high total pore volume, will possess a high maximum adsorption capacity (Saad B.S, 2007).

2.5 Adsorption Isotherm

There are three types of common isotherms which are linear law, the Freundlich isotherm and Langmuir isotherm. The adsorption equilibrium relates q to C. The equilibrium is a function of the temperature. Therefore, the adsorption equilibrium relationship at a given temperature is typically referred to as adsorption isotherm. According to (Geankoplis, 2003), the adsorption isotherm as below:

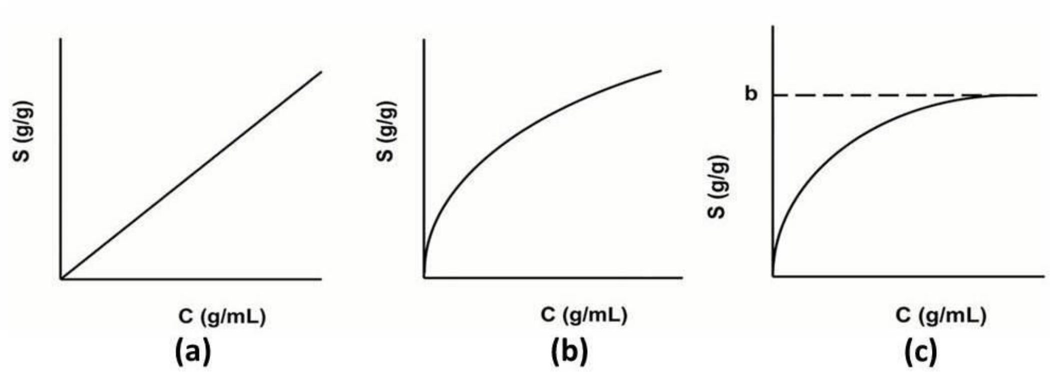


Figure 2.1: Types of adsorption isotherm

Figure above shows:

(a) The linear isotherm which can be expressed by equation similar to Henry's law. The equation is as below:

$$q = Kc$$

(b) Freundlich isotherm - it is the less favorable isotherm and also can be expressed by equation below:

$$q = Kc^n$$

(c) Langmuir isotherm - the most and strongly favored isotherm in adsorption. Below is the Langmuir isotherm equation:

$$q = \frac{q_{\circ}C}{K + C}$$

Where q is the amount adsorbed per unit mass of adsorbent (wt/wt), $q_{\circ}$ and K are empirical constants, and C is the equilibrium concentration of adsorbate in solution after adsorption.

2.6 Types of Adsorption Isotherms

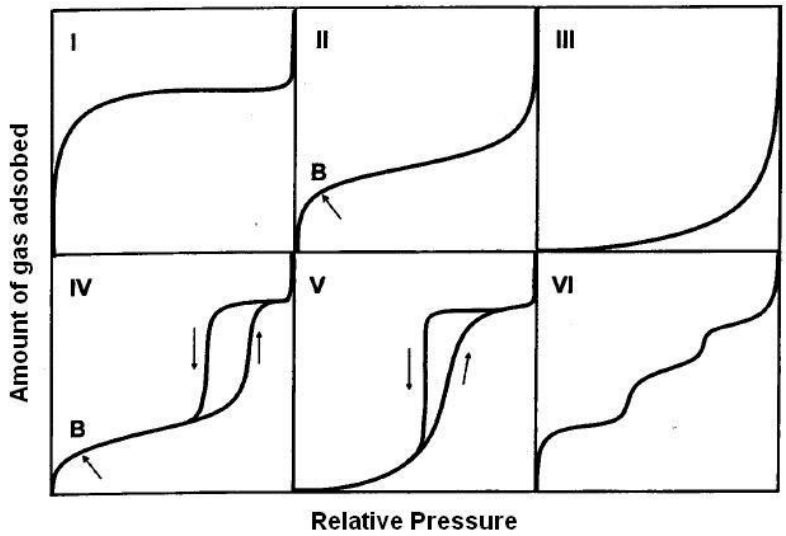


Figure 2.2: Six types of adsorption isotherms by IUPAC

Based on figure 2.2, there are six types of adsorption isotherm based on the IUPAC classification. Type I isotherms are given by microporous solids having relatively small external surfaces (e.g. activated carbons, molecular sieve zeolites and certain porous oxides), the limiting uptake being governed by the accessible micropore volume rather than by the internal surface area. Type II isotherms shows the physical adsorption of gases by non-porous solid. Adsorbents that closely related to this type of isotherms are usually carbons with mixed micro-and mesopores. Type III isotherms is convex, looking upwards and are characteristic of adsorption at sites of low adsorption potential and weak adorbate-adsorbent interaction. Type IV isotherms resemble of Type II but have hysteresis. Instead of adsorption on open surfaces at high relative pressures, adsorption takes place in mesoporosity. Its feature a hysteresis loop generated by the capillary condensation of the adsorbate in the mesopores of the solid. Type V it is related to the Type III isotherms in that the adsorbent-adsorbate interaction is weak, but is obtained with certain porous adsorbents. The Type VI isotherm represents stepwise multilayer adsorption on a uniform non-porous surface. The step height now represents the monolayer capacity for each adsorbed layer and, in the simplest case, remains nearly constant for two or three adsorbed layers.

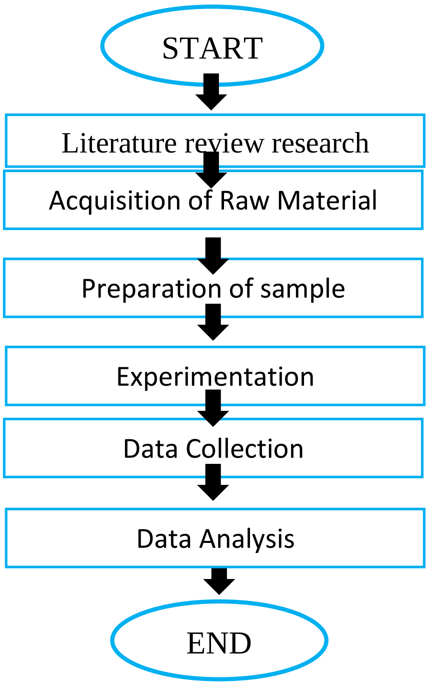
CHAPTER 3

METHODOLOGY

3.1 Research Methodology

The methodology for conducting this project is discovery based on experimental laboratory work. As this project is mainly an empirical research, the results obtained from this research can be used to compare with other literature results. Besides, the result obtained from this research using different raw materials and activating agent to produce activated carbon can be used as a basis of comparison with other researches done. The results can hence further the using of activated carbon as adsorbent in the water treatment process. After literature review is done, experimental laboratory works can be conducted by 5 sections which are acquisition of material, preparation of sample, experimentation of sample, data collection, and data analysis. The adsorption experimental will be done after the best sample is determined. For this project, the proposed raw material to be used is the rubber seed shell.

3.1.1 Research Methodology Flowchart



3.1.2 Raw materials, Equipment, Apparatus and Chemicals needed

In the experimental that are going to be conducted, several raw materials, equipment and chemicals are needed. Different equipment and apparatus as well as the chemical used will be used for different sections in the laboratory works.

Table 3.0: Raw materials, Equipment, Apparatus and Chemicals needed

No.	Item	Material/Chemicals	Equipment/Apparatus
1	Preparation of raw materials	Rubber seed shells	1. Dryer 2.Oven 3.Grinder 4. Siever 5. Desiccator 6. Beaker 7. Volumetric flask
2	Chemical activation & carbonization process	Phosphoric acid	pH meter, Fixed Bed Activation Unit
3	Characterization of activated carbon	-	1.Micrometrics ASAP 2020 2.Field Emission Scanning Electron Microscopy (FESEM) and Energy Dispersive X-ray (EDX)
4	Adsorption test	Hexane	1. InfraCal TOG/TPH Analyzer 2. Filter funnel, filter paper,

3.1.3 Purpose of tools required

Table 3.1: Tools and description

No.	**Equipment/apparatus**	**Description**
1.	Grinder and siever	This tool is needed in order to grind and segregate the raw material of rubber seed shell into two distinct sizes of 1mm, and 500µm.
2.	Beaker, filter funnel, volumetric flask, filter paper, pH meter	All of these tools will be needed throughout the experimentation process**.**
3.	Drying oven	Use to dry and remove moisture contents in the raw materials.
4.	Fixed bed activation unit	Use for carbonization process.
5.	Desiccator	Use to store the produced activated carbon in order to maintain the dryness of the activated carbon.
7.	FESEM and EDX	FESEM-Use to determine the structural images of raw material and activated carbon produced. EDX- Its characterization capabilities are due in large part to the fundamental principle that each element has a unique atomic structure allowing unique set of peaks on its X-ray spectrum.
8.	Micrometrics ASAP 2020	Use to determine the pore size distribution, specific surface area and the porosity of the activated carbon produced.
9.	InfraCal TOG/TPH Analyzer	Use to test the concentration (in ppm) of waste water sample.

3.2 Project Activities

3.2.1 Preparation of raw materials and pretreatment

1. Acquisition of raw material

Description: The rubber seed shell (Hevea brasiliensis) was collected from a local rubber plantation estate

Figure 3.0: Raw rubber seed shell

2. Removal of unwanted material and drying of raw material

Figure 3.1: Drying of raw material

Description: The rubber seed shell is washed with distilled water to remove dust or any unwanted material and then dried in an oven for overnight at temperature 80°c.

3. Grind and segregation of raw material in two different size

Figure 3.2: Process of grinding and sieving of the rubber seed shell

Description: when the rubber seed shell dried, it has been grinded and sieved according to the two particle sizes as required 1mm and 500µm by using grinder and siever.

4. Classification of rubber seed shell size

Figure 3.3: 1mm

Figure 3.4: 500 mm

5. Rubber seed shell storage

Figure 3.5: Rubber seed shell stored in plastic container

3.2.2 Chemical Activation and Carbonization

In the activation process, about 20g of rubber-seed shell was weighed and impregnated with H_3PO_4. Impregnation can be defined as amount of H_3PO_4 is allowed to soak with rubber seed shell for overnight for the full adsorption of the reagent to the raw material. 11.76ml of H_3PO_4 is diluted to a 100ml solution in a volumetric flask for ratio 1:1. For ratio 1:2, 23.5ml of H_3PO_4 is used.

Figure 3.6: The weighing of rubber seed shell

Figure 3.7: Preparation of H_3PO_4 solution

Figure 3.8: The mixture of rubber seed shell and H_3PO_4 solution is stirred

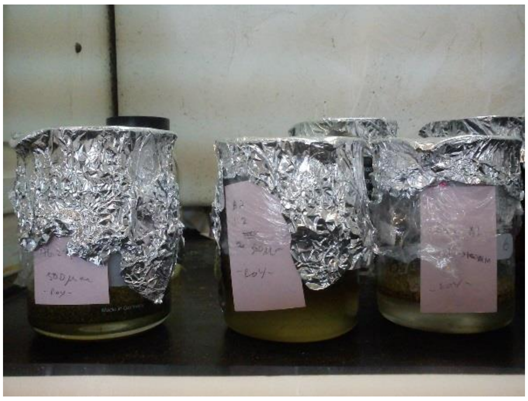


Figure 3.9: The rubber seed shell that has been weighed is soaked with the solution overnight

After an overnight soaked, the treated rubber seed shell is washed with distilled water for several times until pH 6–7 and dried in an oven overnight at 80 °C. After that, the dried sample is stored in an airtight container for carbonization process.

Figure 3.10: Measuring the acidity of the sample by using pH meter

Figure 3.11: The sample is dried by using drying oven

For the carbonization process, the impregnated rubber seed shell is then carbonized in a Fixed Bed Activation Unit (FBAU). The carbonization process is executed at different operating parameter of activating temperature and time under the flow of Nitrogen gas. Next, the activated carbon that is produced is washed with distilled water again to remove the remaining H_3PO_4 and is then dried in oven overnight at 80 °C before been stored in plastic container and a desiccator for locking the dryness of the activated carbon produced.

Figure 3.12: Carbonization process by using Fixed Bed Activation Unit

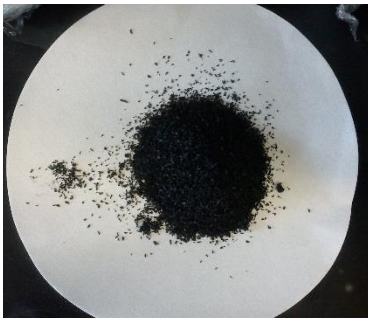
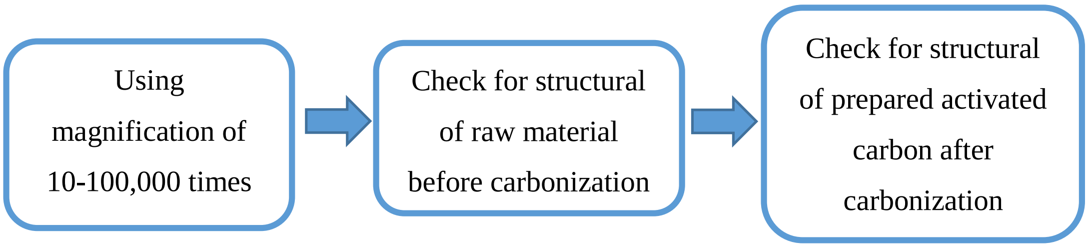


Figure 3.13: Activated carbon produced

Figure 3.14: Activated carbon produced is stored tightly in plastic container

3.2.3 Sample Characterization

FESEM: One of the equipment to characterize the produced activated carbon is Field Emission Scanning Electron Microscope. The structural of the raw material and the produced activated carbon is clearer, less electrostatically distorted images with spatial resolution down to 1 1/2 nm. This is 3 to 6 times better than conventional SEM.



Micrometrics ASAP 2020: In characterization of the activated carbon, the using of micrometrics ASAP 2020 is very important in order to determine the type of surface area, pore size distribution, total pore volume and average pore size diameter. It uses the nitrogen adsorption-desorption isotherms, N_2 as adsorbates. Before the analysis, the samples were degassed under N_2 flow at 350°C for 2 hours in a vacuum of 27°C. The specific surface of area was determined by using BET method.

(a) (b)

Figure 3.15 (a-b): (a) Field Emission Scanning Electron Microscope
(b) Micrometrics ASAP 2020

3.2.4 Overall flow diagram of the experimental procedures

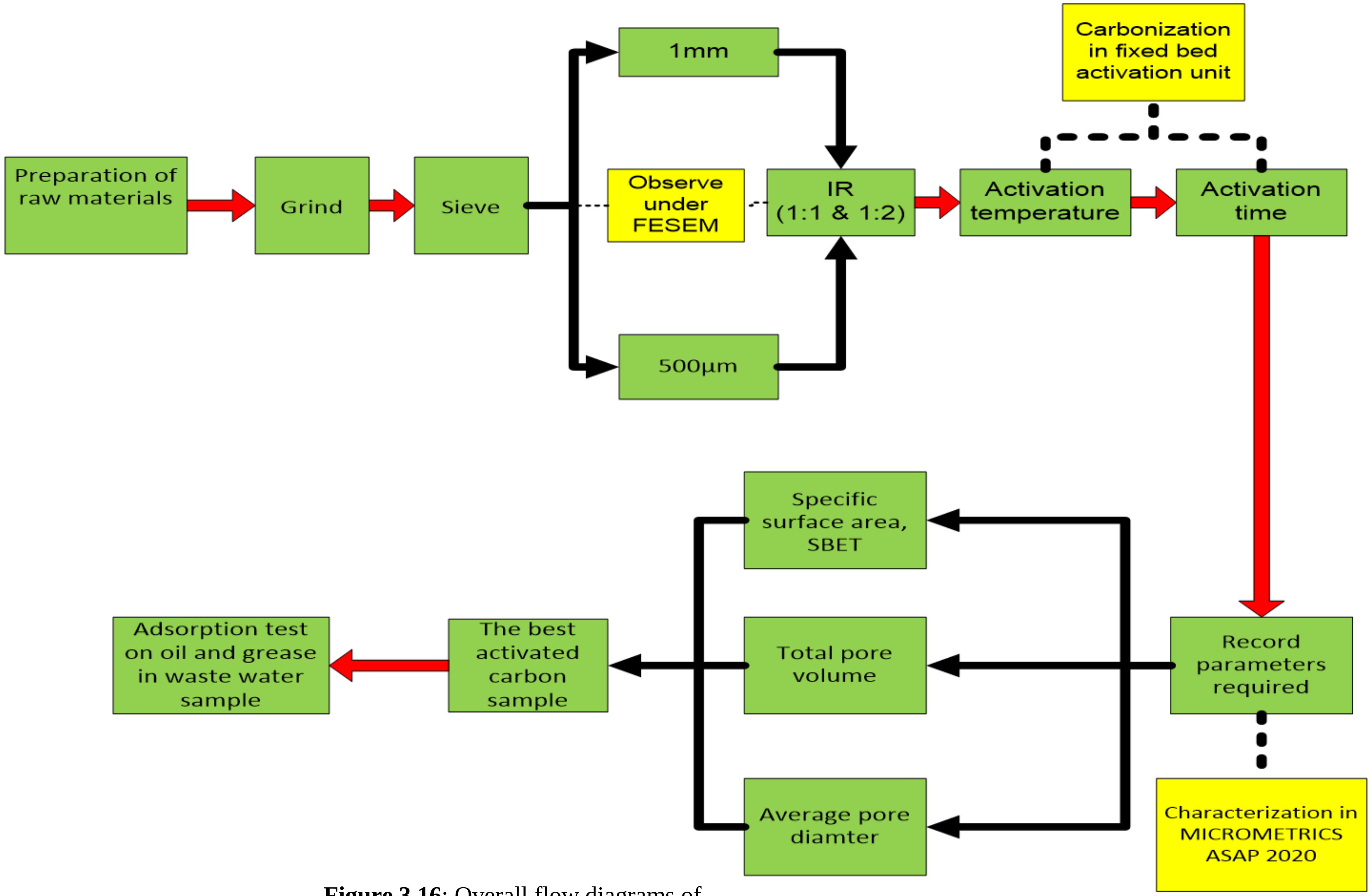
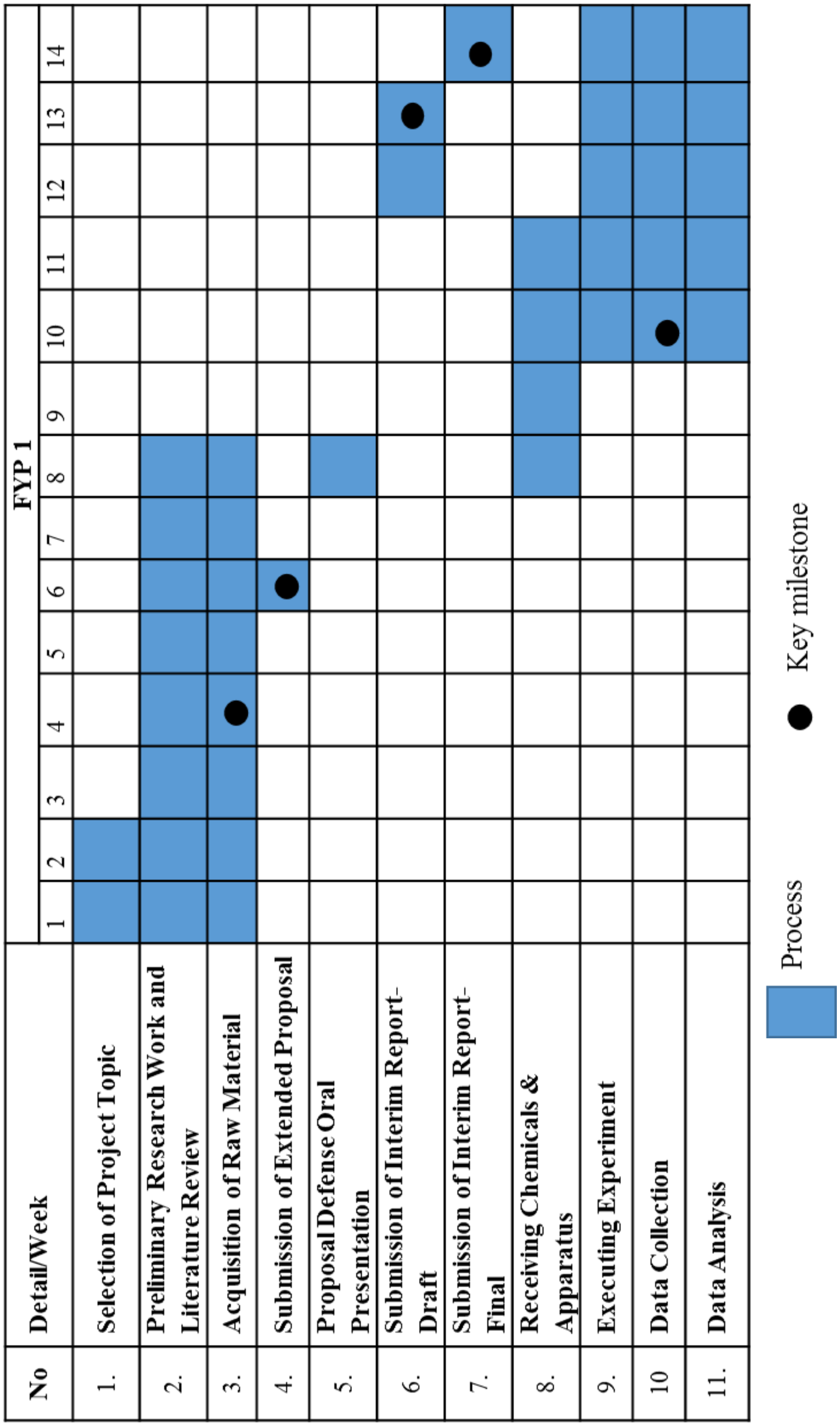


Figure 3.16: Overall flow diagrams of the project

3.3 Project Gantt Chart and Key Milestone

3.3.1 Gantt Chart and Key Milestone FYP 1



No	Detail/Week	FYP 1													
		1	2	3	4	5	6	7	8	9	10	11	12	13	14
1.	**Selection of Project Topic**	🟦	🟦												
2.	**Preliminary Research Work and Literature Review**	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦						
3.	**Acquisition of Raw Material**	🟦	🟦	🟦	🟦 ●	🟦	🟦	🟦	🟦						
4.	**Submission of Extended Proposal**						🟦 ●								
5.	**Proposal Defense Oral Presentation**								🟦						
6.	**Submission of Interim Report-Draft**												🟦	🟦 ●	
7.	**Submission of Interim Report-Final**														🟦 ●
8.	**Receiving Chemicals & Apparatus**								🟦	🟦	🟦	🟦			
9.	**Executing Experiment**										🟦	🟦	🟦	🟦	🟦
10	**Data Collection**										🟦 ●	🟦	🟦	🟦	🟦
11.	**Data Analysis**										🟦	🟦	🟦	🟦	🟦

🟦 Process ● Key milestone

3.3.2 Gantt Chart and Key Milestone FYP 2

No	Detail/Week	FYP 2													
		1	2	3	4	5	6	7	8	9	10	11	12	13	14
1.	**Experimentation**	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	
2.	**Data collection**	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	
3.	**Data Analysis**	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	
4.	**Preparation of progress report**				🟦	🟦	🟦	🟦	🟦	🟦					
5.	**Submission of Progress Report**								●						
6.	**Pre-SEDEX**											●			
7.	**Submission of Technical Paper**												●		
8.	**Submission of Dissertation – Draft**													●	
9.	**Submission of Dissertation – Final**													●	
10.	**Viva**														●
11.	**Submission of Hard Bound of Project Dissertation**														●

🟦 Process

● Key milestone

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Surface Area and Pore Size Distribution

In order to analyze the activated carbon produced, all of the sample is then sent to the analysis laboratory to determine the surface area, pore size and pore volume of it. The equipment used to analyze this characteristics is Micrometrics ASAP 2020. Before characterization process conducted, the sample were degassed under Nitrogen, N_2 flow at 350 °C for 2 hours in a vacuum condition.

Table 4.0: Parameters and results of rubber seed shell activated carbon

Sample	**Size**	**IR**	**Activation Temperature (°C)**	**Activation time (min)**	**S_{BET} (m^2 g^{-1})**	**Total Pore Volume, V_T (cm^3 g^{-1})**	**Avg. pore diameter, D (nm)**
Raw	500µm	-	-	-	0.0420	0.0000482	-
A2	1mm	1:1	400	90	2.5356	0.0104	3.067
A6	1mm	1:2	400	90	2.7632	0.01243	3.123
B3	500µm	1:1	500	30	3.6342	0.0267	3.232
B4	500µm	1:1	500	90	3.9627	0.02632	3.3731
B6	500µm	1:2	400	90	5.9415	0.05887	4.5987
B8	500µm	1:2	500	90	8.2310	0.07918	5.5418
B9	500µm	1:2	600	90	5.7632	0.06782	5.2970

Table 4.0 shows the parameters of preparation condition and results of the rubber seed shell activated carbon produced. Results showed that the raw rubber seed shell surface area is $0.0420m^2g^{-1}$ .This can prove that the fresh rubber seed shell without impregnation of phosphoric acid do not have high surface area compared to the impregnated rubber seed shell. The highest value of S_{BET} ($8.2310m^2g^{-1}$) is shown by sample B8 which is impregnated with ratio of 1:2 H_3PO_4 solution, activated at 500°C in 90 minutes and the total pore volume, V_T ($0.07918\ cm^3\ g^{-1}$) with pore diameter, D (5.5418nm). Sample B9, which is prepared at the same impregnation ratio and activation time with sample B8 but difference in activation temperature which is 600°C shows decreasing in S_{BET} values. The decrement of the S_{BET} values of this sample is due to the excessive heat energy that was given at high temperature to the carbon, which results in knocking and breaking of some porous wall. The sample size is reduced because the cell is destroyed by the high excessive temperature for a long time. As a result, the specific surface area of the activated carbon decreased. This shows that, this temperature and duration is not suitable for the preparation of activated carbon. Sample A2 and Sample A6 which in 1mm size have low surface area compared to other 500µm sample sizes. This can proved that the size of the samples affect the surface area of the activated carbon. Phosphoric acid acts as catalyst by promoting cleavage reactions, forming phosphate, and polyphosphate linkages. The more the phosphoric acid is used the larger the amount of polyphosphates are formed and consecutively the higher pore volume is obtained. This theory proved the results of the samples between IR 1:1 and 1:2 where pore volume of IR 1:2 is higher than IR 1:1. IUPAC standard state that the average pore diameter of activated carbon more than 2.0nm is in mesopores. The average pore diameter of all samples in ranges from 3-6 nm that indicate the pores are mesopores based on (IUPAC, 1994) standard. It is also shown that the increment of the pore volume of the sample will increase the average pore diameter.

4.2 Elemental Composition Analysis

EDX systems are attachments to FESEM instruments where the imaging capability of the microscope identifies the specimen of interest. The data generated by EDX analysis consist of spectra showing peaks corresponding to the elements making up the true composition of the sample being analyzed. This mechanism works by detecting X-rays that are produced by a sample placed in an electron beam. The electron beam excites the atoms in the sample that subsequently produce X-rays to discharge the excess energy. The energy of the X-rays is characteristic of the atoms that produced them, forming peaks in the spectrum. Furthermore, this technique is non-destructive and has a sensitivity of >0.1% for elements heavier than Carbon, C. In this experiment, this mechanism have been used to analyze raw rubber seed shell and activated rubber seed shell. The results are tabulated in Table 4.1 and Table 4.2. Whereas Figure 4.0 and 4.1 show the respective peak of element spectrum.

Table 4.1: Element composition of raw rubber seed shell

Element	Weight%	Atomic %
Carbon, C	52.50	59.55
Oxygen, O	47.50	40.45
Totals	100	

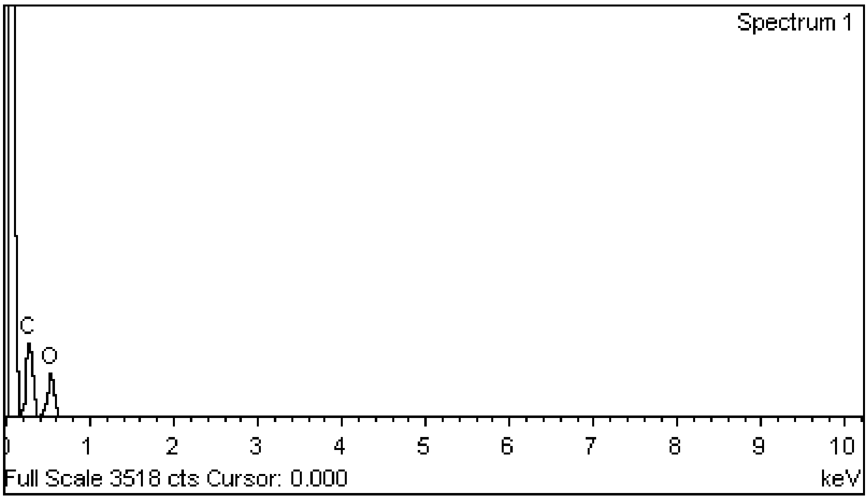


Figure 4.0: Peak of elemental composition of raw rubber seed shell

Table 4.2: Element composition of activated rubber seed shell, B3

Element	Weight%	Atomic %
Carbon, C	80.70	84.78
Oxygen, O	19.30	15.22
Totals	100	

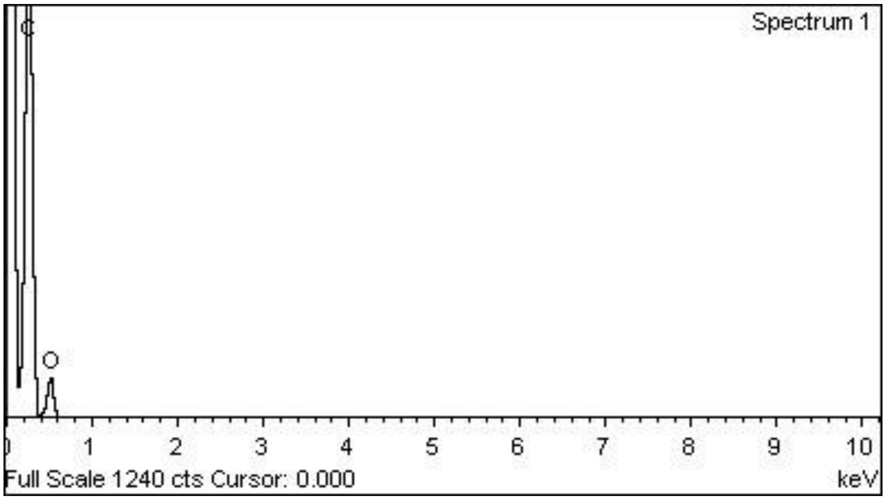


Figure 4.1: Peak of elemental composition of sample B3

From the results above, Figure 4.0 and Figure 4.1 show a distinct different of result before and after activation. Based on figure 4.0 it is shown that the elements exist in raw rubber seed shell is only Carbon, C and Oxygen, O elements. According to Zhu, Wu and Chen (1991), the suitable range of carbon content in raw material must be in between 50-80% .The existence of 52.5% Carbon content in the raw rubber seed shell proved that it is possible to transform the rubber seed shell into valuable activated carbons. In other hand, Figure 4.1 shows the activated rubber seed shell results. The carbon content for this activated rubber seed shell is 80.70%. This results can conclude that the carbon content of the rubber seed shell after activation is higher than raw rubber seed shell.

4.3 Morphological Structure analysis

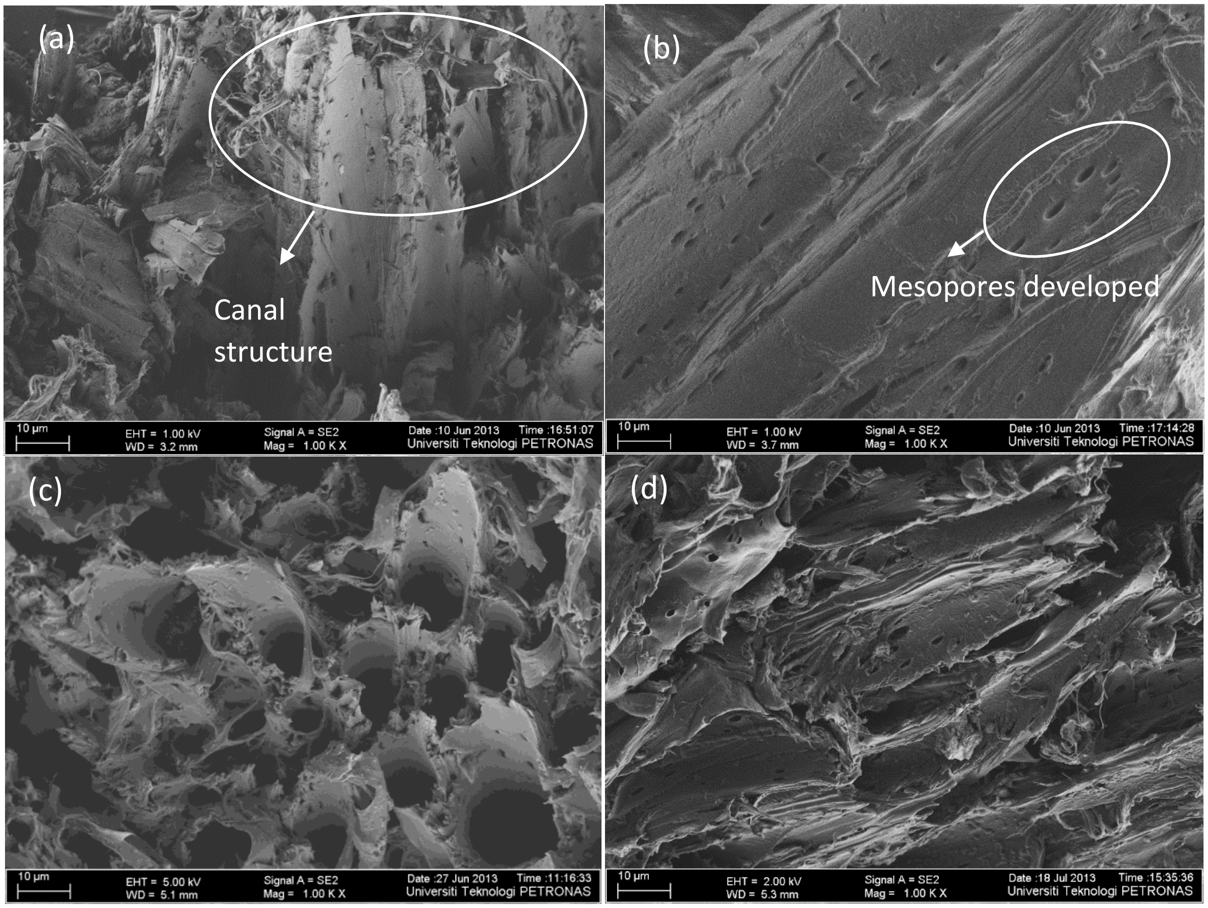


Figure 4.2 (a-d) :FESEM images of sample selected, (a) Fresh rubber seed shell, (b) Sample B6, (c)Sample B8,and (d) Sample B9

Figure 4.2 (a) shows the fresh rubber seed shell at 1000 times magnification. This images shows that there are few pores can be seen. This proved that fresh rubber seed shell without undergo any chemical reaction do not have many pores naturally. However, for this fresh rubber seed shell, it is shown clearly the canal structure existence, which is an important characteristics and good surfaces for preparing activated carbon. This is because the porous and canal structure that exists in the raw rubber seed shell will allow the rubber seed shell to fully adsorb the activating agent and directly undergo chemical reaction to activate the carbon content inside it. The morphological surfaces are different between raw material and others activated carbon samples (b-d). From Figure 4.2 (b-d), it is shown that the pores produced after being activated at different operating parameters.

The existence of pores is shown at 1000 magnifications, with average size of 10 μm. Smaller pores is observed in sample B6 which can probably be the mesopores development for the activated carbon. This sample is carbonized at 400°C which conclude that the pores start to develop at this stage. The pores extensively increased when the impregnation ratio is 1:2 under the same temperature 500°C as shown in sample B8.This proved that impregnation ratio on activated carbon give influence to the pores development. When the temperature is increased to 600°C, the morphology of sample B9 shows that the pores are found to be expanded and partially broken due to excessive duration of high temperature exposure**.** As a result, the volume of the pores is decrease due to the contraction of the wall.

4.4 Characteristics of Isotherm Analysis

Figure 4.3 below shows the N_2 adsorption-desorption isotherm of a selected activated rubber seed shell, B8, B6, B9 and B4 with activation parameters as in Table 4.0 in section 4.1. The isotherm linear plot is plotted on a graph with quantity of N_2 adsorbed at STP onto the sample surface plotted against the relative pressure of p/p° (p = absolute pressure, p° = saturation pressure in mmHg).

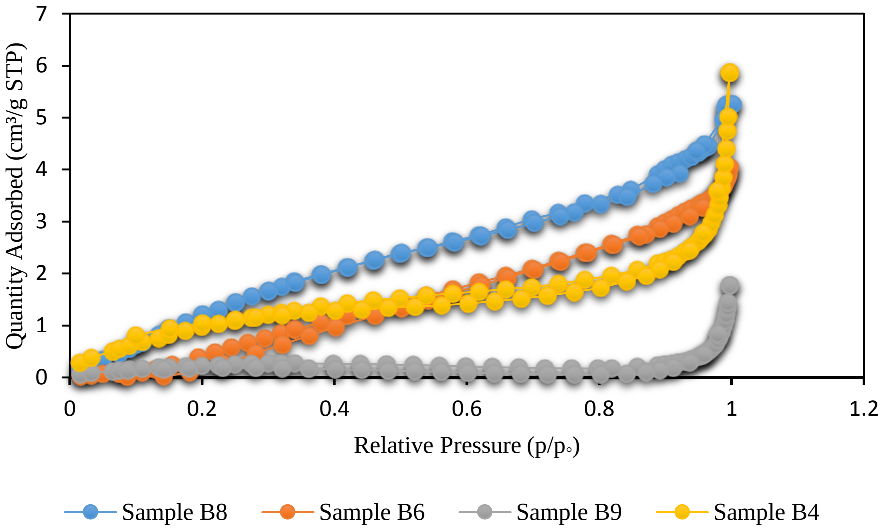


Figure 4.3: Isotherms linear plot

Based on the isotherm linear plot in Figure 4.3, it can be seen that both sample B6 and B8 follows the combination of isotherms of Type I and Type II. This isotherms prove that it is closely related to be as the effect of the mixed of micropores and mesopores structures (Azry et. al, 2012). Sample B6 is prepared at IR 1:2, activation 90 minutes and 400°C .While for sample B8,the sample is also prepared at IR 1:2 ,activation 90 minutes but different in temperature which is 500°C. While for sample B4 and B9 the isotherms type is Type II. According to IUPAC, this type of isotherm is type II adsorption isotherm that shows large deviation from Langmuir model of adsorption. The intermediate flat region in the isotherm corresponds to monolayer formation. For this type, adsorption occurs on the adsorbent with pore diameters larger than micropores, which is mesopores. The results that were obtained from the analysis of FESEM and Micrometrics ASAP 2020 can be the evidence to support all of the isotherms.

4.5 Removal of Oil and Grease Efficiency

The adsorbent (Activated Carbon) was tested on the wastewater taken from PETRONAS Penapisan Terengganu. This waste water sample is used as the medium for adsorption test. InfraCal TOG/TPH Analyzer, Model HATR-T2, is used to perform this adsorption test. The InfraCal TOG/TPH Analyzer makes use of the fact that hydrocarbons such as oil and grease can be extracted from water or soil through the use of an appropriate solvent and extraction procedure. Extraction method is used in extracting oil and grease from the waste water sample by using hexane as the extracting solvent. Hexane which is in the form of liquid help to separate the oil and grease thus forming a distinct layer of oil and grease on top of the wastewater sample as shown in Figure 4.4 and Figure 4.5 . Initial concentration of oil and grease in the waste water sample is taken at time 0 and at an interval of 180minutes. This results proved that the bigger the surface area, the higher the rate of oil and grease removal. The percentage of the removal efficiency is calculated by using this equation:

$$\text{Percentage of removal efficiency} = \frac{Initial\ Concentration - Final\ Concentration}{Initial\ Concentration}\ x\ 100\%$$

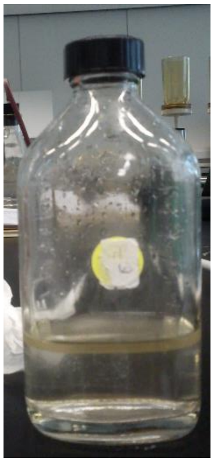


Figure 4.4: Initial concentration before treated with activated carbon

Figure 4.5: Concentration of waste water after treated with activated carbon

Based on the Figure 4.4 and Figure 4.5, the colour of the waste water before treated with activated carbon is yellowish which indicate high concentration of oil and grease while the colour of the waste water after treated with activated carbon is clear.

Figure 4.6 showed the plot of concentration of oil and grease (ppm) versus time (minutes). From the graph, two samples were tested, sample B6 and B8. Sample B8 successfully removes about 84% of oil and grease in the waste water sample while sample B6 removes 71% of oil and grease. It showed that it took about 180 minutes for the activated carbon to fully adsorb the oil and grease. This is explained by the trend of the graph that remained constant at time 180 minutes onwards.

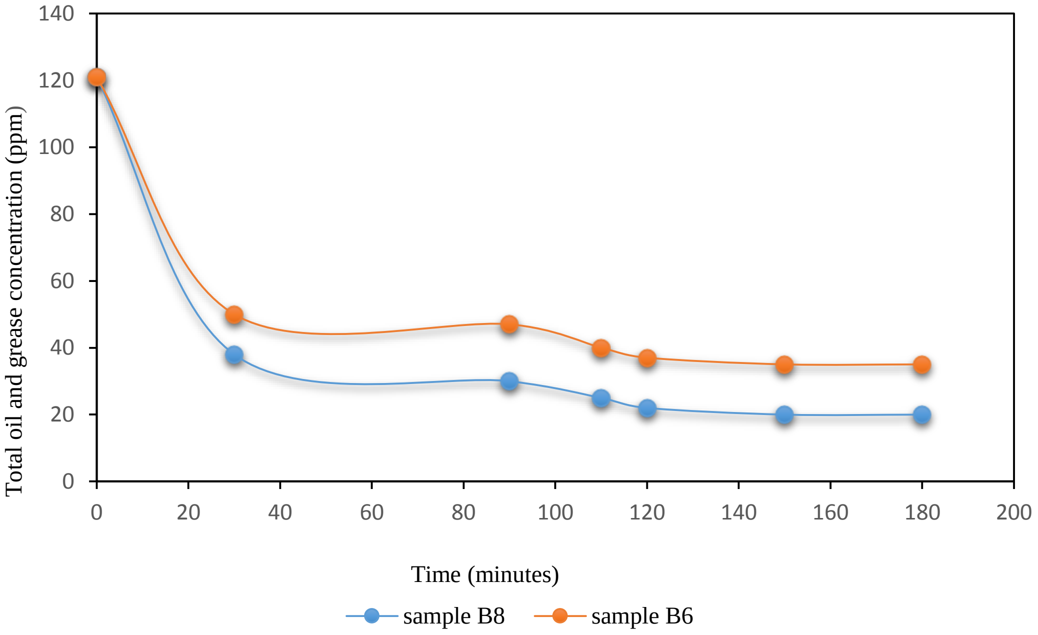


Figure 4.6: Total oil and grease concentration over time

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

The rubber seed shell is very suitable to be converted into valuable activated carbon as it proved by EDX that it has more than 50% of carbon content in it. Furthermore, from the results obtained, the preparation of activated carbon from rubber seed shell through chemical activation is very feasible to be conducted as it has high surface area and pore volumes. The strong acidity of phosphoric acid acts as the best activating agent to activate the carbon contents inside the rubber seed shell over other chemicals. The result showed the highest BET surface area of activated carbon corresponding to an impregnation ratio of 1:2 is found to be 8.2310m^2g^{-1} with total pore volume of 0.07918 cm^3 g^{-1} and average pore diameter 5.5418nm shown by sample B8. The ranges of pore diameter were 3-6 nm that indicate the pores are mesopores according to IUPAC standard. The optimum condition for the preparation condition of this activated carbon is at 500°C activation temperature in 90minutes. It was found that 84 % of oil and grease successfully removed from the waste water sample. This proved that activated carbon prepared from rubber seed shell, an agricultural solid waste, can be effectively used as adsorbent for the removal of oil and grease from waste water sample.

From this study, the objectives of this project have been successfully achieved by determining the characteristics of the rubber seed shell as adsorbent by using phosphoric acid as chemical activated agent. Hence, this can prove that the using of biomass from agricultural waste can be potential material for adsorbent and high potential for commercializing the activated carbon prepared from rubber seed shell.

5.2 Recommendations

Conversely, the specific surface area and total pore volume for this preparation of activated carbon is not high as what has been achieved by previous researchers using the same chemical activating agent. This is because of the suitability of phosphoric acid as chemical activating agent might be not highly recommended to treat rubber seed shell. Thus, the study of the suitability of this chemical agent must be the best recommendation to vary the chemical agent in further research. In addition, further study need to perform adsorption test not only for oil and grease but to another waste water sample to differentiate the result obtained.

REFERENCES

Activated Carbon. Retrieved Feb 24, 2013 from http://www.activated-carbon.com/

Annual Rubber Statistics in Malaysia 2011. Retrieved Feb 25, 2013 from//www.statistics.gov.my/portal/.

Azry Borhan and Ahmad Fikree Kamil, 2012. Preparation and Characterization of Activated Carbon from Rubber-seed Shell by Chemical Activation. *Journal of Applied Sciences, 12: 1124-1129.*

Babatunde, G. M.; Pond, W. G.; and Peo, Jr., E. R., "Nutritive Value of Rubber Seed (*Hevea Brasiliensis*) Meal: Utilization by Growing Pigs of Semipurified Diets in Which Rubber Seed Meal Partially Replaced Soybean Meal" (1990).*Faculty Papers and Publications in Animal Science*.*Paper 688.*

Bukallah, S.B., M.A. Rauf and S.S. Ashraf, 2007. Photocatalytic decoration of coomassie brilliant blue with titanium oxide. Dyes Pig., *72: 353-356.*

Chemviron carbon. What is adsorption? (2013, march 6). Retrieved from Chemviron Carbon Web Site: http://www.chemvironcarbon.com/en/activated-carbon/adsorption

Cheung, C.W., J.F. Porter and G. McKay, 1997. Sorption kinetics for the removal of copper and zinc from effluents using bone char. *Sep. Purf. Technol*., 19: 55-64.

Eka, H. D., Tajul Aris, Y. and Wan Nadiah, W. A., 2010. Potential use of Malaysian rubber (Hevea brasiliensis) seed as food, feed and biofuel. *International Food Research Journal 17:* 527-534.

Geankoplis, C. J. (2003). Transport Processes and Separation Process Principle. *Liquid-Liquid and Fluid-Solid Separation Process*, 4, 760-762.

Girgis B.S., El-Hendawy, Porosity development in activated carbon obtained from date pits under chemical activation with phosphoric acid, *Microporous and Mesoporous Materials, 52, 105-117 (2002)*

Ioannidou, O. and A. Zabaniotou, 2007. Agricultural residues as precursors for activated carbon production - A review. *Renewable Sustainable Energy Rev., 11: 1966-2005.*

IUPAC Recommendations *Pure Appl. Chem*, 1994,66,1739

L. R. Radovic, I. F. Silva, J. I. Ume, J. A. Menendez, C. A. Leony Leon. A. W. Scaroni, Carbon, 35, 1339 (1997).

Man, K. L., & Ridzuan, Z. (2008). *Production of Activated Carbon from Sawdust using Fluidized Bed Reactor*, p. 1.

N.V. Sych, S. T. (2012). Porous structure and surface chemistry of phosphoric acid activated carbon from corncob. *Applied Surface Science 261, 75– 82.*

Qing-Song Liu, T. Z. (2010). Preparation and characterization of activated carbon from bamboo by microwave-induced phosphoric acid activation. *Industrial Crops and Products 31 , 233–238.*

Rao, N.N., K.M. Somasekhar, S.N. Kaul and L. Szpyrkowicz, 2001. Electochemical oxidation of tannery waste water. J. Chem. Technol. *Biotechnol., 76: 1124-1131.*

R.J. and J.B. Sheldon, 1996. Coagulation and precipitation of mechanical effluent. 1. Removal of carbon and turbidity. *Water Res., 30: 781-792.*

Roop Chand Bansal, Jean-Baptiste Donnet, Fritz Stoeckli, 1988, *Active Carbon*, Marcel Dekker Inc, USA.

Salem, I.A. and M. El-Maazawi, 2000. Kinetics and mechanism of color removal of methylene blue with hydrogen peroxide catalyzed by some supported alumina surfaces. *Chemosphere, 41: 1173-1180.*

S. K. W. Sing, Carbon, 27, 5 (1989).

Stephenson, Shrestha Rajeshwar M., Y. A. (2012). Preparation and Characterization of Activated Carbon from Lapsi (Choerospondias axillaris) Seed Stone by Chemical Activation with Phosphoric acid. *Research Journal of Chemical Sciences Vol. 2(10), October, 80-86.*

Steve Kvech and Erika Tull, 1997, Activated Carbon, Available: http://www.cee.vt.edu/ewr/environmental/teach/wtprimer/carbon/sketcarb.html
TIGG Corporation. Granular activated carbon selection. Published 2012-05-8, retrieved 2013-02-27.

V. Go´mez-Serranoa, E. C.-C.-G.-F.-G. (2005). Preparation of activated carbons from chestnut wood by phosphoric acid-chemical activation. Study of microporosity and fractal dimension. *Materials Letters 59, 846– 853.*

Wan Ngah, W.S. and M.A.K.M. Hanafiah, 2008. Adsorption of copper on rubber (Hevea brasiliensis) leaf powder: Kinetic, equilibrium and thermodynamic studies. *Biochem. Eng. J., 39: 521-530*.

Yanhui Li, Qiuju Du, Xiaodong Wang, Pan Zhang, Dechang Wang, Zongha Wang, Yanzhi Xia, Removal of lead from aqueous solution by activated carbon prepared from Enteromorpha prolifera by zinc chloride activation, *J.Hazard.Mater., 183, 583-589 (2010)*

Zhu, S.L., Wu, X.Z. & Chen, Z.Z. (1991) National test standard of activated carbon. GB/T12496.1~22 (1991)

APPENDIX

APPENDIX 1-Raw Data of N_2 Adsorption-Desorption Plot

Sample B8	
Relative Pressure (p/p°)	Quantity Adsorbed (cm³/g STP)
0.015728408	0.156012649
0.032322295	0.245612203
0.049815065	0.340398912
0.074936218	0.45861547
0.089914558	0.550158437
0.110004979	0.676410592
0.134997418	0.828691691
0.149851734	0.926795712
0.174982077	1.062585782
0.1999494	1.180799846
0.224926013	1.305787432
0.24987369	1.434819735
0.274878592	1.563500046
0.29979013	1.659286619
0.319796041	1.752291538
0.339494807	1.846288213
0.379057483	1.984992368
0.41890418	2.119909902
0.458835882	2.249999902
0.498727782	2.379888134
0.538628764	2.494533845
0.578468683	2.618820777
0.618386965	2.740944859
0.658274448	2.889408025
0.698229097	3.046017738
0.738142257	3.172085573
0.777868851	3.353049991
0.827917265	3.515749246
0.847681757	3.612268312
0.888203831	3.908812171
0.899555524	4.011082724
0.909607078	4.0939806
0.919654224	4.137052317
0.929563177	4.202393101
0.939676	4.250584
0.949492	4.331068
0.95497	4.382521
0.960017	4.432644
0.964933	4.451245
0.987881	4.968755
0.99036	5.169622
0.992323	5.247464
1.00068	5.267878
1.00068	5.268788
0.958929	4.484463
0.94681	4.36025
0.921807	3.929331
0.901546	3.856661
0.881407	3.727684
0.842395	3.482529
0.80233	3.338005
0.762202	3.180854
0.74105	3.106869
0.701843	2.975306
0.661724	2.840866
0.621581	2.721832
0.581515	2.59765
0.541372	2.498583
0.501264	2.396906
0.46118	2.269669
0.421077	2.119115
0.380945	1.975538
0.340866	1.825753
0.300729	1.666463
0.250789	1.449796
0.200638	1.215725
0.150023	0.944555
0.1001	0.635819

Sample B6	
Relative Pressure (p/p°)	Quantity Adsorbed (cm³/g STP)
0.016149533	0.025112977
0.03239934	0.042011365
0.04991838	0.066588531
0.074836376	0.070751235
0.109518089	0.098814511
0.129633884	0.156089246
0.154499591	0.246559495
0.194191226	0.389099186
0.219370918	0.483883164
0.244346248	0.578276229
0.269288346	0.669528069
0.294303955	0.760088854
0.319260967	0.8484602
0.339328675	0.924615683
0.340283376	0.926938727
0.378934547	1.052924434
0.419034947	1.190101439
0.45891866	1.317939982
0.498786396	1.443018524
0.538661856	1.571201801
0.578543791	1.691913696
0.618421151	1.82945186
0.658472368	1.955850881
0.698199576	2.094800094
0.73816492	2.247939994
0.778017215	2.404995737
0.817978604	2.56931996
0.857806404	2.744579222
0.88820026	2.904006597
0.899309245	2.972139553
0.909312808	3.048531879
0.919496327	3.12478073
0.929396634	3.187089547
0.939353837	3.254150602
0.949418718	3.312765078
0.954670824	3.348334765
0.959835883	3.374898765
0.964630885	3.411540265
0.969868341	3.462132662
0.97487941	3.506004902
0.979732447	3.558820892
0.982595339	3.595079648
0.985093	3.644487
0.987654	3.680495
0.98958	3.731637
0.991833	3.802477
0.994214	3.870318
0.995105	3.895224
0.997543	4.036312
0.997543	4.036312
0.976585	3.488518
0.956836	3.266696
0.936633	3.105239
0.911893	2.96295
0.891495	2.860061
0.871487	2.761093
0.86069	2.714296
0.82212	2.556601
0.782067	2.396607
0.741954	2.230964
0.701857	2.076289
0.661744	1.924533
0.621685	1.776759
0.581615	1.634519
0.541554	1.493235
0.501485	1.340027
0.461416	1.189142
0.40219	0.96528
0.361461	0.801813
0.321336	0.635569
0.281189	0.4651
0.231363	0.256856
0.181383	0.106301
0.142009	0.025
0.087174	0.018

Sample B9	
Relative Pressure (p/p°)	Quantity Adsorbed (cm³/g STP)
0.015655027	0.065186724
0.032354586	0.091242165
0.064797491	0.125909928
0.074892899	0.138397932
0.089907935	0.153114706
0.109885159	0.169856279
0.134793825	0.19005037
0.15000262	0.201046343
0.174764197	0.216988741
0.199673742	0.226606411
0.224694512	0.237632921
0.249607094	0.25527774
0.274641346	0.266067249
0.299603937	0.271530911
0.319592446	0.273254635
0.339625487	0.272380152
0.398591433	0.267560431
0.438904333	0.260387905
0.478682195	0.252432617
0.518750316	0.240962731
0.558473707	0.228764492
0.598479541	0.215748665
0.638226198	0.201786924
0.678332777	0.191249771
0.718099122	0.180865048
0.758093023	0.176310573
0.797882369	0.176638558
0.818961674	0.181893376
0.857802697	0.206302448
0.888303167	0.234759427
0.899386779	0.252978103
0.909725676	0.268036316
0.919367344	0.289444869
0.929592437	0.312051172
0.939663181	0.347397778
0.9495979	0.392200933
0.954683114	0.422156159
0.959484314	0.45906905
0.964900791	0.506932045
0.969930962	0.560405
0.975013191	0.637854
0.979867798	0.742398
0.982381501	0.801453
0.984804147	0.880563
0.987580124	0.991106
0.990195766	1.101155
0.99199571	1.217697
0.994008248	1.357036
0.994799936	1.450638
0.997372907	1.776264
0.997372907	1.776264
0.979247649	0.840654
0.958101972	0.45021
0.937127914	0.293486
0.912097728	0.193702
0.891505287	0.138918
0.871345118	0.103971
0.84184393	0.0779
0.802249216	0.061384
0.762036547	0.06104
0.721942377	0.062305
0.681894122	0.075372
0.641697348	0.081171
0.601571307	0.094158
0.561549208	0.111322
0.521351135	0.123079
0.481328996	0.132122
0.44120736	0.14744
0.401159098	0.159114
0.361046033	0.171468
0.320935077	0.177584
0.28086406	0.18388
0.230891497	0.185499
0.180953552	0.177528
0.141669656	0.163617
0.086977277	0.138045

Sample B4	
Relative Pressure (p/p°)	Quantity Adsorbed (cm³/g STP)
0.015522	0.281428
0.032333	0.376445
0.064746	0.501642
0.074864	0.550674
0.089895	0.612702
0.109859	0.681634
0.134783	0.761344
0.149991	0.821509
0.174712	0.899432
0.199691	0.973345
0.22463	1.034231
0.249564	1.098593
0.274578	1.151828
0.299521	1.205389
0.319622	1.243466
0.339593	1.282204
0.379069	1.365891
0.419003	1.424986
0.458817	1.483939
0.49885	1.52855
0.538638	1.573282
0.578558	1.615748
0.618422	1.651305
0.658347	1.69905
0.698271	1.739253
0.738205	1.798435
0.77804	1.878669
0.817921	1.959516
0.857803	2.070511
0.888305	2.190721
0.899326	2.231304
0.909414	2.27961
0.919355	2.335464
0.929351	2.418371
0.939349	2.520016
0.949387	2.618824
0.954672	2.689998
0.959575	2.752199
0.964573	2.839485
0.969601	2.976163
0.974723	3.12758
0.979605	3.314069
0.982204	3.464628
0.984831	3.649152
0.987335	3.848458
0.989621	4.113161
0.991758	4.405197
0.993746	4.744847
0.994868	5.011378
0.997207	5.867834
0.997207	5.867834
0.97859	3.592411
0.957474	2.783043
0.93685	2.448347
0.912019	2.2236
0.89155	2.081885
0.871501	1.960569
0.84189	1.855614
0.802427	1.726633
0.762198	1.645418
0.72209	1.574416
0.681974	1.516946
0.641909	1.467522
0.601701	1.42205
0.561654	1.388658
0.521462	1.36278
0.481411	1.340395
0.441324	1.301192
0.401173	1.281016
0.361087	1.242161
0.321019	1.203742
0.28089	1.157954
0.250513	1.106911
0.200668	1.040749
0.150587	0.942755
0.100078	0.806447