Production of Activated Carbon from Waste Palm Oil Shells and Its Adsorption Characteristics on Copper (II)

By

Ch'ng Mei Ling

Dissertation submitted in partial fulfillment of
the requirements for the
Bachelor of Engineering (Hons)
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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the
Chemical Engineering Programme
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Approved by,

(Mr. Khalik Bin Mohamad Sabil)
Main Supervisor

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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.

CH'NG MEI LING

ABSTRACT

The alarming problems of high concentration industrial effluents in the wastewater had awakened the world to the development of the techniques for the removal of these effluents from wastewater. Present of heavy metal such as copper in wastewater especially from plating and semiconductor industries can directly influence human health by impairing mental and neurological functions of the body system. Adsorption has demonstrated efficiency and economic feasibility as a wastewater treatment operation by using activated carbon due to its well-developed porous structure and tremendous surface area. The production of activated carbon from waste palm oil shell via chemical activation and carbonization were done. Various parameters that might affect the adsorption capacities of copper (II) in wastewater for the produced activated carbon were studied. These parameters included the activation agent (H_2SO_4, $ZnCl_2$, $CaCl_2$ and NaOH), carbonization time (1 hr and 3 hrs), carbonization temperature (400°C and 500°C), particle sizes of the raw material (<1mm, 1-2mm and >2mm) and the preparation sequences (sequences of carbonization and activation). In addition to that, the effects of different wastewater conditions included the pH of the wastewater solution and the metal concentrations in the wastewater were investigated. The results showed that the best activation agent for production of high quality adsorbent was NaOH and then followed by the sequence $H_2SO_4 > ZnCl_2 > CaCl_2$ whereas the best adsorption capacity of copper ion from wastewater was the activated carbon produced from particle size < 1mm and then followed by particle size 1 – 2 mm and > 2mm. The maximum adsorption capacity for the activated carbon produced from NaOH activation at particle size < 1mm was the highest among others, 196.06mg/g. The activated carbon produced at 3 hr had shown a higher adsorption capacity than produced at 1 hr. Besides, the higher the carbonization temperature, the better the adsorption capacity will be for that activated carbon. The results also showed that activated carbon prepared by carbonization first and then activation had a better adsorption capacity. From the adsorption study, it can be concluded that the best conditions of industrial wastewater for removal of copper ions were at pH 10 and 10ppm. The adsorption data for the carbons produced obeyed Langmuir Isotherm at which the maximum adsorption capacity was 126.58 mg/g for activated carbon activated by H_2SO_4 at < 1mm and 93.46 mg/g for the particle size 1-2mm.

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NOMENCLATURE

K	the adsorption equilibrium constant ($= k_a/k_d$)
θ	the fraction of the surface covered by adsorbed molecules
q_m,	the maximum loading corresponding to complete coverage of the surface by the gas
W	weight, in grams
q_e	the amount (mg) of copper per gram of activated carbon adsorbed at equilibrium
C_e	the concentration (mg/l) of copper in solution at equilibrium
Q_m	the Langmuir constants, representing the maximum adsorption capacity (mg/g) for the solid phase loading
b	the Langmuir constants, representing the energy constant(mg/ l)$^{-1}$ related to the heat of adsorption, respectively

CHAPTER 1

INTRODUCTION

1.1 Background of the Project

Water is a universal solvent used in every single industrial process. Hence, it is expected to contain a diverse range of organic, inorganic, metallic, hydrocarbonic, and biological effluents of all classes and properties. In Malaysia, the discharge of waste water containing chemicals and metallic ions into nearby watercourses is well documented (Sohaili, 1990). Heavy metals can pose health hazards if their concentrations exceed allowable limits. Heavy metals can directly influence human health by impairing mental and neurological function, influencing neurotransmitter production and utilization, and altering numerous metabolic body processes. Systems in which toxic metal elements can induce impairment and dysfunction include the blood and cardiovascular, detoxification pathways (colon, liver, kidneys, skin), endocrine (hormonal), energy production pathways, enzymatic, gastrointestinal, immune, nervous (central and peripheral), reproductive, and urinary (Farr, 2001). The maximum allowable limit for the heavy metal is as shown in Table 1.1.

Adsorption has demonstrated efficiency and economic feasibility as a wastewater treatment operation. Coupled with air stripping, adsorption by granular activated carbon (GAC) provides tertiary treatment for water contaminated with organics. Air stripping removes the volatiles while GAC completes the treatment. Various study (Toles et al., 1997; Rahman et al., 1999; Othman et al., 1994; Shawabkeh et al. , 2002; Chen et al., 2002) had demonstrated the utilization of activated carbons towards the removal of metal ions from wastewater.

Activated carbon had been reported to have high and fast adsorption characteristics (Chaiwattananont et al., 1998) due to its well –developed porous structure and tremendous surface area (Manahan, 1991). Activated carbon can be produced from a number of precursor materials including coal (Jankowska et al., 1991; Teng and Lin, 1998), coconut shells (Kirubakaran et al., 1991), almond shells (Toles et al.,1999; Rodriguez-Reinoso et al., 1982), palm oil shells (Gua and Lua, 2001; Daud et al., 2001; Daud et al., 2002), olive stones (Lafi, 2000) and other agricultural products (Hayashi et al., 2002; Ahmadpour and Do, 1997) using physical (Toles et al., 2000) and/or chemical processes (Evans et al., 1998; Toles et al., 1999; Ahmadpour and Do, 1997; Hayashi et al., 2002).

Table 1.1 Environmental Quality (Sewage and Industrial Effluents) Regulations, 1979 Maximum Effluents Parameters Limits Standard A and Standard B

Parameters	Units	Standard	
		A[1] (1)	B[2] (2)
Temperature	°C	40	40
pH	-	6.0-9.0	5.5-9.0
Cadmium	mg/l	0.01	0.02
Arsenic	mg/l	0.05	0.10
Cyanide	mg/l	0.05	0.10
Lead	mg/l	0.10	0.50
Copper	mg/l	0.20	1.0
Manganese	mg/l	0.20	1.0
Nickel	mg/l	0.20	1.0
Tin	mg/l	0.20	1.0
Zinc	mg/l	1.0	1.0
Boron	mg/l	1.0	4.0
Iron (Fe)	mg/l	1.0	5.0

In this study, waste palm oil shells were utilized as raw material to produce the granular activated carbon by chemical activation for the purpose of heavy metal effluents removal in wastewater. In Malaysia, palm oil shell is one of the main agriculture wastes from the palm oil processing mills (Daud et al., 2002). It is estimated that for every one million tones of palm oil produced, 0.8 millions tones of palm oil shell is created (Kirkaldy and Sutanto, 1976). Based on a total oil production of 7.4 million tones in 1993, the amount of palm oil shell generated in that year was about 6 million tones. The utilization of palm oil shells as the precursor for the preparation of high quality activated carbon is due to its high density, relatively high carbon content and low ash content (Guo and Luo, 1998).

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[1] Standard A for Discharge Upstream of Drinking Water Take –off

[2] Standard B for inland water

Hussein et al., 1996 found that activated carbon produced form palm oil shell by $ZnCl_2$ activation was essentially microporous with a fairly high surface area of 1500 m^2/g.

1.2 Problem Statement

Activated carbon can be produced from a large variety of carbon-containing feedstocks by the activation of pyrolyzed char (Ahmedna et al., 1999). In general, the activation process can be classified into two different types: chemical activation (J.W. Kim et al., 2001; Toles et al., 1997) and physical activation (E. Vilaplana-Ortego et al., 2002; Toles et al., 2000). In this study, chemical activation was carried out for the production of activated carbon from waste palm oil shells with four different chemicals which include zinc chloride, sulfuric acid, calcium chloride and sodium hydroxide.

In addition to that, the effect of the sequences of these two procedures was studied for three different sizes of activated carbon. The first sequence studied was chemically activated first and then followed by carbonization whereas the second sequence was the reverse. The activated carbons produced were compared with respect to their adsorption efficiency of copper ion in wastewater. There are several critical parameters in the production of activated carbon that would affect its structure included the carbonization time and carbonization temperature. High carbonization temperature would result in a greater amount of volatiles being released from the raw material and eventually influences the product yield and porosity (Daud et al., 2000). Thus, these factors were studied to observe its effects on the adsorption capacity.

For the study of adsorption capacity of the activated carbon produced, the concentration of wastewater and the pH of the wastewater were varies. For the preparation of synthetic copper wastewater, $Cu\ (NO_3)_2.3H_2O$ is dissolved in distilled water for the range from 10ppm to 100ppm. For varying the pH of the wastewater, acid and base were added to adjust the pH of wastewater in the range of pH 2 to pH 12. The concentration of copper ion in the solution after adsorption is measured by Atomic Absorption Spectrophotometer (AAS) and also conductivity meter.

1.3 Objectives and Scope of Study

The main objectives of this study are:

i. To produce activated carbon form waste palm oil shell via chemical activation with four different chemicals included zinc chloride, calcium chloride, sulfuric acid and sodium hydroxide.

ii. To produce activated carbon from waste palm oil shells from two different methods which by carbonization first and chemical activation; chemical activation first and then carbonization.

iii. To study the effect of the sizes of raw materials on the adsorption efficiency on metal removal.

iv. To investigate the effect of carbonization parameters on the efficiency of activated carbon produced, namely the carbonization time, carbonization temperature.

v. To investigate the effect of different wastewater conditions which included the pH of the wastewater solution and the concentration of the metal in the wastewater solution

CHAPTER 2
LITERATURE REVIEW AND/OR THEORY

2.1 Adsorption Process

Adsorption phenomena are operative in most natural physical, biological and chemical systems, and its operations employing solids such as activated carbon and synthetic resins for industrial application and purification of wastewaters. The adsorption process involves separation of a substance from one phase accompanied by its accumulation or concentration at the surface of another. The adsorbing phase is the adsorbent and the material concentrated or adsorbed at the surface of that phase is the adsorbate.

Over the last few decades, adsorption has gained importance as a purification, recovery and separation process on an industrial scale (Tsai et al., 2001).For recovery purposes, adsorption has been applied to recover some biological materials and organics compounds from both aqueous and gaseous streams as well as precious metal, eg. Gold in mines (Noll et al., 1992; Al-Duri, 1996). Adsorption at the surface or interface is largely the result of the binding forces between the individual atoms, ions, or molecules of an adsorbate and the surface, all of these forces having their origin in electromagnetic interactions. Four principal types of adsorption which are exchange, physical, chemical and specific may be distinguished.

2.2 Adsorption Isotherm

Brunauer et al. (1940) had divided isotherms of physical adsorption into five types (refer Appendix, Figure A-1 for illustration). The simplest Type I isotherm represents unimolecular adsorption and applies to microporous adsorbents with small pore sizes (not significantly greater than the molecular diameter of the adsorbate). It applies often to gases at temperature above their critical temperature. The more complex Type II isotherm is associated with multimolecular adsorption of the BET type and is observed for gases at temperatures below their critical temperature and for pressures below, but approaching the saturation pressure (vapor pressure). The heat of adsorption for the first adsorbed layer is greater than that for the succeeding layers, each of which is assumed to have a heat of adsorption equal to the heat of condensation (vaporization). Both types I and II are desirable isotherms, exhibiting strong adsorption.

The Type III isotherm with its convex nature is undesirable because the extent of adsorption is low except at high pressures. According to BET theory, it corresponds to multimolecular adsorption where the heat of adsorption of the first layer is less than that of succeeding layers. An isotherm of type IV is the capillary condensation version of Type II; Type V is the capillary condensation version of Type III. A hysteresis phenomenon can occur in multimolecular adsorption regions for the both isotherms. The upward adsorption branch of the hysteresis loop is due simultaneous multimolecular adsorption and capillary condensation. Only capillary condensation occurs during the downward desorption branch of loop. Hysteresis can also occur throughout any isotherm when strongly adsorbed impurities are present.

In establishing isotherm equations for data representation, only two factors are of practical importance: (1) the accuracy of the representation, and (2) the ease with which the equation may be incorporated into adsorption calculations, as shown in later discussions. The following discussion examines several isotherm equations commonly used for single-component gas-adsorption data.

2.2.1 Langmuir Isotherm

The Langmuir equation which is restricted to Type I isotherms, is derived from simple mass-action kinetics, assuming chemisorption from either gas or liquid solutions. Banat at al. (2003) stated that Langmuir adsorption isotherm is a typical model for monolayer adsorption which can be used to facilitate the estimation of the adsorption capacities of the activated carbon. Assume that all the adsorption sites are identical (energetically) and each site accommodates one adsorbate molecule only ($\Delta H_{ads} = cons\tan t$); the adsorption of adsorbate molecules tales place at well-defined localized states; and that the forces of interaction between adsorbed molecules are negligible. Let θ be the fraction of the surface covered by adsorbed molecules. Therefore, (1 - θ) is the fraction of the bare surface. Then, the net rate of adsorption is the difference between the rates of adsorption and desorption:

$$dp/dt = k_a p(1-\theta) - k_d\theta \qquad \text{Eq. 1.1}$$

At equilibrium, *dq/dt = 0* and Eq. 1.1 reduces to

$$\theta = \frac{Kp}{1+Kp} \qquad \text{Eq. 1.2}$$

where K is the adsorption equilibrium constant (= k_a/k_d). Here,

$$\theta = q/q_m \qquad \text{Eq. 1.3}$$

where q_m, is the maximum loading corresponding to complete coverage of the surface by the gas. Thus, the Langmuir adsorption isotherm is restricted to a monomolecular layer. Combining Eq. 1.3 with Eq. 1.2, we obtain

$$q = \frac{Kq_m p}{1+Kp} \qquad \text{Eq. 1.4}$$

The quantities K and q_m in Eq. 1.4 are treated as empirical constants, obtained by fitting the nonlinear equation directly to experimental data or by employing the following linearized form, numerically or graphically:

$$\frac{p}{q} = \frac{1}{q_m K} + \frac{p}{q_m} \qquad \text{Eq. 1.5}$$

Using Eq. 1.5, the best straight line is drawn through a plot of points p/q versus p, giving a slope of $(1/q_m)$ and an intercept of $1/(q_m K)$. It should be noted that the Langmuir isotherm predicts an asymptotic limit for q at high pressure, whereas the Freundlich isotherm does not.

2.3 Activated Carbon

2.3.1 History of Activated Carbon

Activated carbons are microporous carbonaceous adsorbents whose history can be traced back to 1600 B.C. when wood chars were used for medicinal purposes in Egypt. As one kind of adsorbents, activated carbon is widely used in adsorption for the removal of gaseous (e.g. hydrogen sulphide, H_2S; nitrogen oxide, NO_2; sulphur dioxide, SO_2; and volatile organic compounds) and aqueous pollutants (e.g. acetic acid, dye, phenol, toluene and xylene) (Guo and Lua, 2001). Activated carbon is an effective absorbent primarily due to its extensive porosity and very large available surface area. Thus, such a material has desirable adsorption properties and has been used for purification and elimination of hazardous components in the gas and liquid phases (Hayashi et al., 2002). Hayashi et al. (2002) had also stated that due to the current problems of environmental pollution, activated carbon is expected to play an important role in pollution abatement. The chemical nature of the carbon's adsorptive surface is also important but is usually considered much less significant. The specific properties of an activated carbon are the result of both the raw material used to produce it and the activation process, which boosts its adsorbent qualities.

2.3.2 Classification of Activated Carbon

Activated carbons are complex products which are difficult to classify on the basis of their behavior, surface characteristics, and properties. For example, the BET surface area is in no manner a representative of the quality of the activated carbon because it does not indicate the surface accessible to larger molecules, which may be quite different. The only parameter that can give an idea of the quality of the carbon is its adsorption capacity and that only in the case of a particular application. Activated carbons are therefore classified on the basis of their particle size and particle shapes into powdered, granulated, spherical, or pelleted activated carbons.

a. Powdered Activated Carbons

Powdered activated carbons have a fine granulometry less than 100 pm with average diameter between 15 and 25 μm. Thus they present a large external surface and a small diffusion distance. The rate of adsorption is very high and the problems related to mass transfer are very low. They are thus preferably used for adsorption from solution phase because of their low diffusion rates. To reduce the consumption of the carbon, the treatment is sometimes carried out in a countercurrent principle but the process involves heavy investment.

b. Granulated Activated Carbons

Granulated activated carbons have a relatively larger size of carbon particles in the granules compared to carbon powders and consequently present smaller external surface. Diffusion of the adsorbate thus is an important factor. These carbons are therefore preferred for the adsorption of gases and vapors as their rates of diffusion are faster. Adsorption from the gas phase is carried out almost invariably under dynamic conditions by passing the gaseous mixture and the carrier gas through a bed of the carbon. The size of the carbon granules is an important factor. It should not be too small to prevent excessive pressure drop along the bed and carrying away of the carbon particles with the gaseous steam.

c. Spherical Activated Carbons

Katori et al. and Nagai et al. developed a process for the preparation of spherical carbons from pitch. The activated carbon spheres were found to have a high mechanical strength and excellent SO_2 and NO_2 adsorption capacities. Spherical activated carbons in the form of bellow spheres and in the form of granulated spherical pellets have also been obtained.

d. Impregnated Carbons

Carbons containing several types of inorganic impregnant such as iodine, silver, cations such as aluminum, manganese, zinc, iron, lithium, and calcium, and organic impregnants such as pyridines, ketones , and tertiary amines have also been prepared. The iodine -impregnated carbons can be used as catalysts, in the removal of SO_2 and H_2S from a gas steam and in removing methyl iodide gas from the effluent of a reactor.

2.4 Application of Activated Carbon

Activated carbons can be very useful in some industrial applications where well-developed mesopores and macropores system and a high purity of adsorbents is highly desirable (Torreegrosa-Macia et al., 1996). Hu and Vansant (1994) had stated that carbonaceous adsorbents have been found to be particularly useful due to their good kinetic properties, high adsorption capacities and relative ease of their regeneration. Furthermore, they can adsorb all organic and other non-polar compounds from the gaseous and liquid phase (Hu and Vansant, 1999). Therefore, their important applications relate to their use in the removal of color, odor, taste and other undesirable organic impurities from potable waters, in the treatment of domestic and industrial wastewater, solvent recovery, air purification in inhabited spaces such as restaurants, food processing and chemical industries, for the removal of color from various types of sugar syrup, in air pollution control, in the purification of many chemical, pharmaceutical and food products, and in a variety of gas phase applications as had been proven by Guo and Lua (2001); Toles et al. (1999); Kim et al. (2001); Ahmedna et al. (1999); Rahman and Saad (2003). They are being increasingly used in the field of hydrometallurgy for the recovery of gold and silver and other inorganic and as catalysts or catalyst supports. Due to the superior antacid and antalkali properties and large adsorptive capacity, activated carbons are widely used not only as adsorbent, but also as potential materials for catalytic support, battery electrode material, capacitor and biomedical engineering application (Lu and Chung, 1997). Their use in medicine to combat certain types of bacterial ailment is well known.

2.5 Preparation of Activated Carbon

The basic manufacturing process of activated carbon is based on carbonization and activation processes (Hu and Vansant, 1999). The purpose of carbonization is to enrich the carbon content and create in the char an initial porosity and some ordering in the carbon structure whereas the activation process further enhances this structure to generate a highly porous carbon (Daud et al., 2002). The preparation of activated carbons involves two main steps: the carbonization of the carbonaceous raw material at temperatures below 800°C in the absence of oxygen and the activation of the carbonized product or vice versa. Although the properties of the final product of activated carbon will be different, most carbonaceous materials can be converted into activated carbon depending on the nature of the raw material used, the nature of the activating agent and the conditions of the activation process. Several studies had been carried out by Daud et al. (1999); Lafi (2000); Hayashi et al. (2002); Ahmadpour and Do (1997); Kim et al. (2001); Toles et al. (1997); Rahman and Saad (2003) on the production of activated carbon from various raw materials.

2.5.1 Raw Material

Since the price of commercial activated carbon has dropped continually over the last decades or so, interests are growing in the use of other low – cost and abundantly available lingo-cellulosic materials as precursors for the preparation of activated carbon (Gua and Lua, 2001). Any cheap material with a high carbon content, low in inorganics can be used as a raw material for the production of activated carbon. Younger fossil materials such as wood, peat, and wastes of vegetable origin, which included fruit stones, nutshells, and sawdust were the preferred raw material for production procedures due to the high chars contained that can be easily obtained from them. The usage of these raw material had been proven through several investigators included Daud et al. (2001); Rahman et al. (1999); Tsai et al. (2000); Lafi et al. (2000); Hayashi et al. (2002); Ahmadpour and Do (1997); Kim et al. (2001).Nowadays, various kinds of natural coal, which are cheap and readily available such as waste lignin, sulfite liquors, and wastes from the processing of petroleum and lubricating oil industries are always widely employed. Some criteria are considered when choosing a carbonaceous raw material are:

i. Potential for obtaining high-quality activated carbon.
ii. Presence of minimum inorganics.
iii. Volume and cost of the raw material.
iv. Storage life of the raw material.
v. Workability of the raw material.

In this study, waste palm oil shells were selected as the raw material as the palm oil industries in Malaysia had contributing the largest palm oil production in the world. This industry generated about 6 million tonnes (dry weight) of waste shells annually. With such an abundance of raw material, it is desirable to produce activated carbon on a commercial basis. The possible use of palm shell for the production of good quality activated carbon was highlighted by Chan et al. Reupke and Duff reviewed the possibility of using palm shell for activated carbon production and concluded that the product derived from this material could be technically inferior to the product produced from coconut shell in many applications. Table 2.1 shows the previous study in production of activated carbon form various raw material.

Table 2.1 Various Studies done on Production of Activated Carbon from Various Raw Materials

Researchers	**Raw Material Used**
Guo and Lua, 2000	Waste Palm Oil Shells
Rahman et al., 1999	Rice Husks
Tsai et al., 2000	Waste Corn Cob
Lafi	Acorns and Olive Seeds
Hayashi et al., 2002	Chickpea Husks
Toles et al., 1999	Almond Shells
Ahmadpour and Do, 1997	Macadamia Nutshells
Kim at al., 2001	Waste Walnut Shells
Hu et al., 2000	Coconut Shells
Hu and Vansant, 1994	Walnut Shells
Zandersons et al., 1999	Brazilian Sugarcane Bagasse
Ng et al., 2002	Pecan Shell
Ahmedna et al., 1999	Sugarcane Bagasse, Rice Straw, Pecan Shells
Sirichote et al., 2002	Pericarp of Rubber Fruit, Coconut Shells
Evans et al., 1998	Sugar Carbon
Toles et al., 1997	Almond and Pecan Shells
Rahman and Saad, 2003	Guava Seeds

2.5.2 Carbonization

Carbonization is a particular form of thermochemical process called pyrolysis where complex substances were broken down into simpler molecules by means of heating (Khalik, 2000). According to Brocksiepe et al. (1986), carbonization is a series of decomposition reactions that took place if woods were heated in the absence of atmospheric oxygen above 100°C. The process is usually carried out in rotary kilns or multiple earth furnaces at temperatures below 800°C in a continuous stream of an inert gas. The important parameters that determine the quality and the yield of the carbonized product are the rate of heating, the final temperature, the soaking time at the final temperature, and the nature and physical state of the raw material. Low heating rate during pyrolysis results in lower volatilization and higher char yield because of increased dehydration and better stabilization of the polymeric components. However, the char microporosity was found to be independent of the precursor composition and the pyrolyzing heating rate. The basic microstructure was formed by 500°C, although some of these pores were blocked by the pyrolysis products and could be available only when high -temperature treatment was given.

According to Daud et al. (2001), several parameters that affect the properties of the char produced during carbonization are carbonization temperature, carbonization time and the heating rate. Carbonization temperature is considered as the most important parameter in the carbonization process because it is associated with the amount of energy required to break the chemical bonds of the raw materials (Daud et al., 2001). Ahmadpour and Do (1997) had proved that as the carbonization time increases, the weight loss of the activated carbon will increases. This result was also proven by Hu and Vansant that the micropore volume and surface area increase with increasing carbonization time, but the change of the adsorption energy is in reversed order. Lozano-Castello et al. (2002) showed that an increase in the carbonization time produces an increase in the N_2 adsorption capacity. This statement can further confirm that high carbonization time will lead to a higher pore volume and surface area which will then resulted in higher adsorption capacity.

2.5.3 Activation

The objective of the activation process is to enhance the volume and to enlarge the diameters of the pores which were created during the carbonization process and to create some new porosity. The structure of the pores and their pore size distribution are largely predetermined by the nature of the raw material and the history of its carbonization. The activation process removes disorganized carbon, exposing the aromatic sheets to the action of activation agents in the first phase and leads to the development of a microporous structure. In the latter phases of the reaction the significant effect is the widening of the existing pores or the formation of the large-sized pores by the complete burnout of the walls between the adjacent pores. This results in an increase in the transitional pores and macroporosity, whereas the volume of the micropores decreases. According to Dubinin and Zaverina (1949) that a microporous active carbon is produced when the degree of burn off is less than 50% and a macroporous active carbon when the extent of burn off is greater than 75%. When the degree of burn off is between 50 and 75%, the product has a mixed porous structure and contains all types of pores. Two types of activation processes are normally utilized which are chemical activation and physical activation. Table 2.2 shows the several activation processes used and the activating agents. According to Ahmadpour and Do (1997), chemical activation normally takes place at a temperature lower than that used in the physical activation process, therefore it can improve the pore development in the carbon structure and because of the effects of chemicals, and the yields of carbon are usually high. Hence, from the literature, it is obviously shown that the chemical activation process is more favorable than physical activation process.

Table 2.2 Various Activation Processes and Activating Agents used for Production of Activated Carbon

Researchers	**Activation Process**	**Activating Agents**
Guo and Lua, 2001	Physical activation	CO_2 gas
Rahman and Osman, 1999	Chemical activation	Nitric Acid
Hu et al., 2002	Chemical Activation	$ZnCl_2$ and KOH
Tsai et al., 2000	Chemical Activation	KOH and K_2CO_3
Lafi, 2001	Chemical Activation	Phosphoric Acid
Hayashi et al., 2002	Chemical Activation	K_2CO_3
Toles et al., 1999	Chemical Activation	Phosphoric Acid
Ahmadpour and Do, 1997	Chemical Activation	$ZnCl_2$ and KOH
Kim et al., 2001	Chemical Activation	$ZnCl_2$ and $CaCl_2$
Hu et al., 2000	Chemical Activation	$ZnCl_2$
Hu and Vansant, 1994	Chemical Activation	KOH
Ng et al., 2002	Physical Activation	Steam
Ahmedna et al., 1999	Chemical and Physical Activation	N_2 gas and H_3PO_4
Sirichote et al., 2002	Chemical Activation	$ZnCl_2$
Evans et al., 1998	Chemical Activation	KOH

a. Chemical Activation

Chemical activation usually is carried out when the raw material is of wood origin. The starting material is impregnated with the activating agent in the form of concentrated solution usually by mixing and shaking. This results in the degradation of the cellulose material. On calcination, the impregnated chemicals dehydrate the raw material, which results in charring and aromatization of the carbon skeleton and the creation of a porous structure. The most widely used activating agents are phosphoric acid, zinc chloride and sulfuric acid, although potassium sulfide, potassium thiocyanate hydroxides and carbonates of alkali metals, chlorides of calcium, magnesium, and ferric iron have also been suggested. The common feature of these activating agents is that they are dehydrating agents which influence the decomposition and inhibit the formation of tar. They also decrease the formation of acetic acid, methanol, etc and enhance the yield of carbon.

b. Physical Activation

Physical activation is the process through which the carbonized product develops an extended surface area and a porous structure of molecular dimensions, as previously mentioned. This step is generally carried out at temperatures between 800 and 1100°C in the presence of suitable oxidizing gases such as steam, carbon dioxide, air or any mixture of these gases. The heating is carried out by the combustion of coke oven or natural gas, when available, because it is most economical as both the required heat and the activation agent are supplied simultaneously. However, in directly fired activators, which could be rotary kilns or multiple hearth furnaces, extra steam is added to moderate the temperature. The active oxygen in the activating agent basically burns away the more reactive portions of the carbon skeleton as CO and CO_2, the extent of burn off (gasification) depending on the nature of the gas employed and the temperature of activation. The burning out of the carbon skeleton also occurs at different rates at different parts of the exposed surface.

2.6 Structures and Pore Size Distribution of Activated Carbon

Activated carbons are similar to the turbostatic carbon, having microcrystallites only a few layers in thickness and less than 100 Å in width. Activated carbons owe a large portion of their remarkable adsorption properties to their porous nature. Tsai et al. (2001) had stated that high adsorptive capacities of activated carbon are related to the properties such as surface area, pore volume and porosity. Guo and Lua (2000) had stated that the decreased in the apparent densities will result in the development of the porosity for the activated carbon. In addition to that, their results showed that the surface area of the activated carbon increased due to the development of new pores at high carbonization temperature and high carbonization time. Figure A-2 in Appendix is a scanning electron photomicrograph of a sample carbon which is a particularly good example of this porous characteristic. This is an activated carbon purposely prepared so as to induce a very high degree of transition pore porosity for increasing the diffusion-limited rate of adsorption from solution. The pores observed in this figure are about 0. 1 - 0.5 Å in diameter. A granule of a less porous carbon is shown in Figure A-3 (Appendix) for comparison. It is important to point out that the physical parameters such as porosity can be controlled to some degree to produce carbons suited for special applications. Adsorption of molecules from solution is in a sense strongly dependent on the porous nature of the activated carbon. In the solution adsorption, this arises from the fact that mass transfer through the carbon pores limits the rate at which a carbon can adsorb any species. Figure A-4 (Appendix) illustrates the rate of uptake of p-nitrophenol by four commercial activated carbons, and the highly porous carbon shown in Figure A-2. As Figure A-4 illustrates, the rate of approach to equilibrium varies considerably from the less porous carbons (Darco Barneby-Cheney) to the highly porous materials.

Activated carbons are characterized by their strong adsorption capacity, which can be as high as 0.6-0.8 cm^3/g, and which occurs mostly in cavities of molecular dimensions called micropores. Depending on their preparation, activated carbons also contain larger pores, known as mesopores and macropores. The definition of the different types of pores is based on their width w, which represents the distance between the walls of a slit-shaped pore or the radius of a cylindrical pore. One distinguishes micropores, for which does not exceed 2 nm; macropores, for which w exceeds about 50 nm; and mesopores, of intermediate size (2.0-50 nm). Several studies had been carried out to study the effect of various parameters on the pore development and surface area in activated carbon by Daud et al. (2002, 2001); Ahmadpour and Do (1997); Hu and Vansant (1999).

2.7 Factors Affecting Adsorption Capacity of Activated Carbon

In testing adsorption processes, a number of factors are concerned which also affect final design of the process. Three factors which have particular impact on experimental design are as below:

2.7.1 Characteristics of Adsorbate

The chemical character of the adsorbate is important for a number of reasons. It is this character which determines the size as well as the configuration of the particular molecule to be adsorbed. Molecular size is important for two reasons. First, for any homologous series of organic molecules, as size increases solubility generally decreases. A material which has low solubility in water, will have a higher affinity for solid surfaces than for the water and will therefore have a tendency to concentrate on those surfaces, i.e. , to adsorb. Molecular size is also important for the perspective that all adsorbents depend upon internal surface area for the full use of their adsorption capabilities. If the molecular size is too large, adsorption will be hindered and adsorption capacity will decrease as very large molecules block or cannot penetrate pores or pathways within the adsorbent. One further aspect of molecular size is that larger molecules will tend to diffuse more slowly from solution and therefore will require longer times for full equilibrium adsorption capacity to be realized.

The molecular form of the particular adsorbate is also of significance. Whether the molecule is in an ionic or neutral state, whether it is a branched isomer or straight chain can have significant effect on the removal of this material from solution by adsorption. The molecular form can have consequences affecting the solubility of the adsorbate and it can also determine the energy of adsorption, i.e., the force with which the particular molecule is held on the adsorbent. Further, these characteristics can affect the rate of diffusion of the molecule through the liquid. The rate of diffusion is usually a function of both molecular size and form for a given solvent.

2.7.2 Characteristics of Adsorbent

The chemical and physical properties of the adsorbent used to remove a material from solution are quite important. Chemical properties include the degree of ionization of the surface of the adsorbent, the types of functional groups which are present on the adsorbent, and the degree to which these properties may be changed by contact with the solution. Toles et al. (1999) and Ahmedna et al. (1999) had done the study on the chemical and physical properties of the activated carbon produced. The presence of ionized or otherwise active functional groups on the adsorbent surface allow chemical interactions of "chemisorption" which usually produces effects different from and less reversible than physical adsorption. This effect may be advantageous or not, depending on a particular application. Further, the general ability of the chemical nature of the adsorbent to change the chemical characteristics of the solution to be treated can also have either beneficial or adverse effects on the adsorption process. This is particularly important where the treated solution is to be reused, or is for human consumption. Ahmedna et al. (2000) had concluded that high ash binders may explained the richness of minerals in the cane and beet molasses which in turn may have contributed to their relatively high pH of the activated carbon.

The physical properties of the adsorbent are like-wise important. The adsorbent can be in the form of granules or particles which may have a density near or very different from the solution to be treated; or the adsorbent may be in very fine powdered form which may be easily suspended in the solution to be treated. These physical properties have most effect on the selection of the mode of application of the adsorption process using that particular adsorbent. Attrition is another physical property of any activated carbon, especially granular activated carbon which may encounter intraparticle abrasion due to the nature of their applications (Toles et al., 2000).

Some physical properties such as surface area and size and distribution of pores in the particles directly affect adsorption performance by determining the amount of adsorbent capacity available and the molecular sizes which can be adsorbed. According to Tsai et al. (2001), high adsorptive capacities of activated carbons are related to properties such as surface area, pore volume and porosity.

2.7.3 Characteristics of Solution

The three major waste solution characteristics which have particular impact on adsorption are: the solution pH; its temperature; and, the presence of other competing adsorbate compounds.

The pH of a solution is of significance for its effect on the adsorbent, as well as on the adsorbate. Both adsorbate and adsorbent may have chemical characteristics which are affected by the concentration of hydrogen ions (H^+) in the solution. Some adsorbents have affinity for H^+ or OH^- ions and can directly affect the solution pH and therefore solubility and adsorption capacity. This effect must be considered during test design where large quantities of virgin adsorbent may be used per volume of solution. The pH change may not be quite so evident in full-scale operation where large volumes of solution are treated.

Thus significant differences between laboratory and full scale results can be realized. Adsorption from solution can be highly pH sensitive in aqueous systems where an adsorbate exhibits an isoelectric point or neutral point on the pH scale. It is at this point where maximum adsorption can be achieved since solubility is minimized and the non-polar adsorbent has greatest affinity for U911-ionic materials. In many cases solution pH change is possible in full scale, and it is a relatively simple effect to simulate in laboratory testing; it should not be overlooked.

The temperature of a solution has two major effects on adsorption. First, the rate of adsorption is usually increased at higher temperatures. This is due primarily to the increased rate of diffusion of adsorbate molecules through the solution to the adsorbent. Further, since solubility and adsorption are inversely related, as temperature affects solubility it will therefore affect the extent of adsorption or capacity of the adsorbent for the particular adsorbate. Temperature effects should be simulated carefully in the laboratory to reproduce expected full-scale conditions. In cases where change of process temperature is possible, it should be evaluated for possible beneficial effects.

A major influence of the solution character on adsorption is the presence of competing adsorbate compounds. Few adsorbents demonstrate controllable selectivity for specific compounds and therefore all adsorbable compounds present will compete for adsorption sites. Further, since physical adsorption is a reversible phenomenon, the presence of materials with a particularly high affinity for the adsorbent will, under continued application, tend to displace from the adsorbent materials of lesser affinity. This effect can result in what is known as a chromatographic effect. For the adsorbent system operated in a fixed bed mode, this effect can have particularly dramatic consequences for the quality of an effluent.

CHAPTER 3

METHODOLOGY/PROJECT WORK

3.1 Raw Material

The waste palm oil shells were obtained from a palm-oil processing mill in Perak. The shells were pretreated with drying at 110°C in an oven for 24 hours to reduce the moisture content. It is then grinded to a particle size fraction of 1 – 2 mm, <1mm and > 2mm with the assistance of mortar and sieve. The chemicals needed for as the activating agent included zinc chloride, calcium chloride, sodium hydroxide and sulfuric acid.

3.2 Characterization of Raw Material

3.2.1 Moisture Content (ASTM D2667 – 99)

1 – 2g of representative sample dipped out with a spatula. It is then put into a predried crucible with lid, close and weighed at once to the nearest 0.5 mg. Heat the sample in a preheated furnace at 145 to 155°C until a constant weight (3 hours normally sufficient). The sample was cool to ambient temperature in a dessicator and weighed. The moisture content was then calculated with:

$$\boldsymbol{Moisture, weight\%} = \left[\frac{(W_1 - W_2)}{W_1}\right] \times 100\% \qquad \text{Eq. 3.1}$$

where W_1= weight of the sample before drying, in grams

W_2= weight of the dried sample, in grams

3.2.2 Total Ash Content (ASTM D2866 – 94)

The crucible ignited in the furnace at 650 ± 25°C for 1 hour and then cooled to room temperature in a dessicator. A known weight of dried sample was then placed in the ignited crucible. It was then placed in the furnace at temperature 650 ± 25°C. Ashing will require from 3 to 16 hours, depending on the size and type of activated carbon.

Ashing can be considered complete when constant weight is achieved. After that, the sample was cooled to room temperature in a dessicator and weighed it. The total ash content was then calculated as below:

$$\mathit{Total\ Ash, weight\%} = \left[\frac{(W_4 - W_3)}{W_2}\right] \times 100\% \qquad \text{Eq. 3.2}$$

where W_2= weight of the dried sample, in grams

W_2= weight of empty crucible and lid, in grams

W_4= weight of crucible, lid and ash residues, in grams

3.2.3 Volatile Matter Content Test (ASTM D5832 – 98)

Approximately 1 g of the sample was dipped and placed in the predried crucible and weighed. Cover the crucible was then placed in the furnace regulated at 950 ± 25°C for 7 min ± 10s with lid tightly closed. The covered crucible was then removed from the furnace and cooled to room temperature in a dessicator. The cooled sample was then weighed and the volatile matter content can be calculated from:

$$\mathit{Weight\ Loss,\%} = \left[\frac{(W_6 - W_7)}{(W_6 - W_5)}\right] \times 100\% \qquad \text{Eq. 3.3}$$

where W_5= weight of the crucible and cover, in grams

W_6= weight of crucible, cover and sample, in grams

W_7= weight of crucible, cover and de – volatilized sample, in grams

$$\mathit{Volatile\ Matter,\%} = \mathit{Weight\ Loss,\%} - \mathit{Moisture,\%} \qquad \text{Eq.3.4}$$

3.2.4 Fixed Carbon Content

The percentage of fixed carbon Content was then calculated as follows:

$$\mathit{Fixed\ Carbon, FC\%} = 100 - (\mathit{Moisture} + \mathit{Ash} + \mathit{Volatile\ Matter}) \qquad \text{Eq. 3.5}$$

3.3 Production of Activated Carbon

The production of activated carbon can be summarized in the Figure 3.1.

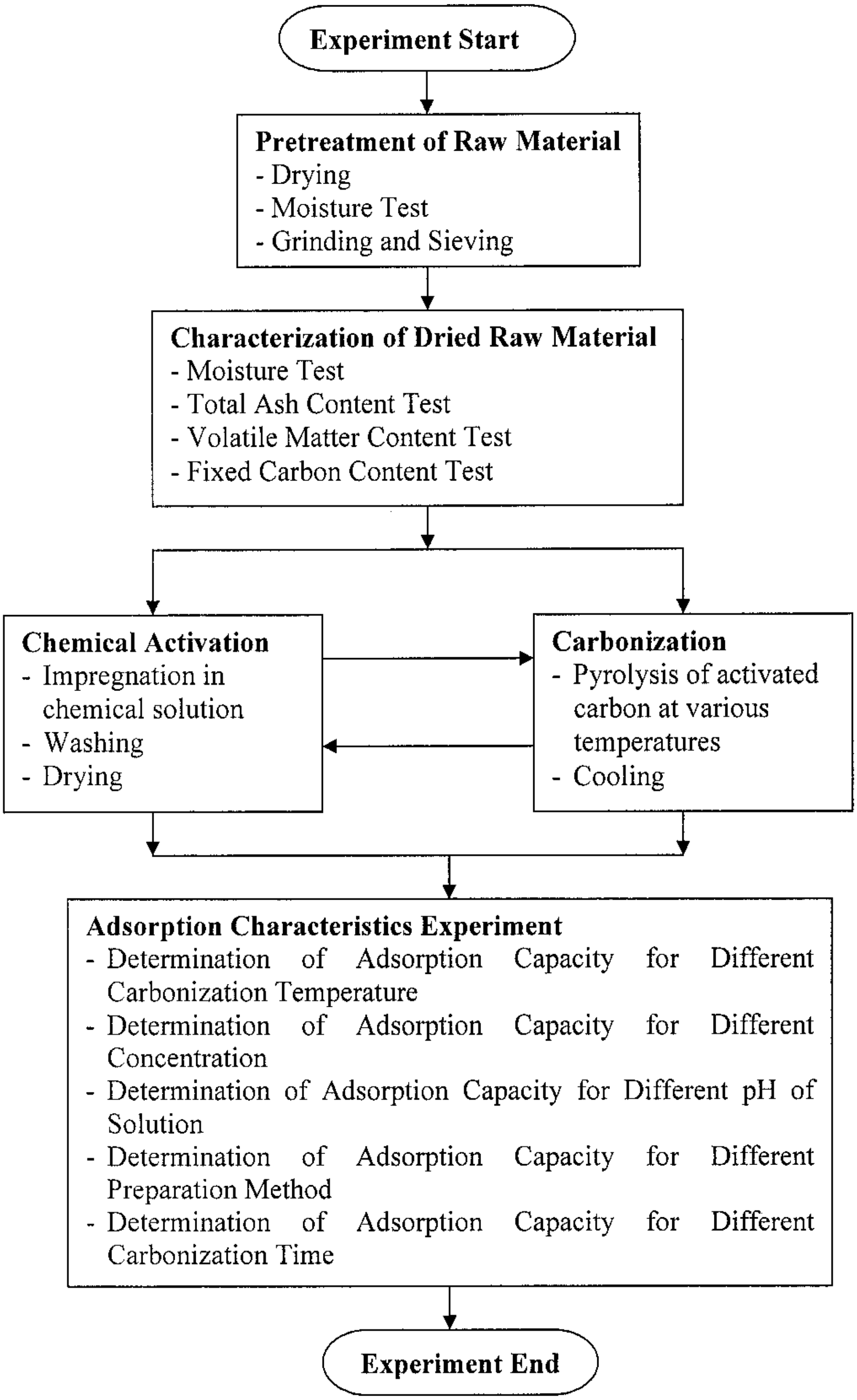

Figure 3.1 Process Flow for Preparation of Activated Carbon

3.3.1 Chemical Activation

20 g of the dried shells was impregnated with a solution of $ZnCl_2$ in the Erlenmeyer flask. The Erlenmeyer flask was shake for 24 hours by using the shaker. The obtained activated carbon was washed with distilled water until the pH is in the range of 6 - 8 to remove chloride including zinc compounds. After that, the washed activated carbon was dried at 110°C for 3 hours until constant weight obtained. Then, the activated carbon was cooled to room temperature in a dessicator for 24 hours. The method was repeated for different types of chemical: H_2SO_4, $CaCl_2$ and NaOH.

3.3.2 Carbonization

Pyrolysis of the activated carbon was carried out at 500°C for 1 hour using an furnace. The pyrolyzed activated carbon was then cooled to room temperature and then kept in a dessicator to prevent oxidation. This procedure was repeated with different carbonization temperature and carbonization time which are 400°C and 3 hours respectively.

3.3.3 Characterization of Activated Carbon

a. Percent Burn – off

Percent Burn – off of the produced activated carbon were calculated from the equation provided by Daud et al. (2002):

$$\theta = \frac{W_i - W_f}{W_i} \times 100\% \qquad \text{Eq. 3.6}$$

3.4 Adsorption Testing

0.5g of activated carbon was added to different copper solutions that have different copper concentration solution in 250 ml conical flask. One conical flask that contained only water sample is also prepared to act as a control sample. Samples were agitated for 24 hour. After the mixing activated carbon with copper solution, contents were filtered through filter paper by neglecting the first 5 ml of the filtrate in order to saturate the filter paper with Cu $(NO_3)_2.3H_2O$ solution. Concentration of

Cu^{2+} in the filtrate was then determined by Atomic Adsorption Spectrophotometer (AAS) and also conductivity meter. The amount of Cu^{2+} ion adsorbed was calculated based on the difference between the Cu^{2+} ion concentration in aqueous solution before and after adsorption. The same procedure was repeated for different pH in the copper solution for different activated carbon produced.

3.4.1 Preparation of different pH copper solution

100ml of 100ppm copper solution was prepared in an Erlenmeyer flask. Few droplets of 1M HCl was added until the pH of the copper solution was at pH 2. The pH of the copper solution was measured by using pH meter. Same procedure was repeated to produce copper solution at pH 4. For copper solution at pH 8, 10 and 12, NaOH was added instead of HCl.

CHAPTER 4

RESULTS AND DISCUSSION

As can be seen from the literature, voluminous researches had been done on the production of activated carbon from various raw materials and its adsorption characteristics on metal removal. Thus, utilization of the waste palm oil shells which is capacious in Malaysia as the precursors for the production of activated carbon was proposed and studied. As the achievement in the production of the activated carbon from waste palm oil shells, its adsorption characteristics on removal of heavy metal was also analyzed.

To present a systematic and resourceful report for this study, the results and discussion have been structured into several sections as follows:

Section 1: Characterization of Raw Material
Section 2: Production of Activated Carbon
Section 3: Adsorption Studies
Section 4: Study of Isotherm

4.1 Characterization of Raw Material

For the production of activated carbon, it is interesting to note that whether the precursors exploited is a high carbon content starting material such as carbon black. In this study, waste palm oil shell which has no specific technical uses and creates huge disposal problem was used. A proximate analysis was completed for determination of the moisture content, volatile matter, fixed carbon contents and the ash content present in the raw material.

Table 4.1 shows the results for the proximate analysis of the waste palm oil shells and from literature review. The results showed that the moisture content in the palm oil shell is very low as compared with the palm oil shell used by Daud et al. (200[illegible]) for the production of activate carbon. The low moisture content promotes energy efficient and fast – highly productive – carbonization. The total ash content from the waste palm oil shell is relatively larger than the one used by Daud et al. (2001) and Guo et al. (2001) as shown in Table 4.1. Raw materials of relatively high ash content are always activated to adsorptive capacities equal to or greater than those of lower ash raw materials. However, the high ash content will lead to present of soluble inorganic matter which is not a good criteria for the selection of a carbonaceous material.

The volatile content is considered high for the waste palm oil shells. A high volatile content will produce activated carbon with large micropore volume. As the density for the palm oil shell is considerably high, thus it is suitable for the liquid phase applications and also vapors adsorption. In addition to that, the fixed carbon content is low for the raw materials. Thus, it is not suitable for the utilization of raw material as the adsorbents without modification such as carbonization. Carbonization process involves thermal decomposition of the raw material by eliminating the noncarbon species and producing a fixed carbon mass and a rudimentary pore structure.

As the waste palm oil shell is relatively low in moisture content and high in volatile matter, it is suitable to act as a raw material for producing activated carbon.

Table 4.1 Proximate Analysis of Raw Material (Waste Palm Oil Shell) using ASTM Method and from Literature Review

Proximate Analysis	Palm Oil from Perak	Daud et al., 2001	Guo et al., 2001
Moisture Content (wt %)	2.92	7.96	-
Total Ash Content (wt %)	7.39	1.10	2.6
Volatile Matter (wt %)	67.07	72.47	77.6
Fixed Carbon (wt %)	22.62	18.7	19.8

4.2 Production of Activated Carbon

In this study, activated carbon was produced from waste palm oil shells by using chemical activation and carbonization. The activated carbons that were successfully produced are sorted in Table 4.2 and Table 4.3. Parameters that might affect the adsorption capacity of the activated carbon produced were varied which included the particle sizes, activating agent, carbonization time, carbonization temperature and sequences of carbonization and activation.

Three different particle sizes were chosen for the study waste palm oil shell in less than 1mm, 1 – 2 mm and more than 2mm. The activating agents used in this study can be characterized to three main groups which is acid, base and salt. The acid used was acid sulfuric whereas the base used was sodium hydroxide. In addition to that, two different salts, zinc chloride and calcium chloride, were used as the activating agent. Besides, carbonization time were also varied which are one hour and three hours. The carbonization temperatures for preparing the activated carbon were varied for this study which are 400°C and 500°C. Last but not least, the sequences of carbonization and activation were studied; these included two different sequences which are carbonization first and then activation; activation first and then carbonization.

Table 4.2 Activated Carbon Produced with Activation First and then Carbonization

Chemicals	**500°C, 1 hour**			**500°C, 3 hours**			**400°C, 1 hour**		
	<1	**1-2**	**>2**	**<1**	**1-2**	**>2**	**<1**	**1-2**	**>2**
$ZnCl_2$	x	x	x	x	x	x			
H_2SO_4	x	x	x	x	x	x	x	x	x
NaOH	x	x	x	x	x	x			
$CaCl_2$	x	x	x	x	x	x			x

Table 4.3 Activated Carbon Produced with Carbonization First then Activation

Chemicals	**1 hour**		
	<1	**1-2**	**>2**
H_2SO_4			x
$CaCl_2$			x

4.2.1 Characterization of Activated Carbon

The burn – off (%) for the activated carbon produced form waste palm oil shell was studied. Burn – off can be considered as the weight loss during the carbonization process. In order to characterize the surface area and pore volume development in the activated carbon produced, burn –off is an important factors to be considered.

Figure 4.1- 4.3 shows the effect of carbonization time on burn – off (%) for various activated carbons produced. As shown in the figure, it indicates that as the time of activation increases, the percentage burn – off increases linearly. Besides, for the activated carbon with activating agent of NaOH shows the higher percentage burn – off among others activated carbon produced. In addition to that, Figure 4.4 shows the effect of carbonization temperature on the burn-off percentage for activated carbon activating by H_2SO_4. It shows that as the carbonization temperature increases, the % burn –off will also increases. Besides, it is shown clearly from the figure that as the particles sizes of the activated carbon increases, the percentage burn –off decreases. As from the literature, the surface area of the activated carbon as well as the micropore volume, macropore volume and mesopores volume development increase, the percent burn –off will increase.

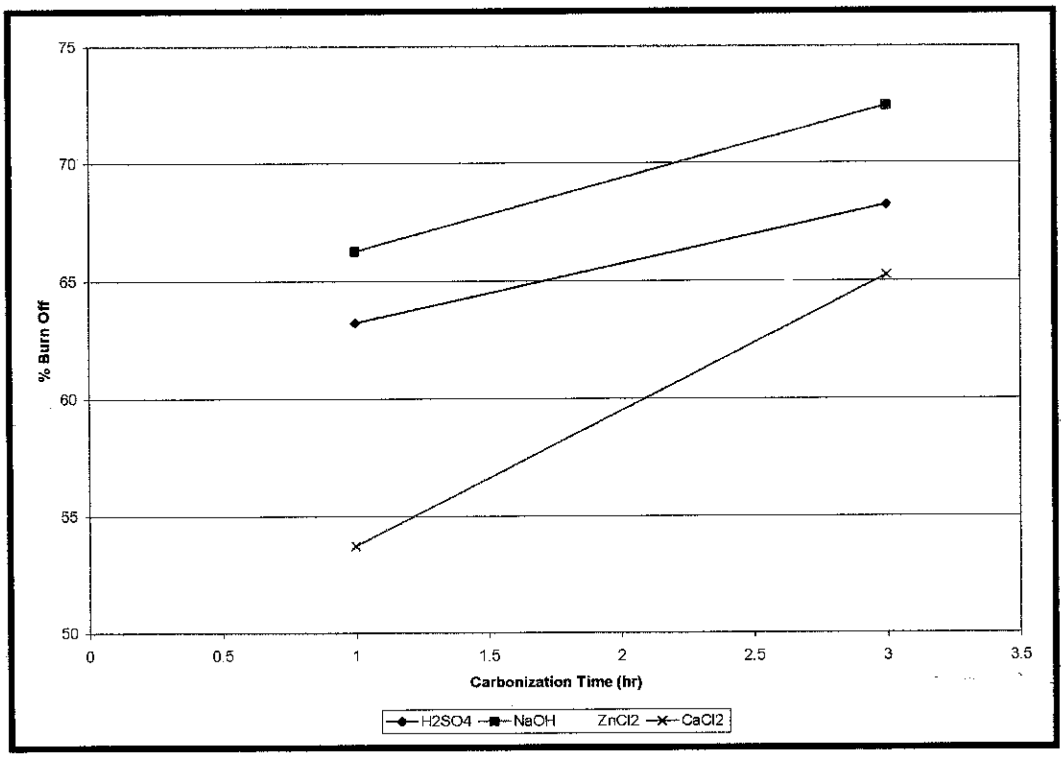

Figure 4.1 Effect of Carbonization Time on the Burn Off % for Different Activating Agent (Particle Size = <1mm, Carbonization Temperature = 500°C)

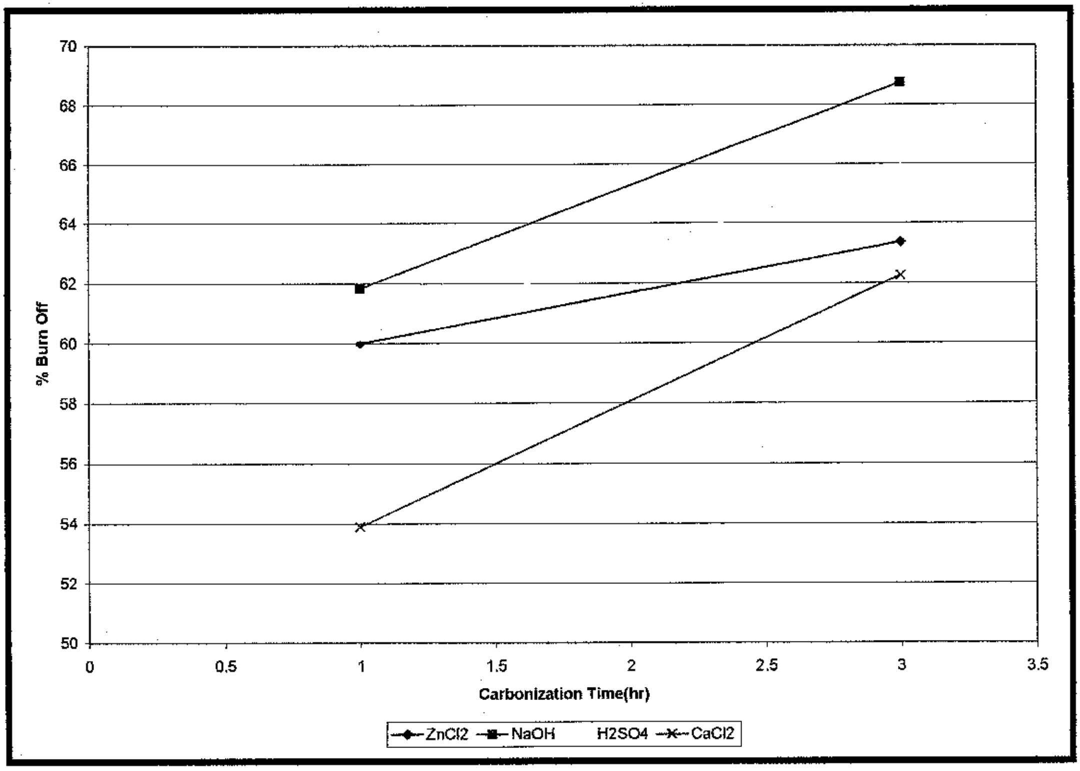

Figure 4.2 Effect of Carbonization Time on the Burn Off % for Different Activating Agent (Particle Size = 1-2 mm, Carbonization Temperature = 500°C)

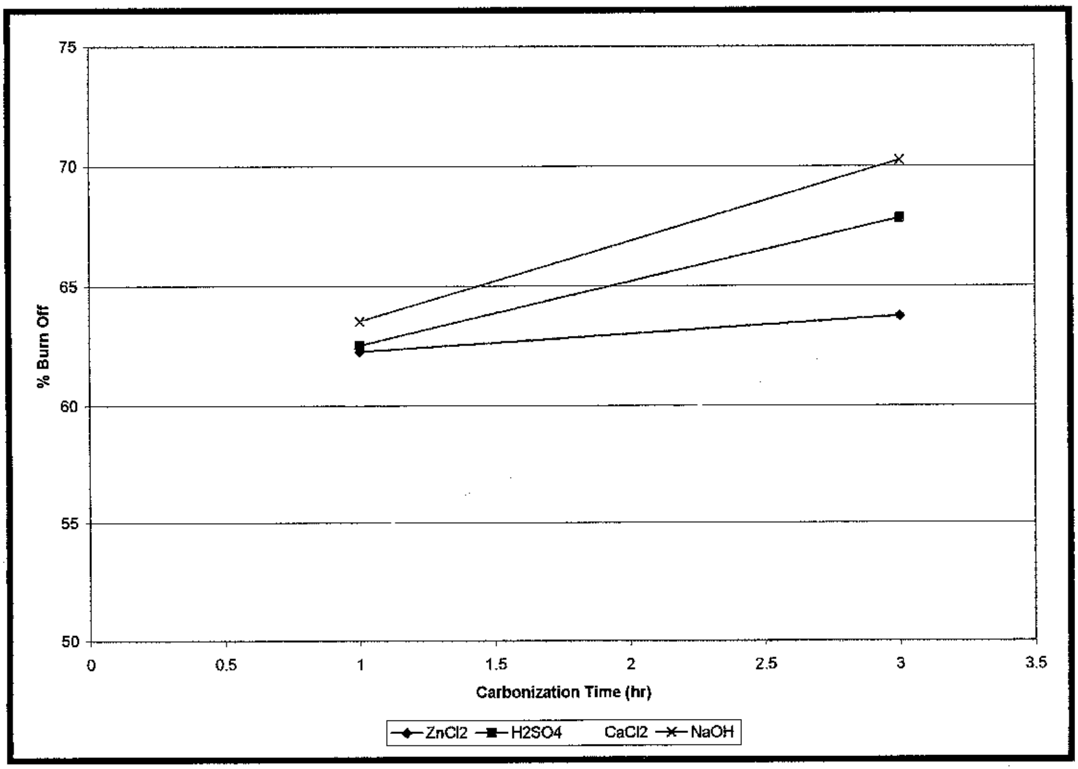

Figure 4.3 Effect of Carbonization Time on the Burn Off % for Different Activating Agent (Particle Size = > 2mm, Carbonization Temperature = 500°C)

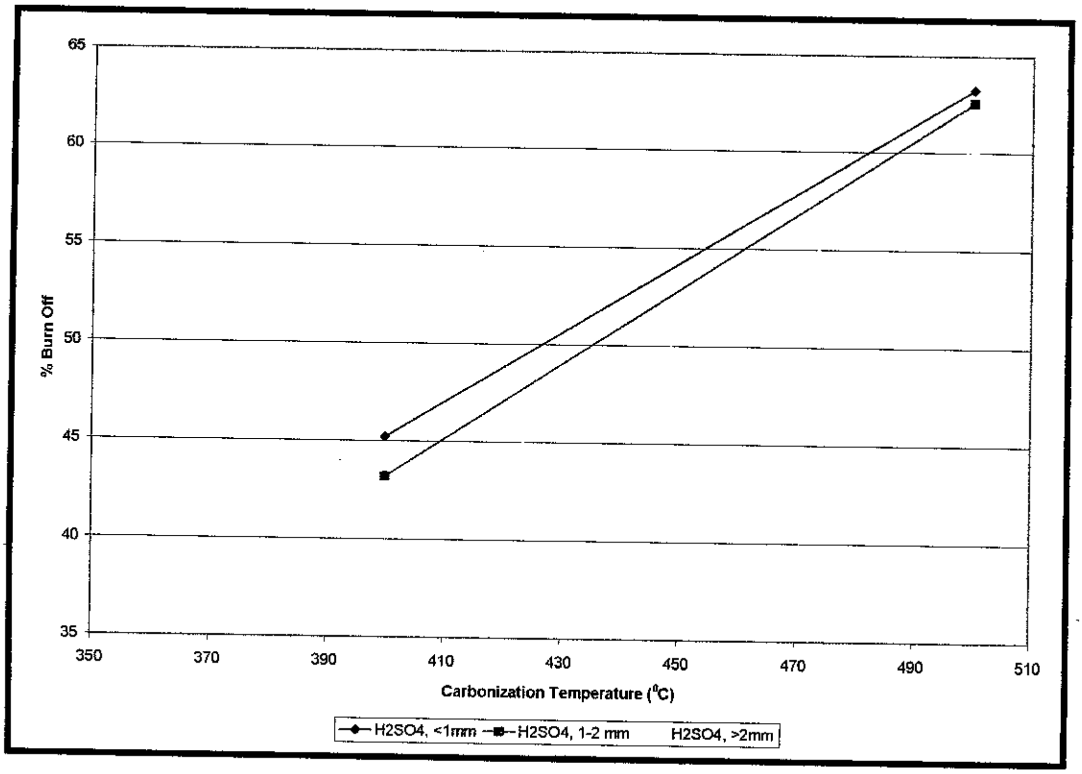

Figure 4.4 Effect of Carbonization Temperature on the Burn Off % for Different Particle Sizes (Activating Agent = H_2SO_4Carbonization Time = 1 hr)

Daud et al. (2002) stated that at high percentage of burn – off, the BET surface area will consequently increased as shown in Table 4.4. Kimber et al. (1995) and Burchell et al. (1997) had also produced the same results. In addition to that, the surface area based on Langmuir equation and Dubinin-Raduskevish equation will increased. Thus, it showed that the percent burn – off of the activated carbon varies proportionally with surface area. For the micropore volume development, the increase in the burn – off, the micropore volume developed increases almost linearly as shown in Appendix (Daud et al., 2002; Vilaplana-Ortego et al., 2002). Similar results were reported by Rodriguez-Reinoso and Sabio (1992) on peach stone and by Tomkow et al. (1977) on brown coal. In addition to micropores, mesopores and macropores are also developed during the carbonization (Daud et al. 2002; Burchell et al., 1997). Thus, it can be concluded that the exploitation of percent burn – off for the indication of pore volume available in activated carbon is proven. As stated in Daud et al. (2002), the mesopores volume and macropore volume developed in the activated carbon produced from waste palm oil shell is less dominant than the micropore volume developed which is at the average of 0.01-0.15cm^3/g as compared with 0.8 cm^3/g.

Thus, by comparing the burn – off percent of the activated carbon produced with the literature, it can be concluded that the activated carbon prepared by using NaOH as activation agent produced highest surface area as well as micropore, macropore and mesopores volume development. It follows by activated carbon with activation agent of sulfuric acid, zinc chloride and lastly calcium chloride. On the other hand, for the different particle sizes, the particle size of less than 1 mm provides the highest surface area as well as micropore, macropore and mesopores volume development. It is most obvious that at increasing carbonization time, the percent burn – off of activated carbon increases linearly and thus as the surface area as well as micropore, macropore and mesopores volume development. Based on the literature results, BET surface area, Langmuir surface area and Dubinin-Raduskevich surface area were estimated and shown in Table 4.5, Table 4.6 and Table 4.7.

Table 4.4 Surface Area of Activated Carbon Produced from Waste Palm Oil Shell at Various Burn - offs and Activation Temperature by Daud et al., 2002

Carbonization Temperature (°C)	Burn – off (%)	S_{BET}[3] (m^2g^{-1})	S_{Lang}[4] (m^2g^{-1})	S_{DR}[5] (m^2g^{-1})
800	36.2	533	794	790
	37.6	561	834	829
	49.4	797	1187	1179
	58.5	954	1425	1413
	63.9	1022	1530	1514
850	35.2	516	768	763
	43.4	593	1030	1025
	51.9	839	1250	1248
	57.3	935	1395	1348
	77.4	1400	2129	2019
900	38.8.	544	810	806
	49.4	783	1168	1162
	64.2	1111	1666	1652
	70.4	1232	1862	1977

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[3] Surface area based on BET equation

[4] Surface area based on Langmuir Equation

[5] Surface area based on Dubinin-Raduskevich Equation

Table 4.5 Estimated Surface Area for Activated Carbon Produced at Carbonization Temperature = 500°C, Carbonization Time = 1hr

Activated Carbon Produced	Burn – off (%)	S_{BET} (m^2g^{-1})	S_{Lang} (m^2g^{-1})	S_{DR} (m^2g^{-1})
Carbonization Time = 1 hr, Carbonization Temperature = 500°C				
$ZnCl_2$, <1 mm	61.44	1032.19	1557.84	1545.22
1-2 mm	62.28	1049.66	1584.04	1571.08
>2 mm	60.00	1002.24	1512.92	1500.90
$CaCl_2$, <1mm	54.48	887.44	1340.75	1330.99
1-2 mm	53.90	875.37	1322.65	1313.14
>2 mm	53.74	872.04	1317.66	1308.21
NaOH, <1mm	66.29	1133.06	1709.11	1694.51
1-2 mm	63.54	1075.86	1623.34	1609.86
>2 mm	61.83	1040.30	1567.00	1557.23
H_2SO_4, <1mm	63.25	1069.83	1614.29	1600.94
1-2 mm	62.56	1055.48	1592.77	1579.70
>2 mm	60.26	1007.65	1521.03	1508.90
Carbonization First, then Activation				
$CaCl_2$, >2mm	60.95	1022.00	1542.55	1530.14
H_2SO_4, >2mm	65.26	1111.64	1676.98	1662.81

Table 4.6 Estimated Surface Area for Activated Carbon Produced at Carbonization Temperature = 500°C, Carbonization Time = 3hr

Activated Carbon Produced	Burn – off (%)	S_{BET} (m^2g^{-1})	S_{Lang} (m^2g^{-1})	S_{DR} (m^2g^{-1})
Carbonization Time = 3 hr, Carbonization Temperature = 500°C				
$ZnCl_2$, <1 mm	65.82	1123.28	1684.45	1680.05
1-2 mm	63.76	1080.44	1630.20	1616.64
>2 mm	63.37	1072.33	1618.03	1604.63
$CaCl_2$, <1mm	65.26	1111.64	1676.98	1662.81
1-2 mm	63.26	1070.04	1614.60	1601.25
>2 mm	62.26	1049.24	1583.41	1570.47
NaOH, <1mm	72.46	1261.38	1901.56	1884.43
1-2 mm	70.24	1215.21	1832.32	1816.10
>2 mm	68.75	1184.22	1785.84	1770.23
H_2SO_4, <1mm	68.24	1173.62	1769.93	1754.54
1-2 mm	67.85	1162.50	1757.77	1742.53
>2 mm	65.87	1124.32	1696.01	1681.58

Table 4.7 Estimated Surface Area for Activated Carbon Produced at Carbonization Temperature = 400°C, Carbonization Time = 1hr

Activated Carbon Produced	Burn – off (%)	S_{BET} (m^2g^{-1})	S_{Lang} (m^2g^{-1})	S_{DR} (m^2g^{-1})
Carbonization Time = 1 hr, Carbonization Temperature = 400°C				
H_2SO_4, <1mm	45.22	694.85	1051.92	1045.96
H_2SO_4, 1-2mm	43.21	653.02	989.22	984.09
H_2SO_4, >2mm	40.35	593.56	900.02	896.05

4.3 Adsorption Characteristics

One of the most widespread uses of activated carbons for liquid phase adsorption is in waste water treatment. Recent years have seen an increase in the level of heavy metal content in industrial waste water. As stated before, the most critical parameters that are hazardous to the health and environment in wastewater are the concentration of the metal and the pH of the wastewater. Thus, the study on the activated carbon produced on the removal of Copper (II) content in wastewater was done. In order to present in a systematic way, the discussion on the results obtained are divided into two subsections:

Section 1: adsorption capacity of activated carbon at various copper concentrations
Section 2: adsorption capacity of activated carbon at various pH

4.3.1 Adsorption Capacity of Activated Carbon at Various Copper Concentrations

The adsorption test was carried out at various concentrations which are 10ppm, 20ppm, 40ppm, 60ppm, 80ppm and 100ppm.

a. Effect of Particle Size on the Adsorption Capacity

Particle size is a known parameter that has a direct effect on the physical properties of the resulting carbon during the carbonization stage (Ahmadpour and Do, 1997). Figure 4.5 shows that the adsorption capacity, as defined the difference between initial and final Cu^{2+} concentration divided by the weight of activated carbon used, of the activated carbon produced by activation agent of zinc chloride at three different particle sizes which are <1 mm, 1 – 2 mm and > 2mm. As the concentration of the copper solution increases, the amount of Cu^{2+} adsorbed per gram of activated carbon used will relatively increases. It is evident that activated carbon from was palm oil shell produced at particles sizes less than 1 mm has the highest adsorption capacity which is varied between 20 and 112 mg/g for the initial copper concentration of 20 – 200mg/g.

As discussed before, the smaller the particle sizes, the higher the percent burn – off and thus the higher the surface area as well as the micropore, macropore and mesopores volume development. As can be seen from the figure, all the adsorption isotherms are of type I, indicating a high microporosity. The adsorption capacity of an activated carbon depends largely on the presence of micropores on the surface area (Daud et al., 2002). Daud et al. (2002) also stated that a measure of the adsorption capacity of the activated carbon is the micropore volume. Ahmadpour and Do (1997) stated that activated carbon with small particle size are superior in terms of their surface area and micropore volume due to the higher surface of the small particles compared to that of the larger particles. As the micropore volume in the activated increases, there is the ease for the activated carbon to attract the copper from the solution. In addition to that, the storage of activated carbon for keeping copper atom will also increase and thus increase in the adsorption capacity. Same results were obtained for the activated carbon produced by activating with calcium chloride, sodium hydroxide and sulfuric acid. The graphical results were shown in Appendix VII. For the micropore volume development in the activated carbon, an important adsorption mechanism applicable is called microporous filling. Bering et al. (1996, 1972) studied the adsorption in micropores and suggested that adsorption in pores of less than 15Å should follow a mechanism of pore filling of the adsorption space rather than the mechanism of surface coverage. In these micropore solids, micropore walls are in proximity to each other, providing an enhanced adsorption potential within the micropores which is due to the dispersive forces. Theories based on this force include that of Polanyi and particularly that of Dubinin, who coined the term micropore filling. As stated before that the micropore network provides the most of the adsorption capacity resides as its pore dimension comparable to the dimension of the adsorbate molecule. The mechanism of micropore filling is due to the adsorption force field encompassing the entire volume of micropores. Such an enhancement in the adsorption potential would lead to higher heat of adsorption in micropore compared to that on a surface.

For the micropore filling, the chemical potential is a function of the amount adsorbed (Bering et al., 1972). The fundamental quantity in the micropore filling is the differential molar work of adsorption given by

$$A = R_g T \ln\left(\frac{P_0}{P}\right) \qquad \text{Eq. 4.1}$$

The standard state is the bulk liquid phase at the temperature T, which is in equilibrium with saturated vapor. The parameter P_0 is the vapor pressure of the free liquid.

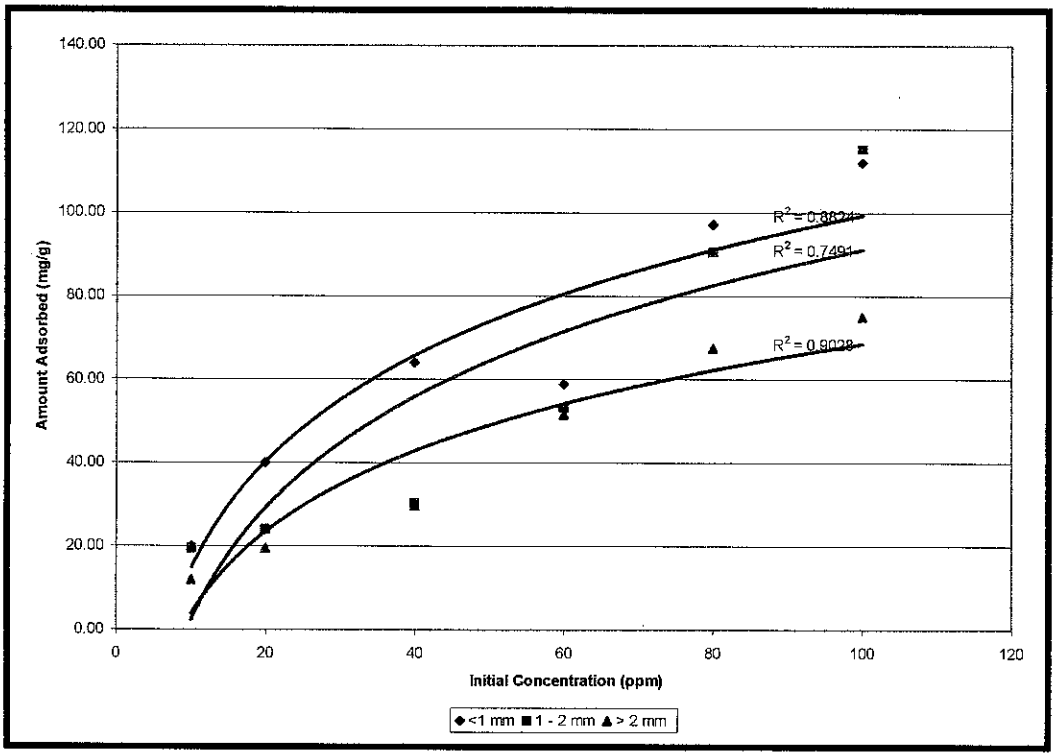

Figure 4.5 Effects of Different Particle Sizes on the Adsorption Capacity of Copper 2+ on Activated Carbon Produced (Activating Agent = $ZnCl_2$, Carbonization Time = 1hr, Carbonization Temperature=500°C)

b. Effect of Activation Agent on the Adsorption Capacity

Four different activation agents had been used for production of activated carbon from waste palm oil shells which includes zinc chloride, calcium chloride, sodium hydroxide and sulfuric acid. These activation agents can be classified as acid, base and salt. Figure 4.6, 4.7 and 4.8 show the effect of different activation agents on the adsorption capacity of copper solution at different concentration of activated carbon produced form waste palm oil shell at different particle sizes. From the figure, the best adsorbent is the activated carbon produced from activation of sodium hydroxide and then followed by sulfuric acid, zinc chloride and lastly is calcium chloride for all three particle sizes.

As stated before, the percent burn –off for the activated carbon with NaOH is relatively the highest among others three activating agents which is 66.29% for < 1mm, 63.54% for 1 – 2 mm and 61.83% for > 2mm. Ahmadpour and Do, 1997 stated that the burn – off percentage in the KOH series is more than that in the $ZnCl_2$ series . Hu et al., 2002 stated that the BET surface area and micropore volume developed in activated carbon produced from KOH are higher than that produced by $ZnCl_2$. As NaOH and KOH both are very strong acid, thus the comparison can be done with the aid of the activated carbon produced from KOH. From the adsorption capacity, it showed that activated carbon activating with H_2SO_4 can adsorb less copper form the copper solution as compared with NaOH. Guo and Luo, 1999 stated that the adsorption of SO_2 showed that the activated carbons pre-treated with KOH can adsorb more SO_2 than those pre-treated with H_2SO_4, even though they had almost identical BET and micropore surface areas. Thus, it can be concluded that activated carbon activating with NaOH has higher adsorption capacity than those in H_2SO_4. For the activated carbon produced by activating with $CaCl_2$ provides the less percent burn –off as compared with $ZnCl_2$ and thus the BET surface area and micropore development. Kim et al., 2001 stated that the activation is more promoted by employing $ZnCl_2$ as the activating agent rather than $CaCl_2$. Hence, it can be concluded that $CaCl_2$ is less efficient in the adsorption of copper solution as compared with the other three chemicals.

The different adsorption capacity based on different activating agents can be referred to the different reaction mechanism associated with these four chemicals acting on the carbonaceous structures. in this regard, several mechanism have been proposed by Rodriguez-Reinoso et al. (1992); Otawa et al. (1990); Laine and Calafat (1991) on the effect of strong base and Lewis acid on porosity creation. These suggested mechanisms indicate that zinc chloride which is a Lewis acid promotes the aromatic condensation reactions while KOH which is a strong base catalyzes the oxidation reaction (Ahmadpour and Do, 1997). The results of experimental work on activation of carbonaceous materials with $ZnCl_2$ by Ibarra et al. (1991) and Kandiyoti et al. (1984) have shown that the evolution of molecular hydrogen is more pronounced that other gaseous product. These hydrogen gases are developed from the hydroaromatics structure of the precursor and leave behind some sites for reactions. At this stage some cross-linking or aromatization reactions are taking place among the adjacent molecules which result in stabilizing some of the molecules that are normally volatile at that temperature. The consequential effect of these aromatization processes is an increase in the carbon yield (Ahmadpour and Do, 1997). On the other hand, for a strong base activation, some surface metal complexes are produced which are responsible for further carbon gasification and release of gaseous products such as CO_2, CO and H_2. Also, a number of oxygen functional group, as a result of the oxidizing atmosphere, are found (Otowa et al., 1993, 1995) to be formed on the carbon surface. This phenomenon results in widening of the spaces between carbon layers and increasing the pore volume (Ahmadpour and Do, 1997).

Guo and Luo (1999) stated that chemical characterization results showed that impregnation affected significantly both inorganic components and surface organic functional groups of the activated carbons. Surface organic functional groups were related to the adsorptive capacity of the activated carbon due to the change of the surface nature. The role of the impregnating agent was to minimize the formation of tars and any other liquids that could possibly clog up the pores and inhibit the development of porous structures in the activated carbon (Guo and Luo, 1997). As can be seen from Figure 4.6, the maximum adsorption capacity for the best activated carbon (activated carbon with activating agent NaOH) was 196.06 mg/g for particle size < 1mm.

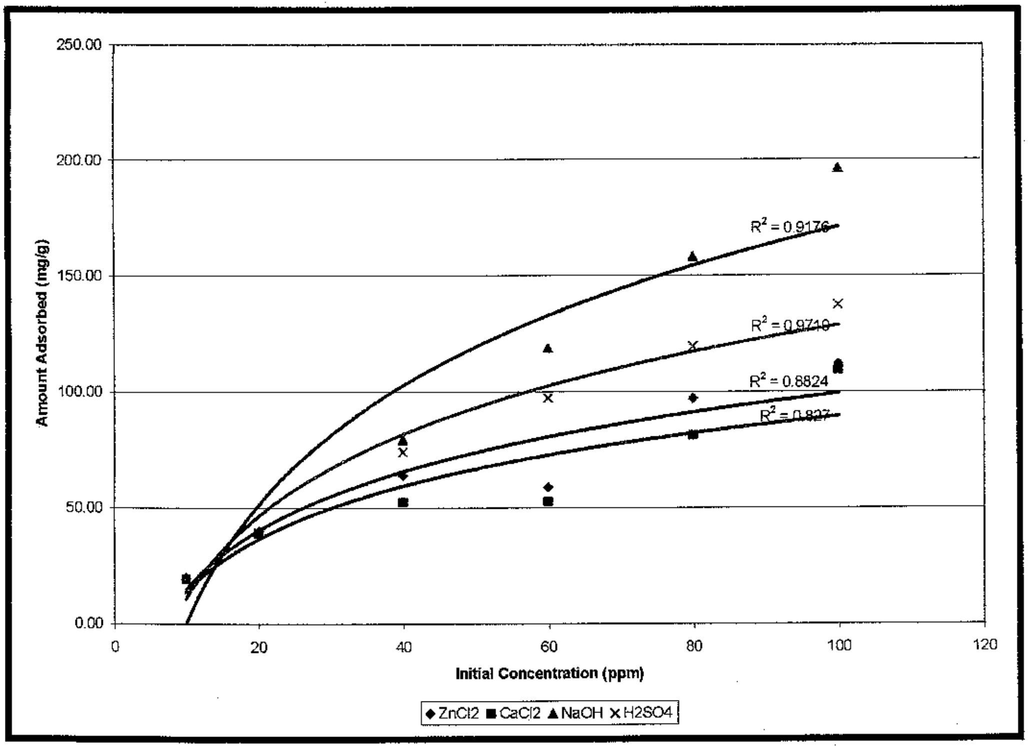

Figure 4.6 Effects of Different Activating Agents on the Adsorption Capacity of Copper 2+ on Activated Carbon Produced (Particle Size <1mm, Carbonization Time = 1hr, Carbonization Temperature=500°C)

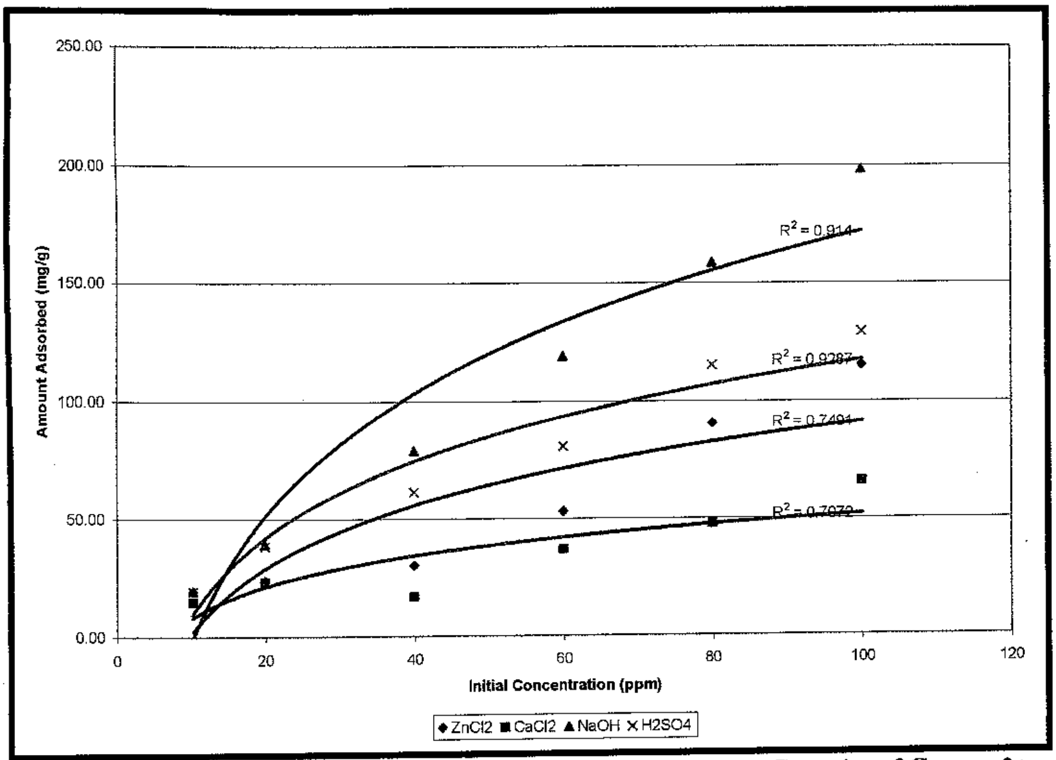

Figure 4.7 Effects of Different Activating Agents on the Adsorption Capacity of Copper 2+ on Activated Carbon Produced (Particle Size 1-2mm, Carbonization Time = 1hr, Carbonization Temperature=500°C)

carbonization time, but the change of the adsorption energy is in a reversed order. This indicates that at a given carbonization temperature, the micropores are formed in shorter time. When increasing the carbonization time, the pore size is widened by a burning off effect of carbon in the pores resulting in an increase of the pore volume and a decrease of the adsorption energy (Hu and Vansant, 1995). As the time for carbonization is increased, the percent burn – off in the activated carbon will also increased. As stated above, the increase in percent burn –off will relatively increase the surface area as well as the micropore, macropore and mesopores volume development. The increase in pore volume will then lead to the increase in amount of copper adsorbed and thus the adsorption capacity. The metal uptake for the highest adsorption capacity is at 131.89 mg/g for activated carbon produced from $ZnCl_2$ activation at particle size <1mm.

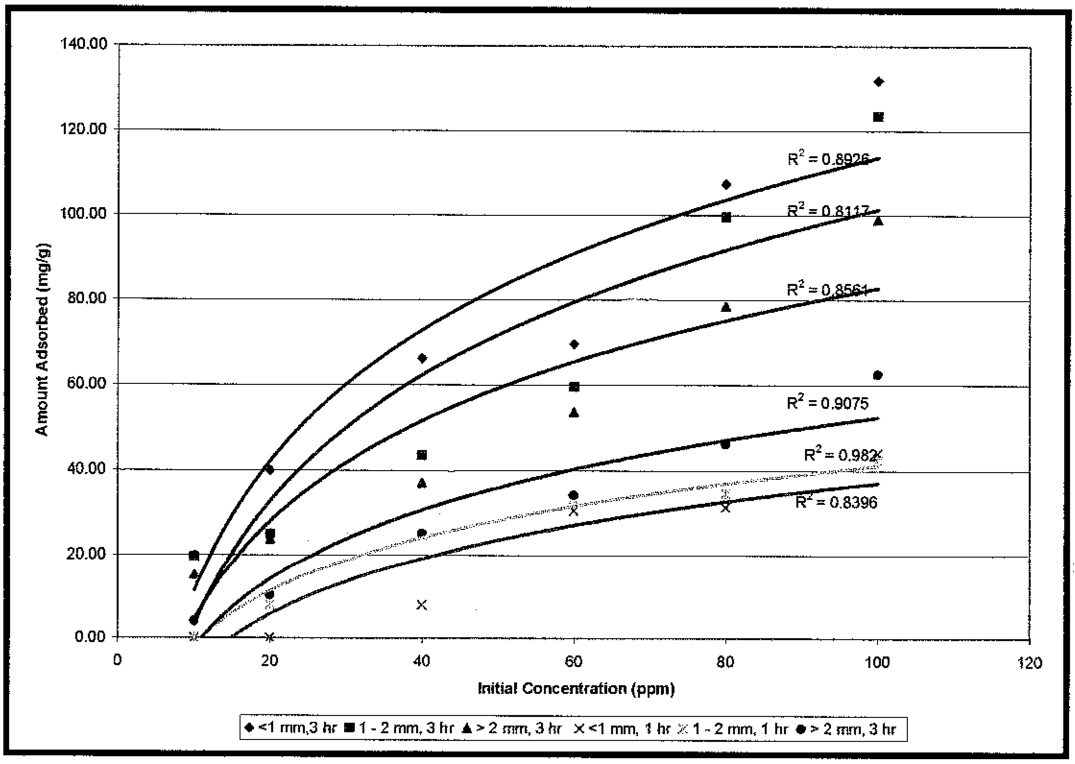

Figure 4.9 Effects of Carbonization Time on the Adsorption Capacity of Copper 2+ on Activated Carbon Produced (Activating Agent= $ZnCl_2$, Carbonization Temperature=500°C)

d. Effect of Carbonization Temperature on the Adsorption Capacity

Figure 4.10 shows the result for the effect of carbonization temperature on adsorption capacity for the activated carbon produced by activating agent of sulfuric acid for 1 hour. The result shows that the activated carbon produced at low temperature had low adsorption capacity on the copper solution and vice versa. This result can also be concluded for particle at various sizes that low temperature will adsorbed less copper content form the solution. This also means that the percent removal of cooper content of activated carbon decreases with lowering the carbonization temperature.

Hayashi et al., had stated that the micropore is well developed in the produced activated carbon and the total pore volume (micropore volume +mesopores volume) increases with an increase of carbonization temperature. Besides, Ahmadpour and Do (1997) had found the similar results for activated carbon activated with KOH. In general, carbonization temperature is known to be very influential on the micropore structures of activated carbon, which determines the adsorption capacity (Hu and Vansant, 1995). Lazano-Castello et al. (2002) had proven that for activated carbon, the higher the pyrolysis (carbonization) temperature results in higher BET surface area and the micropore volume.

As adsorption capacity increases with increasing carbonization temperature, the adsorption energy increases remarkably from 500 to 700°C with a maximum of 700°C (Hu and Vansant, 1995). High carbonization temperature will slightly increase the development of micropore volume in the activated carbon due to the higher percent burn – off at higher temperature. It also can be observe that increasing the carbonization temperature, the micropore size distribution becomes wider (Lazano-Castello et al., 2002). As expected considering the micropore volumes, the activated carbon prepared at 400°C to 500°C show an increase in the copper uptake with the carbonization temperature. This increase is progressive for the activated carbon produced at 500°C. The increase in the micropore volume could be attributed to a higher internal rate of carbonization thus creating more pore volume as a result of rearrangement of the carbon layer resulting in the creation of smaller-sized pores. These results also seem to indicate that within this temperature range, the reaction rate is primarily controlled by chemical activation (Daud et al., 2002).

The increasing in carbonization will significantly reduces the mesopores volume development (Daud et al;, 2002). The analysis had been done by Daud et al. (2002) based on the incremental pore volume shows that for all curves, the largest increments occurred at a pore diameter of around 9 nm and the increments gradually decreased for larger size pores. Another analysis also by Daud et al. (2002) based on cumulative pore volume indicates that mesopores volume almost linearly decreased upon increasing the carbonization temperature on the macropore volume. Increasing the carbonization temperature decreases the interlayer spacing of the carbon and causes the arrangement of carbon become more orderly. Thus, it can be concluded that at higher carbonization, the micropore volume development is more dominant that macropore volume and hence, the theory of micropore fillings discussed above was proven satisfied the condition.

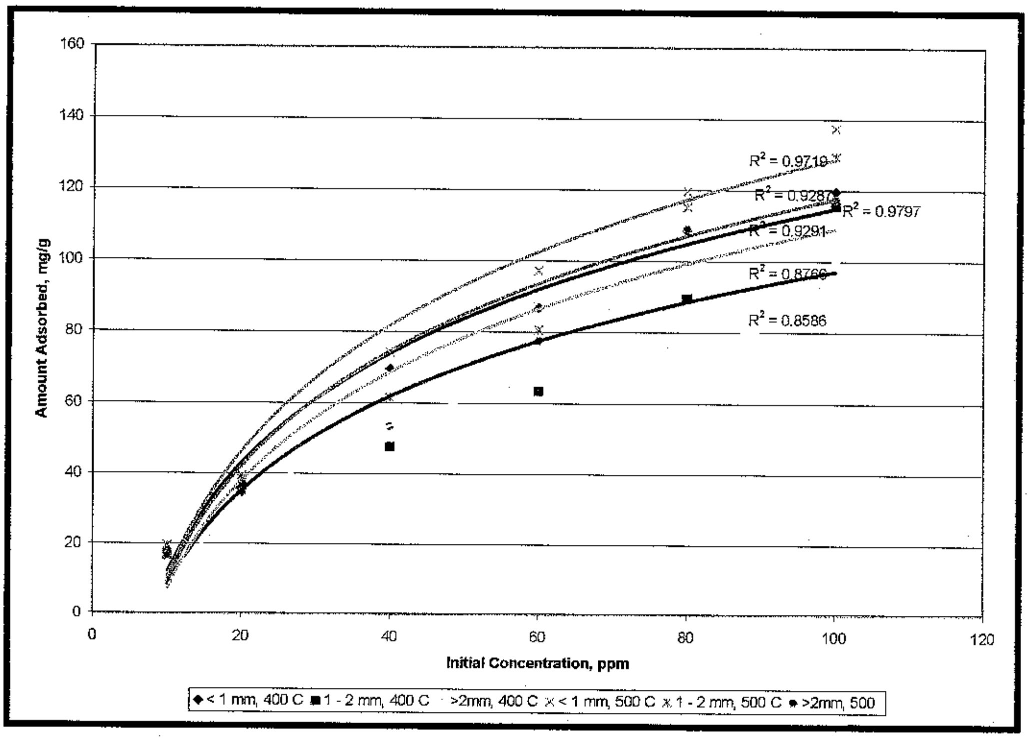

Figure 4.10 Effects of Carbonization Temperature on the Adsorption Capacity of Copper 2+ on Activated Carbon Produced (Activating Agent=H2SO4, Carbonization Time=1 hr)

In addition, Guo and Lua (2002) stated that as the carbonization temperature increased from 500°C to 900°C, the sample weight lost significantly due to a combination release of volatile natters in a continual carbonization process and carbon burn – off through carbon weak oxidation. This will then lead to an increase in the fixed carbon content of the activated carbon produced. Besides, increasing carbonization temperature will increased the solid density progressively and decreases the apparent density, resulting in the development of porosity (Guo and Lua, 2002). Guo and Lua (2002) had also proven that the higher the carbonization temperature will relatively increase the BET and micropore surface areas. The fairly high BET and micropore surface areas of the activated carbons prepared from waste palm oil shells render them to be suitable as effective adsorbents.

e. Effect of Preparation Sequences on the Adsorption Capacity

Figure 4.11 shows the result obtained from the study of effect of preparation sequence on the adsorption capacity. Two different chemicals acted as activating agents were studied at particles sized of > 2mm. The preparation methods were divided into types which are carbonization first and then only activation; and activation first and then carbonization. The result shows that the adsorption capacity is higher for the preparation sequence of leading by carbonization and followed by activation. This on the other hand had stated that the preparation sequence of activation first and then carbonization had showed a comparatively lower adsorption capacity. The results can be applied to both different activating agents which is sulfuric acid and calcium chloride.

The main reason in resulting this conclusion is that as the raw material had been carbonized first, the thermal decomposing of he carbonaceous raw material will resulting in elimination of noncarbon species and producing a fixed carbon mass and a rudimentary pore structure. The following chemical activation steps will then further enhance the volume and enlarge the diameters of the pores which were created during the carbonization process and to create some new porosity. With this, the pore structure created at the initial stage can be further expand and resulting in a high BET surface area as well as high pore volume development. .

On the other hand, as the carbonaceous raw material were activated first, then the expansion of pore volume is based on the original pore structure of the raw material which is relatively low compared with the carbonized raw material. The following carbonization step will only eliminating the noncarbon species and producing a fixed carbon mass but with no pore structure development. Hence, it can be concluded that the surface area and pore volume for activated carbon produced by carbonization first is relatively higher than those produced by activation first. This result will lead to a lower adsorption capacity of the activated carbon produced by activation first.

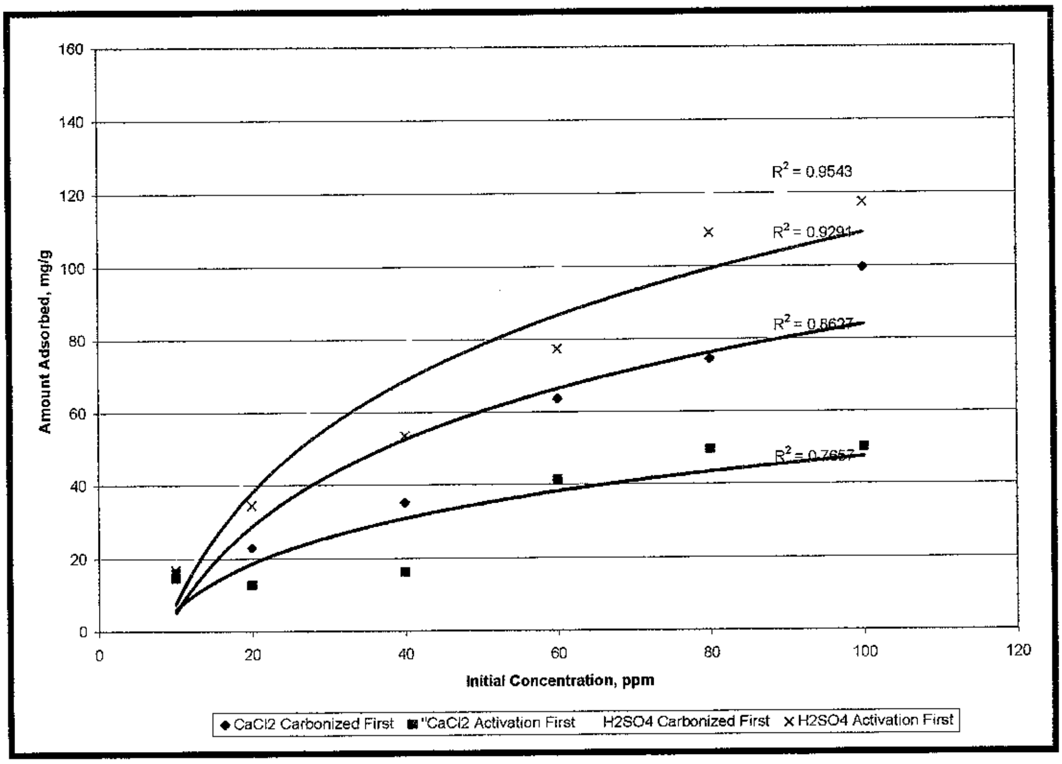

Figure 4.11 Effect of Preparation Sequences on the Adsorption Capacity on Activated Carbon produced with activating agents, sulfuric acid and calcium chloride (Carbonization Time=1 hr, Carbonization Temperature = 500°C)

4.3.2 Adsorption Capacity of Activated Carbon at Various pH

As the pH in the industrial waste water will always varies, this will then lead to a different adsorption capacity for the utilization as adsorbent for heavy metal removal. The value of pH used in the study of adsorption characteristics are in the range of pH 2 to pH 12. As the behavior of the activated carbon produced by varying the particles sizes, activation agents, carbonization time, carbonization temperature and the preparation sequence were known in the study of its effect on adsorption capacity, only four different activated carbons produced were selected for the studied of the effect of pH on the adsorption characteristics which are:

i. activated carbon produced with activating agent of $ZnCl_2$ at 500°C, <1 mm particles size at 1 hour carbonization time
ii. activated carbon produced with activating agent of $ZnCl_2$ at 500°C, 1-2 mm particles size at 1 hour carbonization time
iii. activated carbon produced with activating agent of $ZnCl_2$ at 500°C, >2 mm particles size at 1 hour carbonization time
iv. activated carbon produced with activating agent of H_2SO_4 at 500°C, 1-2 mm particles size at 1 hour carbonization time

From Figure 4.12, it is clearly demonstrates that the copper adsorption by the activated carbons produced from waste palm oil shell are strongly pH dependent. The copper adsorption sharply increases when the solution pH is increased from 2 to 4, which is in consistence with the observations reported in the literature (Corapcioglu and Huang, 1987; Chen and Lin, 2001). It is obvious that the extent of copper ion removal increases significantly with increases pH of the solution. The maximum adsorption seems to be related to the hydrolysis and precipitation of the metal ions as reported by Panday et al. (1988). The percent removal of copper for the activated carbon activating by zinc chloride at different particles sizes followed the trend of that for various concentration. On the other hand, the activated carbon produced from activating agent of sulfuric acid and zinc chloride at same particle size was also obeys the trend of that adsorption capacity at different concentration.

Generally, it was also agreed that the adsorption of metal ions at the solid-solution interface was controlled by the formation of surface complexes between free metal ions and the deprotonated sites (Mmari and Liew, 1998; Huang, 1984). As pH increases, more surface functional groups dissociate to provide metal binding sites, which results in higher metal ion adsorption. Chen et al., 2003 describes the interaction of copper ions with activated carbon as:

$$\begin{gathered} SOH + Cu^{2+} \rightarrow SOCu^{2+} + H^+ \\ SOH + Cu^{2+} + H_2O \rightarrow SOCuOH + 2H^+ \end{gathered} \qquad \text{Eq. 4.2}$$

The pH of the aqueous solution is an important variable that controls cationic adsorption on the carbon surface. This is due to the change of the carbon surface properties with an increase of pH. Carbons behave as a base for pH<pH_{zpc} (zpc, zero point charge) by adsorbing H^+ ions and behave as an acid for pH>pH_{zpc} by adsorbing OH^- ions. It is known that increases of pH decreases the competition between the protons and metal ions for surface sites and results in increased uptake of metal ions by the activated carbon (Savova et al., 2003). Savova et al. (2003) stated that activated carbon samples in aqueous solutions carry a surface charge, which is very much dependent on the pH of the solution and the results might be explained by the changes in the carbon surface charge at different pH values. Cation adsorption is favorable at pH values greater than that for pH_{zpc}. The results might indicate that the zero point of charge for different carbons obtained lies between pH 3.5 and 5.5. As the surface of carbons became positively charged the hydrated manganese cations can hardly be adsorbed in the pH range lower than pH_{zpc} (Savoca et al., 2003). Figure 4.9 shows that at pH values lower than 4 the electrostatic repulsion between the carbon surface and the metal ions prevent their adsorption which leads to a smaller percent removal

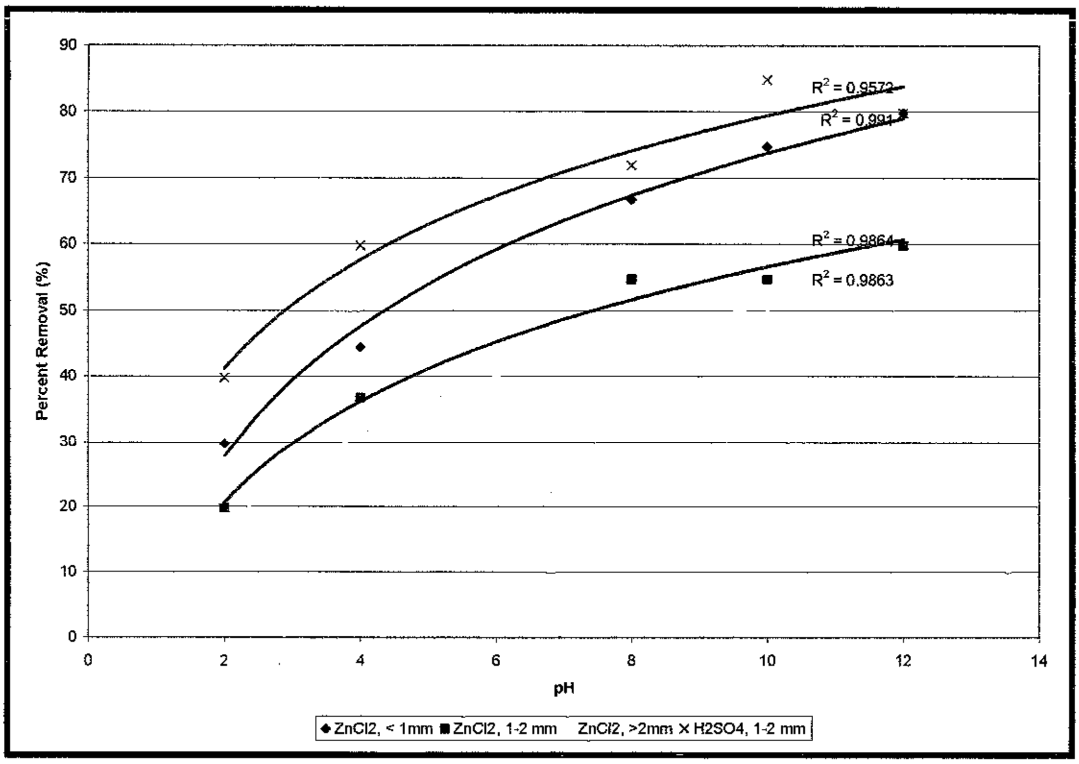

Figure 4.12 Effect of pH of Copper Solution on the Adsorption Capacity on Activated Carbon Produced (Carbonization Time=1 hr, Carbonization Temperature = 500°C)

4.4 Study of Adsorption Isotherm

In order to facilitate the estimation of the adsorption capacities at various conditions, Langmuir adsorption isotherm was used for fitting the adsorption data into the model. For the development of adsorption isotherm, three activated carbons were selected which are the activated carbon at particle size <1mm and 1-2mm and >2mm and were activated with sulfuric acid (H_2SO_4) and sodium hydroxide (NaOH) and carbonized for 1 hour at 500°C.

Langmuir isotherm is a typical model for monolayer adsorption which is based on a kinetic principle that is the rate of adsorption (which is the striking rate at the surface multiplied by a sticking coefficient, sometimes called the accommodation coefficient) is equal to the rate of desorption from the surface. The linearized Langmuir model can be written as

$$\frac{1}{q_e} = \frac{1}{Q_m} + \frac{1}{bQ_m} - \frac{1}{C_e} \qquad \text{Eq. 4.3}$$

where q_e is the amount (mg) of copper per gram of activated carbon adsorbed at equilibrium, C_e is the concentration (mg/l) of copper in solution at equilibrium, Q_m (mg/g) and b $(mg/\ l)^{-1}$ are the Langmuir constants, representing the maximum adsorption capacity for the solid phase loading and the energy constant related to the heat of adsorption, respectively (Banat et al., 2003). The constants Q_m and b can be evaluated from the intercept and the slope of the linear plot of the experimental data of $1/q_e$ versus $1/C_e$, respectively.

Figure 4.13 shows a linear relationship of $1/q_e$ versus $1/C_e$ for the adsorption of copper ions on activated carbon produced, suggesting the applicability of the Langmuir model. The Langmuir constants that can be obtained form the graph is shown in Table 4.8. The maximum adsorption capacity, Q_m, indicates that activated carbon produced by activating with NaOH at particle size <1mm is a superior adsorbent. It is then followed by the activated carbon produced with NaOH at particle size 1-2mm, Activated carbon produced with H_2SO_4 at particle size <1mm and lastly the activated carbon produced with H_2SO_4 at particle size 1-2mm. The high adsorption capacity can be attributed to the high surface area of the activated carbon and also widening of the micropores in the presences of the NaOH that an increase of the pore volume can be assumed.

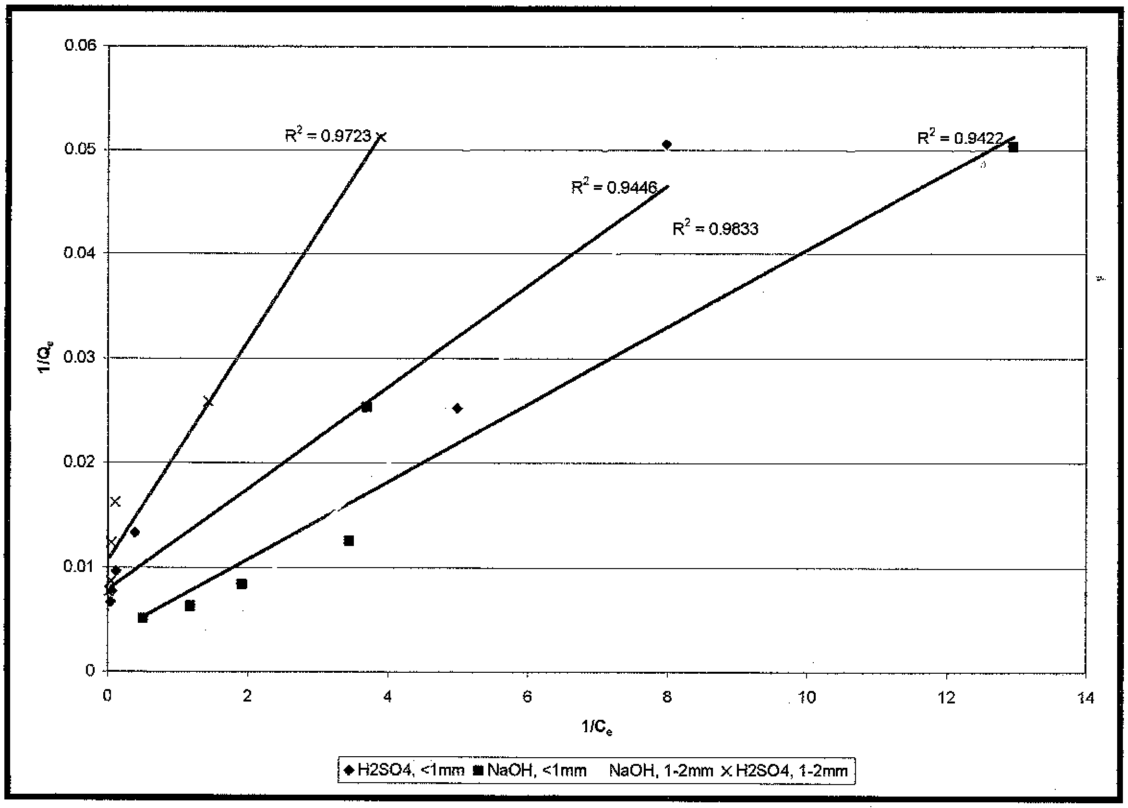

Figure 4.13 Langmuir Isotherm on the Adsorption Process of Activated Carbon Produced from H_2SO_4 and NaOH at Carbonization Time = 1 hr, Carbonization Temperature = 500°C

Table 4.8 Langmuir Constant for the Adsorption of Copper ion on Activated Carbon Produced at Various Sizes with Activating Agent H2SO4 (Carbonization Time =1 hr, Carbonization Temperature = 500°C)

Adsorbent	Q_m (mg/g)	b $(mg/l)^{-1}$	R_2
H_2SO_4, < 1mm	126.58	1.646	0.9446
H_2SO_4, 1-2mm	93.46	1.019	0.9723
NaOH, <1mm	294.12	0.919	0.9422
NaOH, 1-2mm	212.77	0.758	0.9833

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

The utilization of waste palm oil shells as the raw material for production of activation carbon for heavy metal removal was proven to be workable. In addition to that, various parameters affecting the adsorption capacity on different heavy metal concentration and pH in industrial wastewater were studied. From the experimental work, the best activation agent for production of high quality adsorbent was NaOH and then followed by he sequence H_2SO_4 > $ZnCl_2$ > $CaCl_2$ whereas the best adsorption capacity of copper ion from wastewater was the activated carbon produced from particle size < 1mm and then followed by particle size 1 – 2 mm and > 2mm. The maximum adsorption capacity for the activated carbon produced from NaOH activation at particle size < 1mm was the highest among others, 196.06mg/g. As discussed before, the carbonization time that produced superior adsorption capacity's activated carbon is at 3 hr. in addition to that, the higher the carbonization temperature, the better the adsorption capacity on the metal ion removal. The activated carbon prepared by carbonization first and then activation showed a higher adsorption capacity than the activated carbon produced by activation first and then carbonization. From the adsorption study, the best conditions of industrial wastewater for removal of copper ions were at pH 10 and 10ppm. The adsorption isotherm that fit the adsorption characteristics of the activated carbon produced by activating with H_2SO_4 and NaOH is Langmuir Isotherm. From the Langmuir Isotherm, the maximum adsorption capacity for the activated carbon can be determined. The maximum adsorption capacity for the activated carbon activated by H_2SO_4 at < 1mm was 126.58 mg/g and for the particle size 1-2mm was 93.46 mg/g.

5.2 Recommendations

The result presented above indicate the significance of using waste palm oil shells as a starting material to produced activated carbon for wastewater treatment purposes.

This procedure, if scaled up, will eventually reduce the cost of wastewater treatment and will help Malaysia, to reduce the solid waste produced from palm oil after proceeding in the palm oil mill. Thus, some recommendations had been proposed for future work to be done:

i. The produced activated carbon can be characterized by using thermogravimetric analyzer (TGA) and AUTOSORB-I for analyzing the fixed carbon content in the activated carbon and the surface area available in the activated carbon. The availability of the surface area can further support the experimental results.
ii. Analysis of the adsorption kinetics and development of the adsorption model relating the adsorption kinetics with the performance of the activated carbon.
iii. Produce the activated carbon by varying more parameters that will affect the adsorption capacity such as the weight ratio of activated carbon to weight ratio of the activating agents.
iv. Study on the effect of the adsorption temperature on the adsorption capacity of the produced activated carbon and analyze the apparent enthalpy of the adsorption.
v. Study on the effect of adsorption time on the adsorption characteristics of the produced activated carbon and evaluation of the equilibrium concentration of copper solution and equilibrium time.

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APPENDIXES

Appendix I: Brunauer's Five Types of Adsorption Isotherm

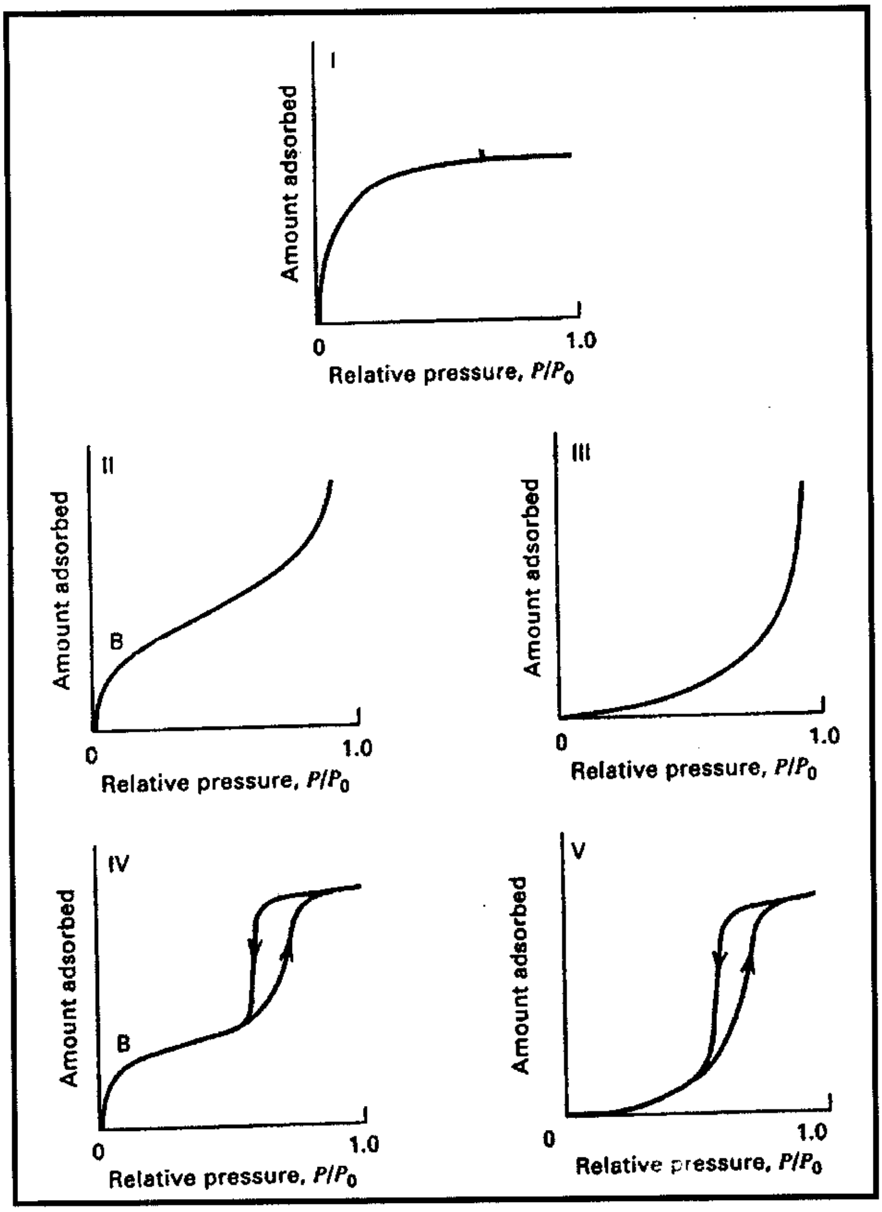

Figure A-1 Brunauer's Five Types of Adsorption Isotherm (Source: Separation Process Principles, Seader and Henley, John Wiley and Sons)

Appendix II: Structures and Pore Size Distribution of Activated Carbon

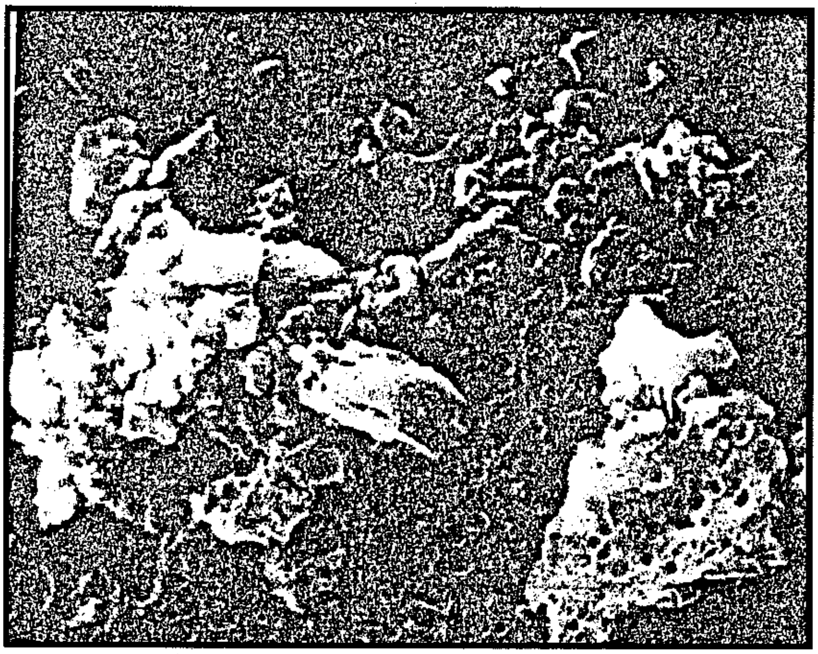

Figure A-2 Scanning Electron Photomicrograph of an Activated Carbon Surface showing Highly Developed Porosity in the Macroporous Range (Source: Activated Carbon, Surface Chemistry and Adsorption from Solution, Mattson and Mark, Marcel Dekker, Inc.)

Figure A-3 Scanning Electron Photomicrograph of A relatively "nonmacroporous" Carbon Granule (Source: Activated Carbon, Surface Chemistry and Adsorption from Solution, Mattson and Mark, Marcel Dekker, Inc.)

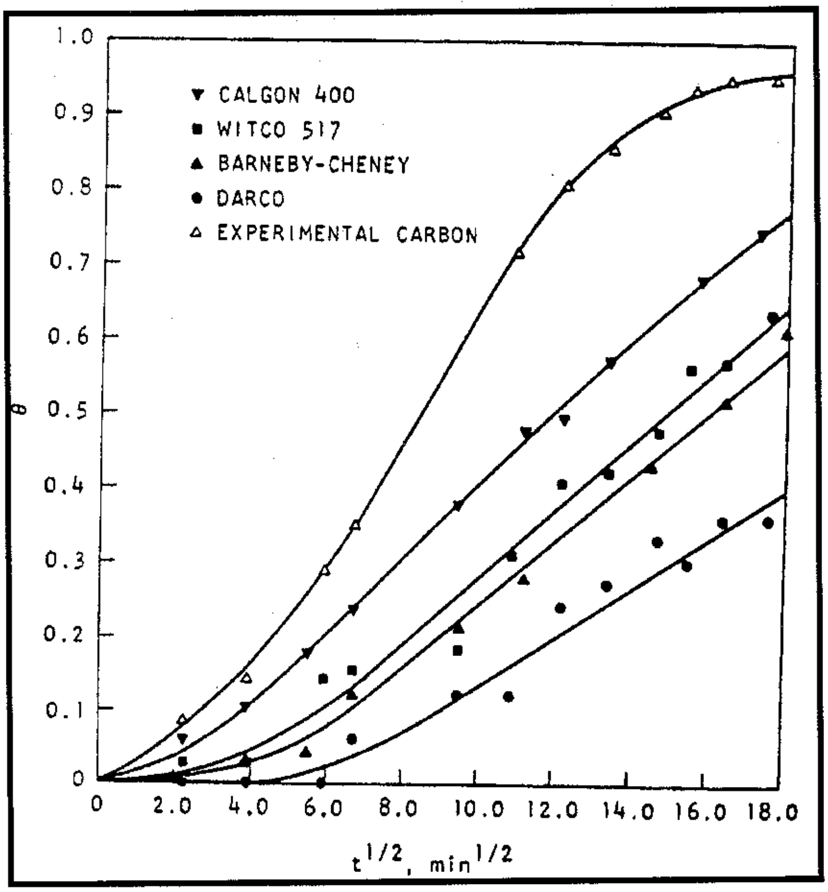

Figure A-4 Diffusion-limited Uptake of p-nitrophenol by 16 x 20-mesh Granular Activated Carbons (Source: Activated Carbon, Surface Chemistry and Adsorption from Solution, Mattson and Mark, Marcel Dekker, Inc.)

Appendix III: Calibration Curve from AAS

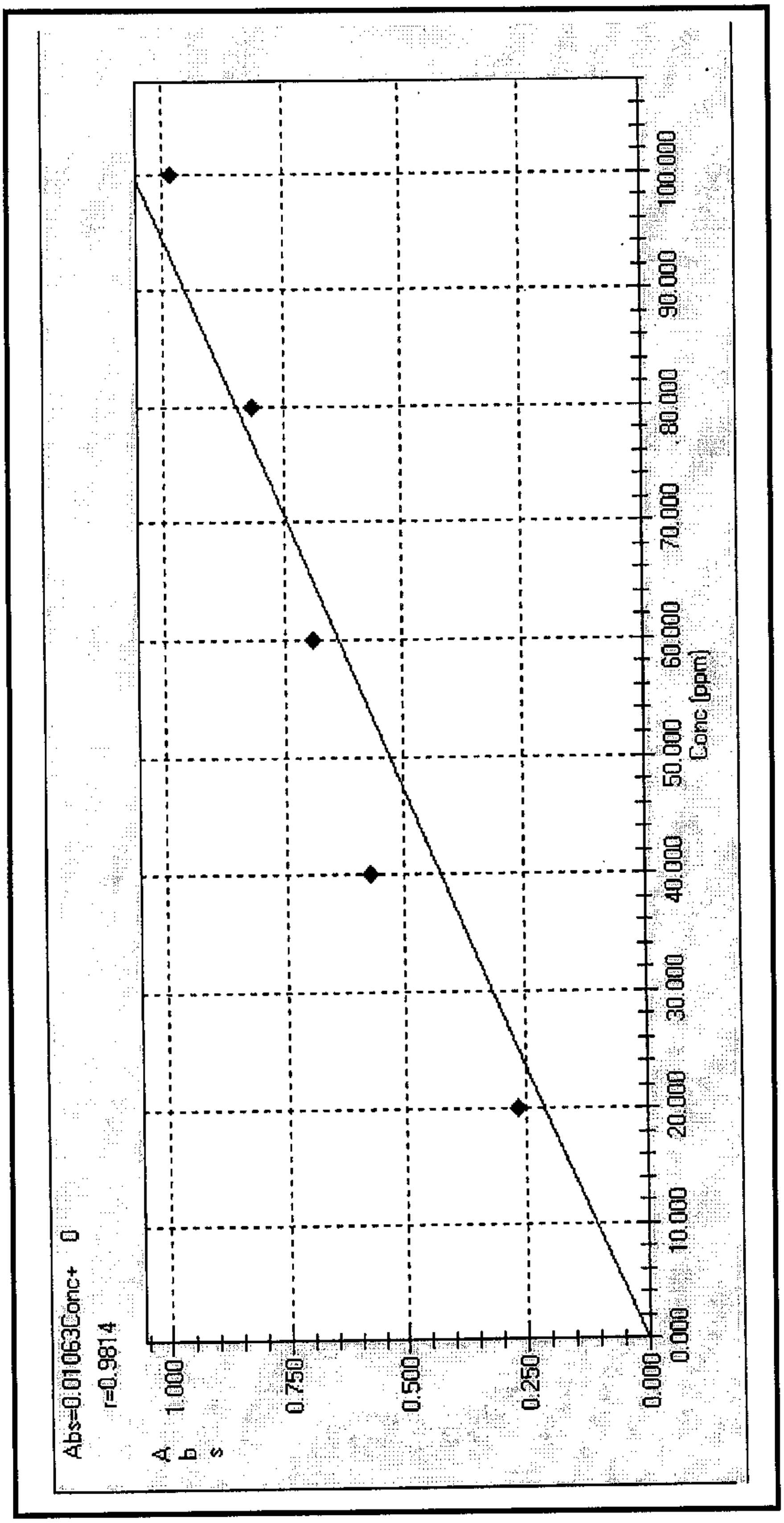

Figure A-5 Calibration Curve Obtained from AAS

Appendix IV: Calibration Curve Obtained from Conductivity Meter

a. pH 2

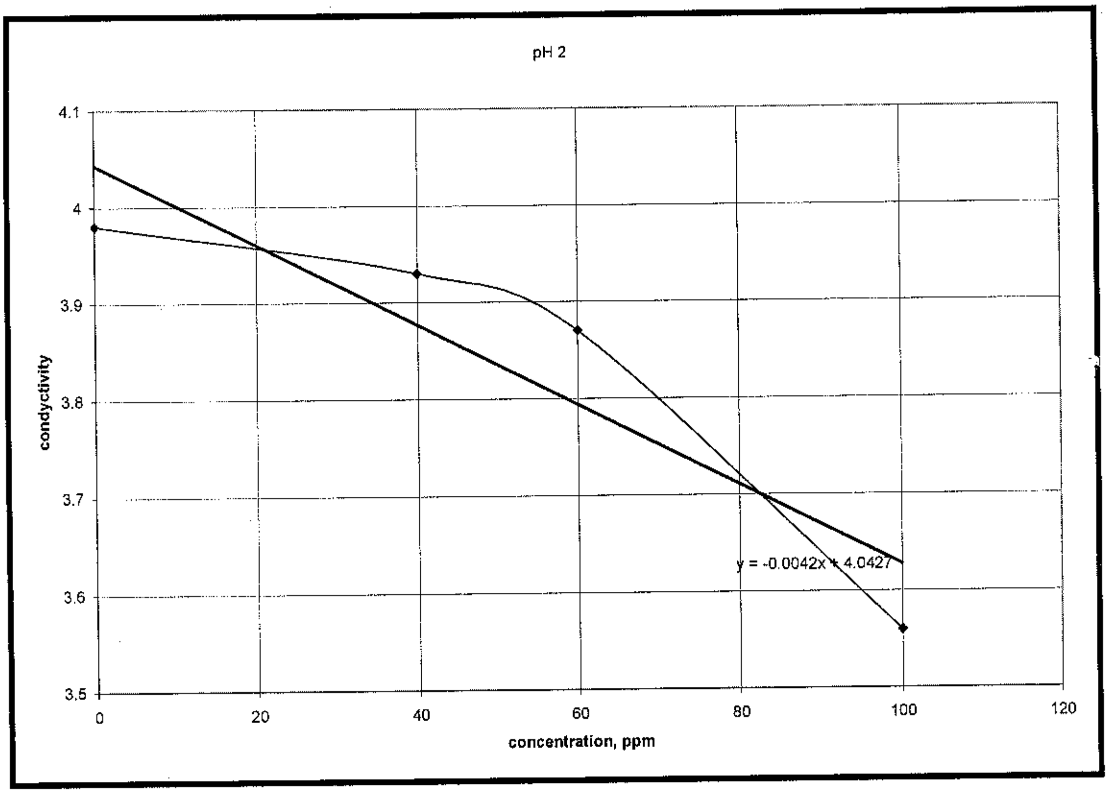

Figure A-6 Calibration Curve at pH 2 from Conductivity Meter

b. pH 4

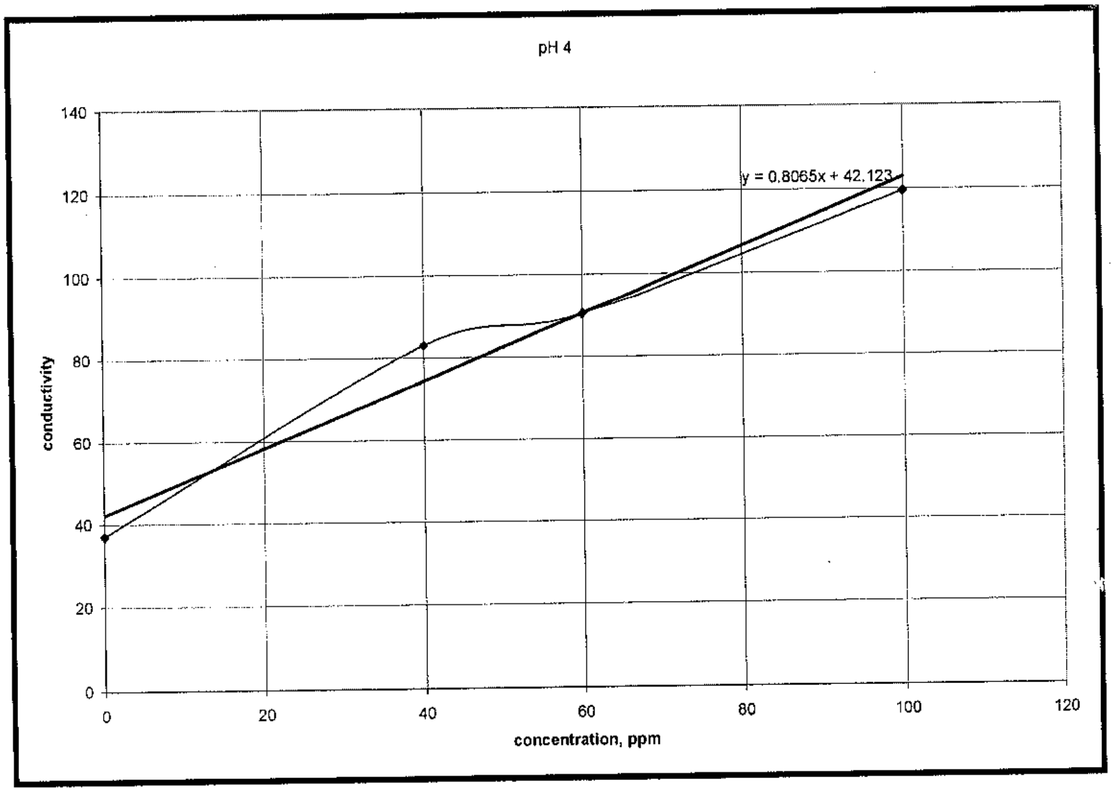

Figure A-7 Calibration Curve at pH 4 from Conductivity Meter

c. pH 8

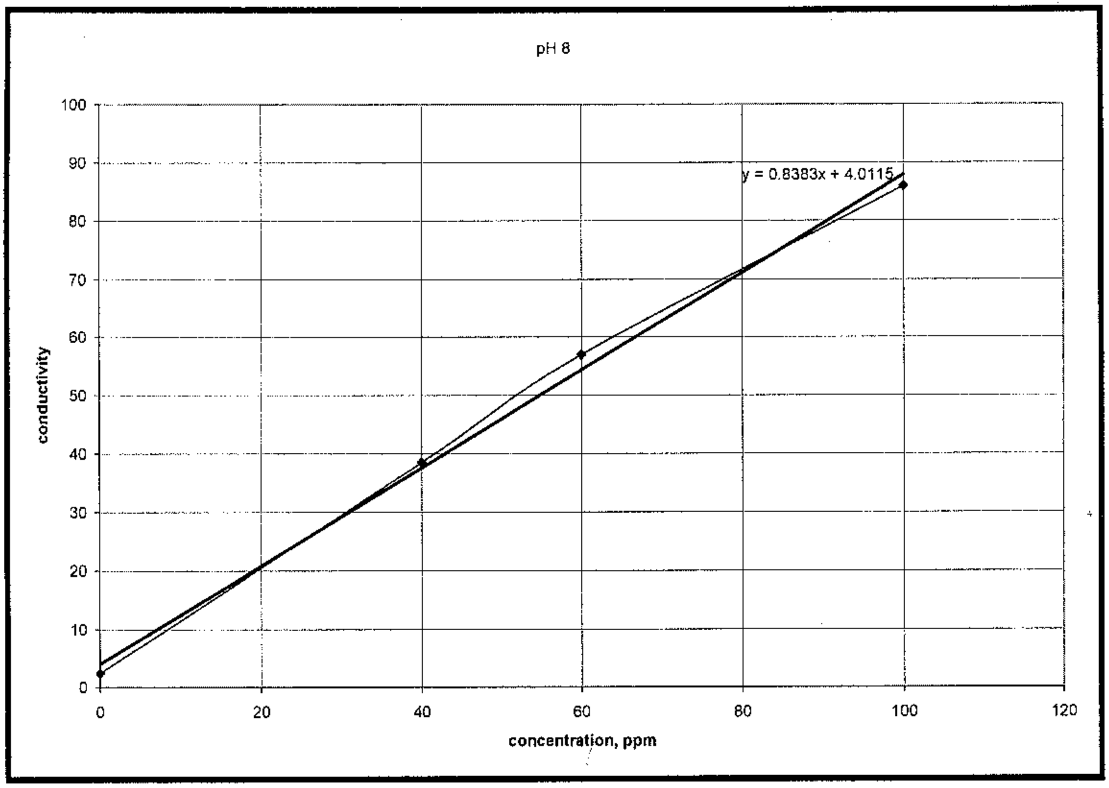

Figure A-8 Calibration Curve at pH 8 from Conductivity Meter

d. pH 10

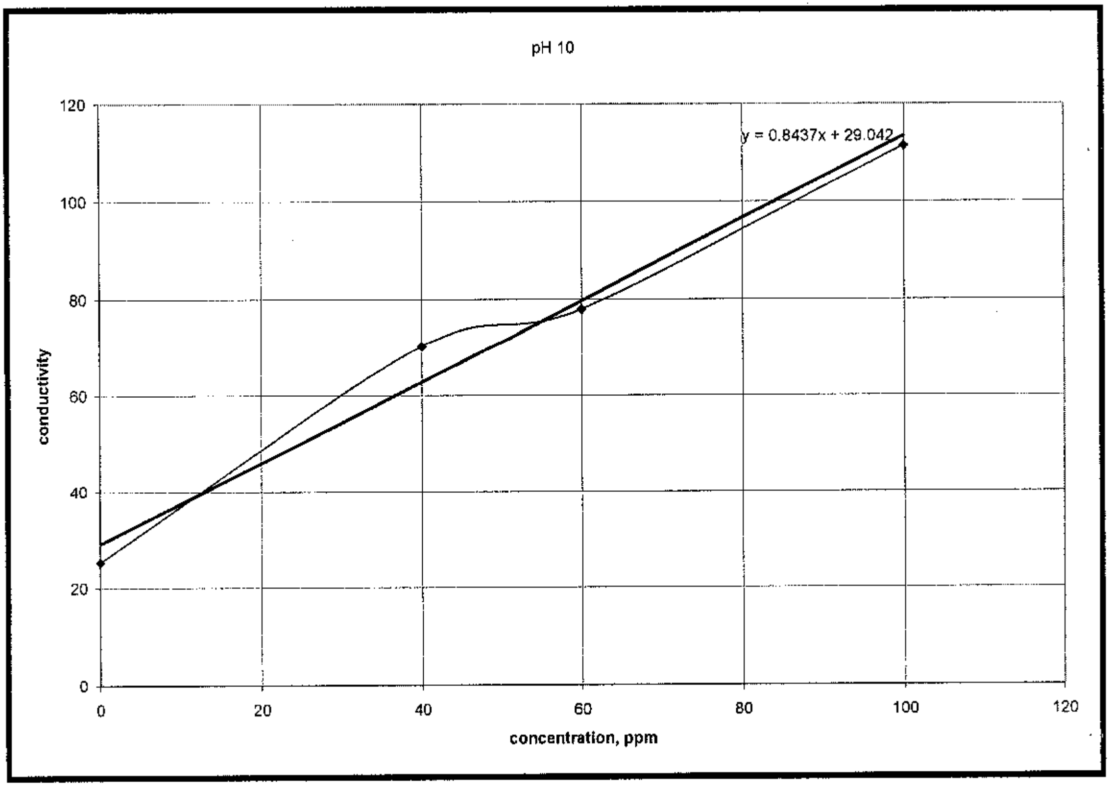

Figure A-9 Calibration Curve at pH 10 from Conductivity Meter

e. pH 12

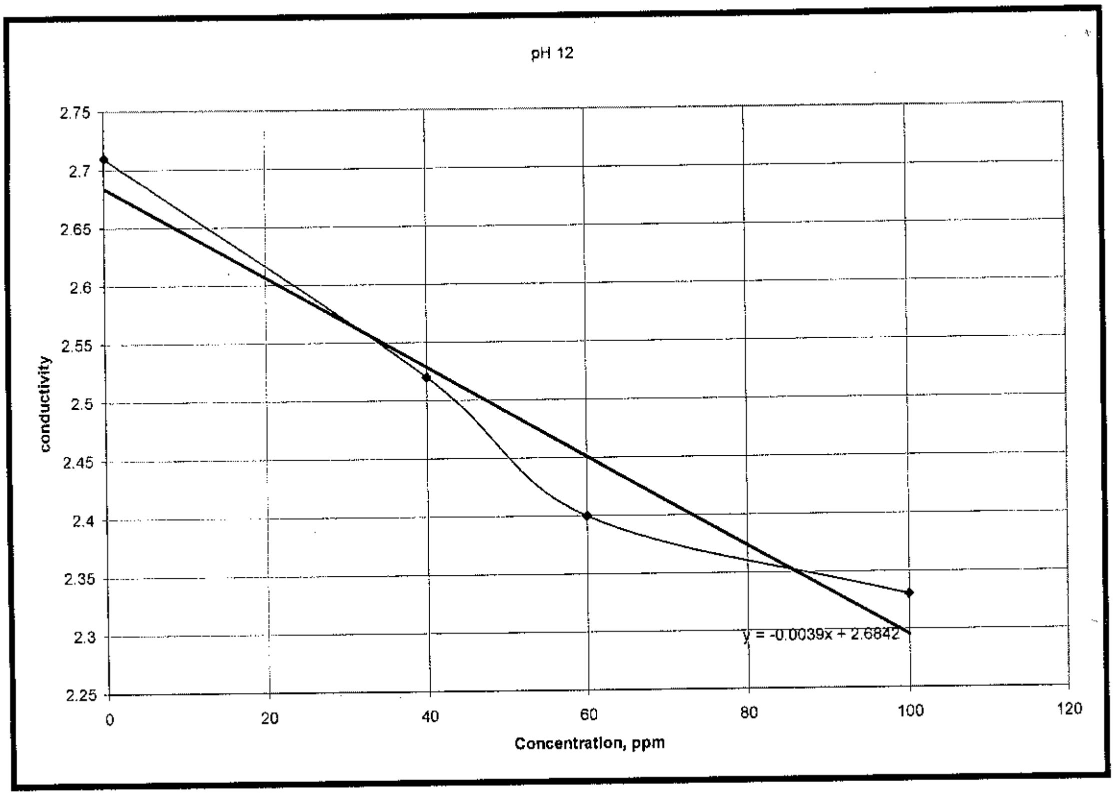

Figure A-10 Calibration Curve at pH 12 from Conductivity Meter

f. Varies Concentration

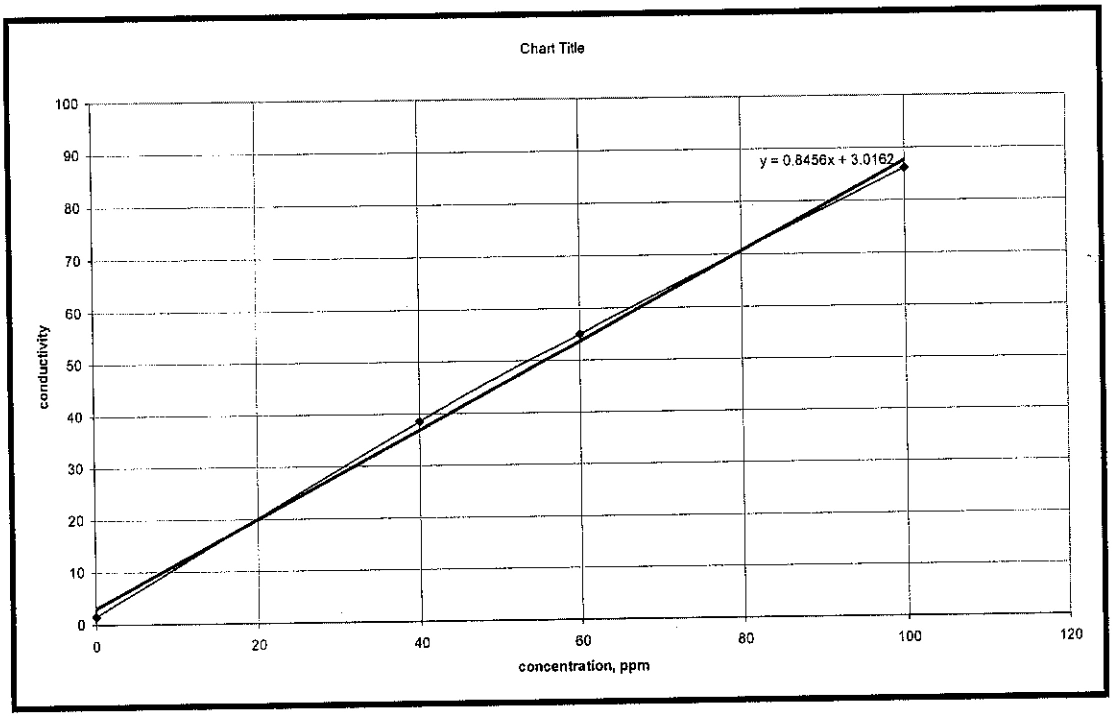

Figure A-11 Calibration Curve at Various Concentration for Copper Solution

Appendix V: Calibration Curve for Estimating the Surface Area

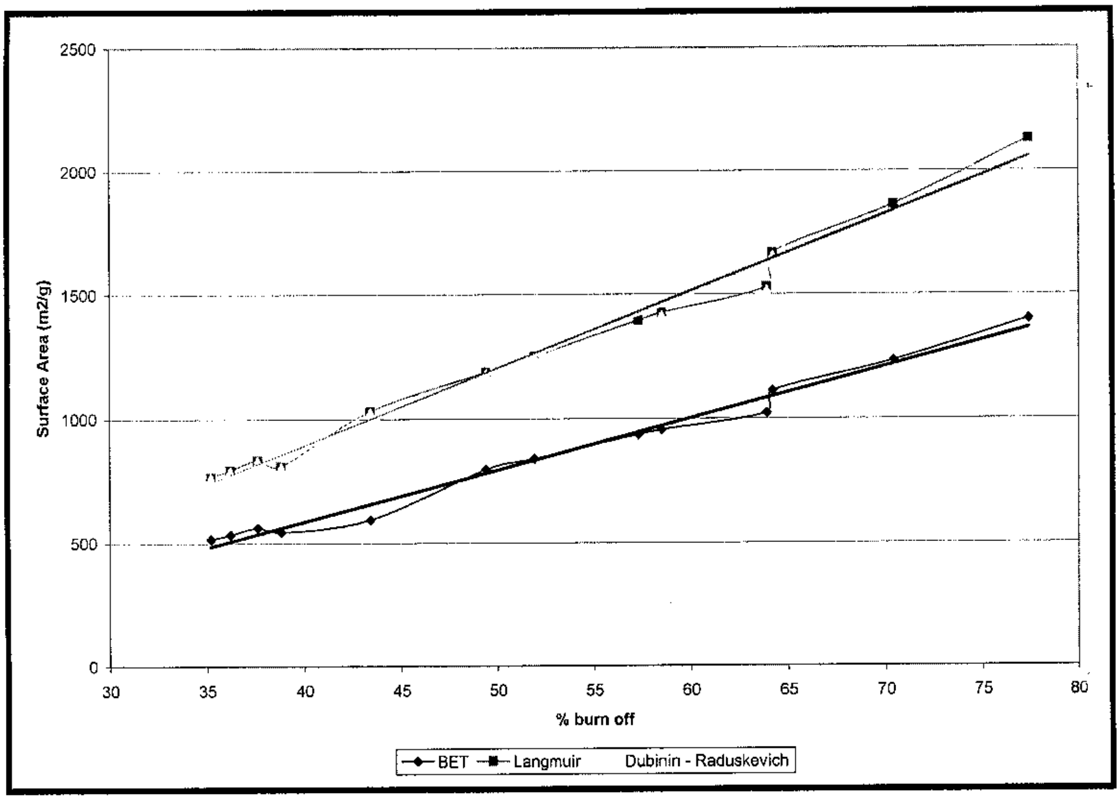

Figure A-12 Calibration Curve for Estimating Surface Area of Activated Carbon Produced (Source Data: Daud et al., 2002)

Appendix VI: Relationships of the pore volumes towards the % Burn-Off

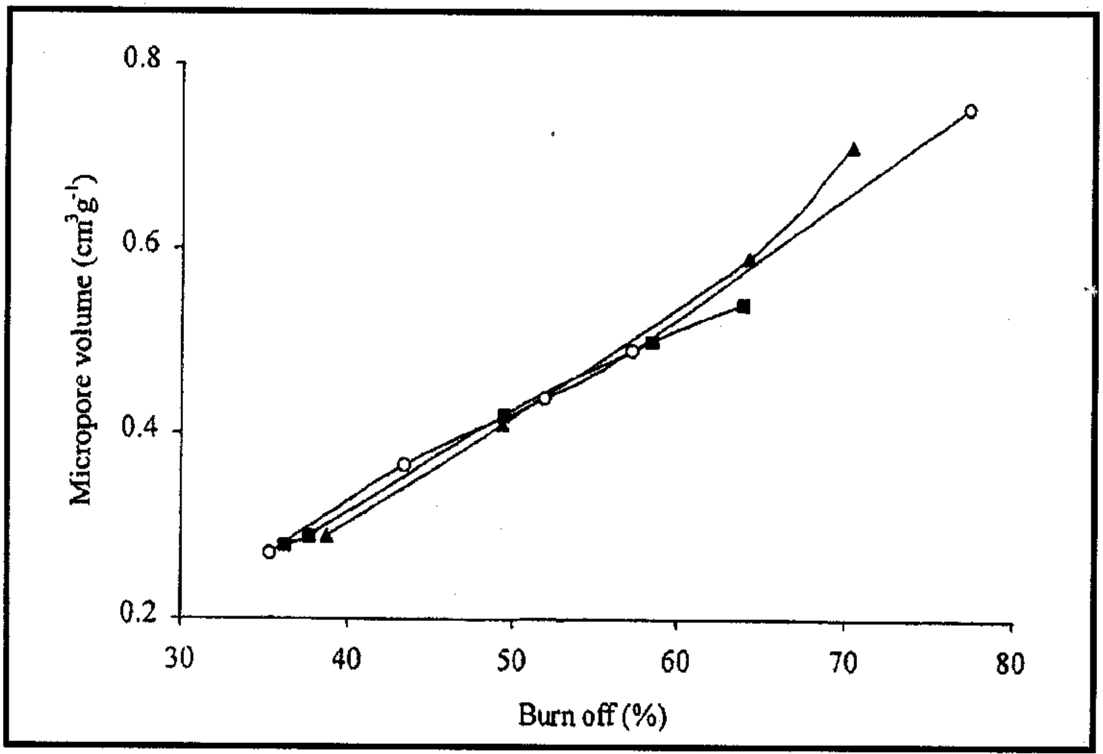

Figure A-13 Effects of the % Burn- Off on the Micropore Volume Development (Source: Daud et al., 2002)

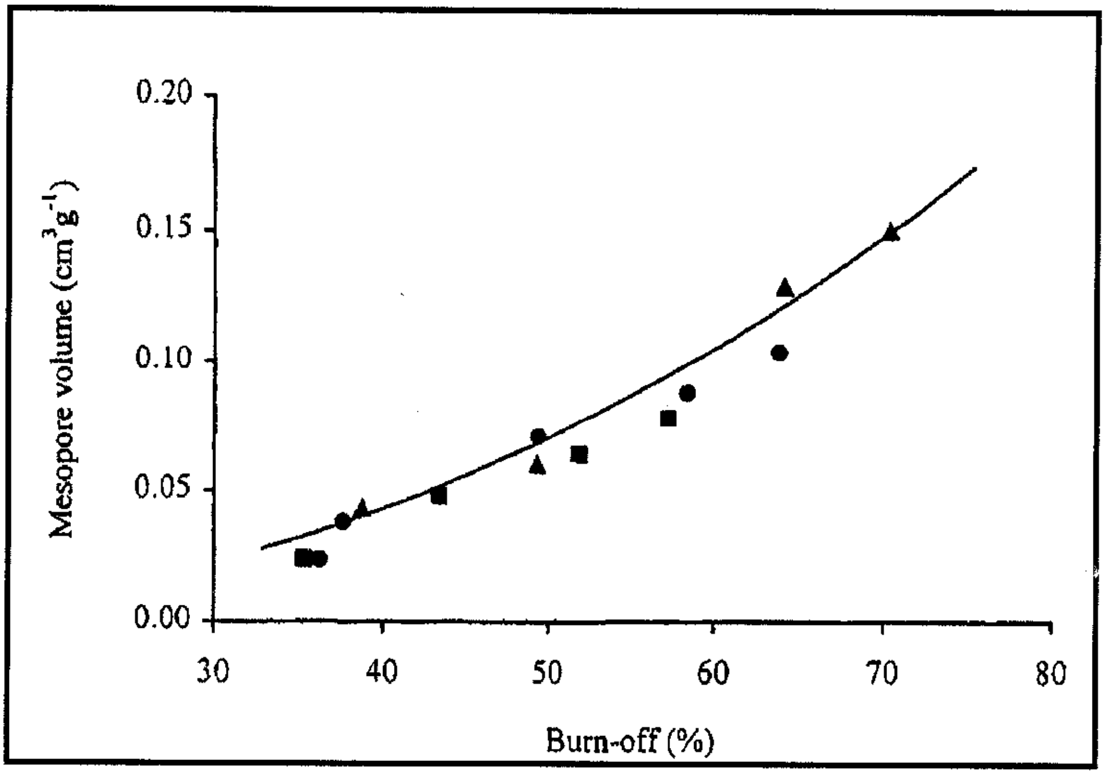

Figure A-14 Effects of the % Burn- Off on the Macropore Volume Development (Source: Daud et al., 2002)

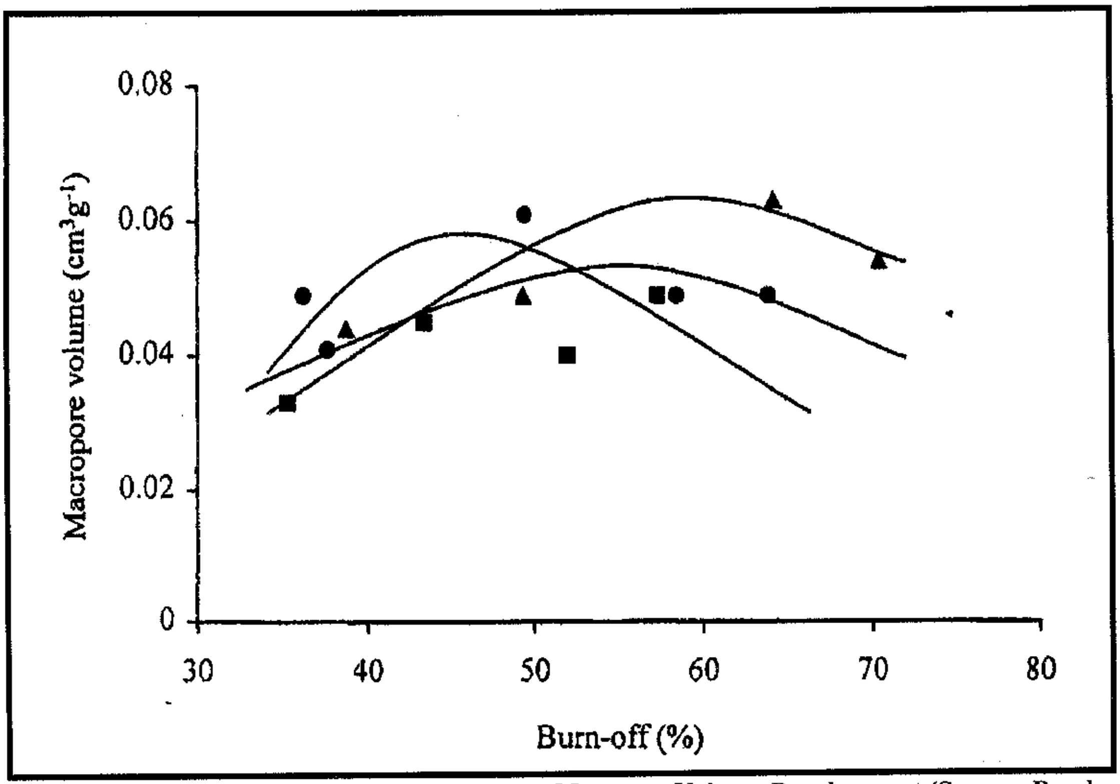

Figure A-15 Effects of the % Burn- Off on the Mesopore Volume Development (Source: Daud et al., 2002)

Appendix VII: Results Obtained on the Effect of Particle Sizes on the Adsorption Capacity

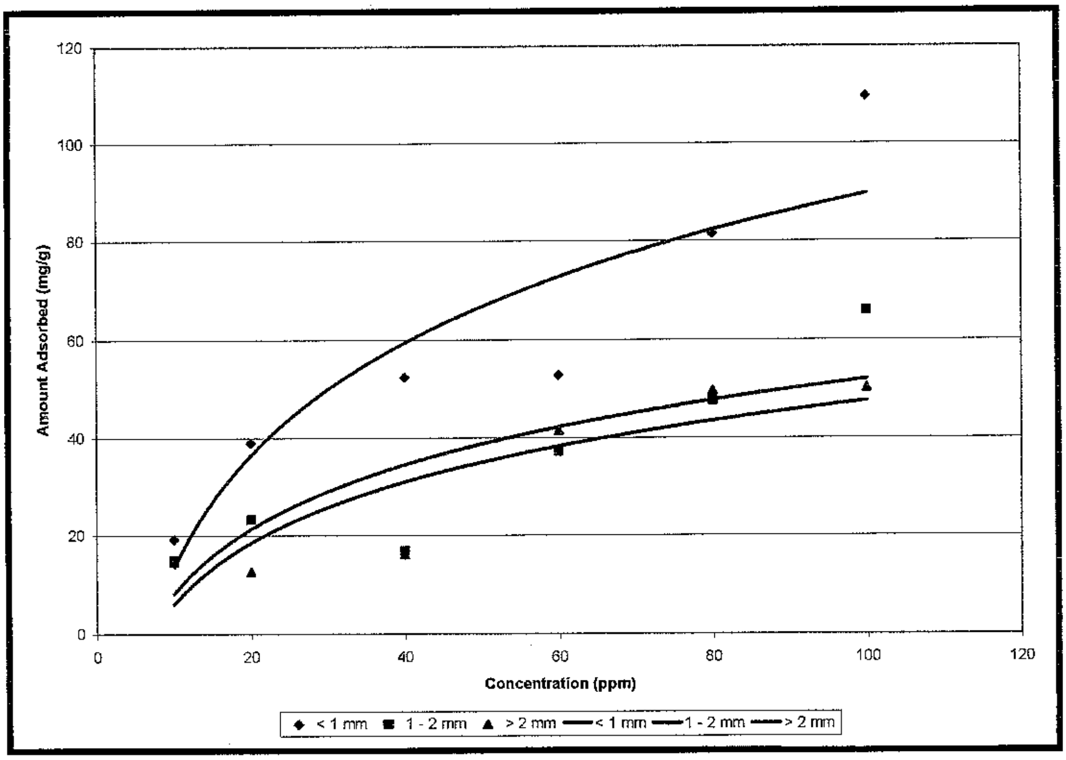

Figure A-16 Effects of Different Particle Sizes on the Adsorption Capacity of Copper 2+ on Activated Carbon Produced (Activating Agent = $CaCl_2$, Carbonization Time = 1 hr, Carbonization Temperature = 500°C)

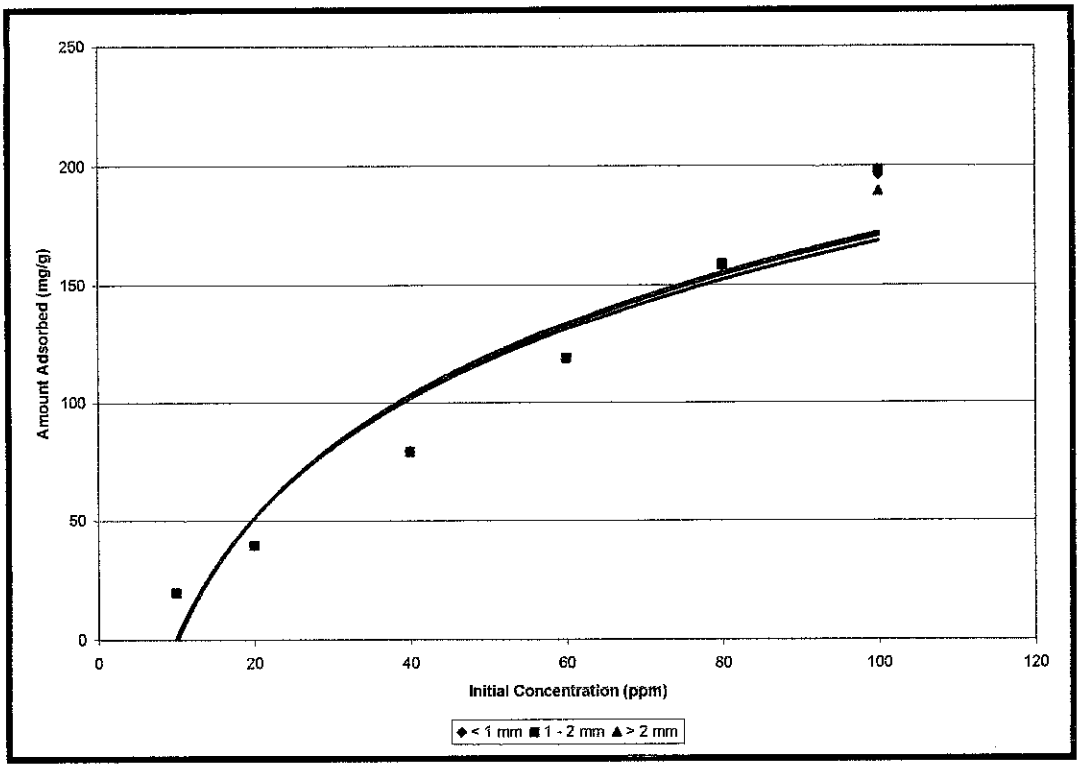

Figure A-17 Effects of Different Particle Sizes on the Adsorption Capacity of Copper 2+ on Activated Carbon Produced (Activating Agent = NaOH, Carbonization Time = 1 hr, Carbonization Temperature = 500°C)

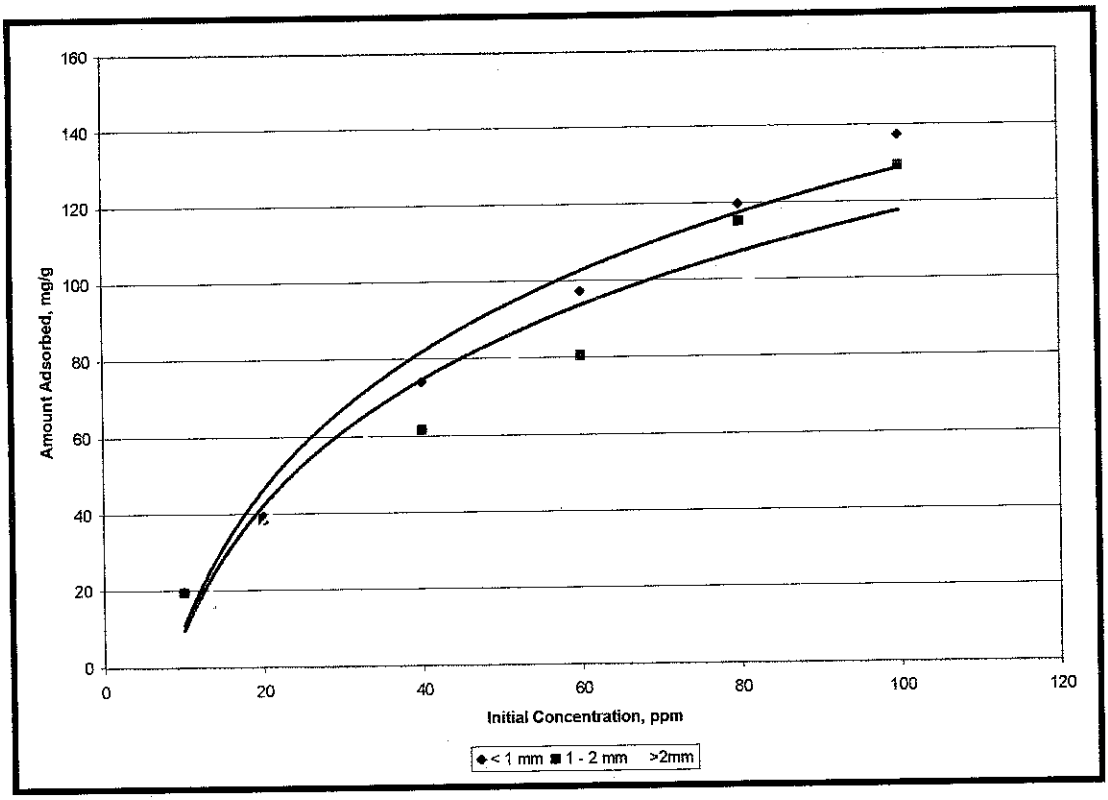

Figure A-18 Effects of Different Particle Sizes on the Adsorption Capacity of Copper 2+ on Activated Carbon Produced (Activating Agent = H_2SO_4, Carbonization Time = 1 hr, Carbonization Temperature = 500°C)