CERTIFICATION OF APPROVAL

Production of Granular Activated Carbon from Waste Palm Oil Shells and Its Adsorption Characteristics for Cu^{2+}

by

Nor Zalina Zamri

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(Khalik M Sabil)

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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 the original work contained herein have not been undertaken or done by unspecified sources of persons

NOR ZALINA ZAMRI

ABSTRACT

The utilization of waste palm oil shells as activated carbons has been proven reliable and environmental friendly. The study emphasized on the preparation of activated carbons from the abundant waste of palm oil shells and their ability to adsorb heavy metals in synthetic wastewaters. Waste palm oil shells were grinded and sieved before going for carbonization and chemical activation. Carbonization temperature was within the range of 700°C to 900°C for and carbonization goes for 3 hours. Sodium hydroxide as the chemical activation agent was varied at the range concentration of 0.05M to 0.15M. For adsorption process purposes, the produced activated carbons were tested at different copper solutions concentrations (50ppm, 100ppm and 200ppm), copper solutions pH (pH3, pH7 and pH12) and loading ratio (0.5g, 1.0g and 1.5g in 100mL of copper solutions) to study their adsorption capacity. From the study, it can be observed that at higher carbonization temperature, the better the adsorption will be. The pore volume of the activated carbon increases at higher temperature due to excessive vaporization in shells. Activated carbon activated at lower concentration of sodium hydroxide, 0.05M, is a superior adsorbent due to much larger external surface area. The best conditions for removal of copper ions are at 200ppm and pH 12. In addition, adsorption process at higher loading gives the most adsorption capacity. For the development of adsorption isotherm, the activated carbons suited with Freundlich isotherm instead of Langmuir isotherm.

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CHAPTER 1
INTRODUCTION

1.1 Background of Study

Palm oil shells are an abundant agricultural solid waste from palm oil processing mills in tropical countries such as Malaysia [Guo, 2001]. It is estimated that a total of 42 tonnes of Fresh Fruit Bunches (FFB) were produced in 1995 [ASEAN COGEN, 2000].FFB contain approximately 21% palm oil and 6-7% palm kernel. The resulting waste together with fiber and shells amounts to 42% of the FFB and would translate to a total waste volume of over 17 million tones of waste. Thus, the employment of waste palm oil shells as a raw material to produce activated carbon is a useful recycling process.

Activated carbons can be produced from a number of precursor materials including almond shells [Toles et al, 2000], macadamia nutshells [Ahmadpour et al, 1997], pecan shell [Ng et al, 2002], walnut shells [Hu et al, 1994], waste corn cob [Tsai, 2000], chickpea husk [Hayashi et al, 2002] and etc. The activated carbon is used widely and favored as absorbents for adsorption of pollutant removal process.

Activated carbon is especially known for its effectiveness in removing organic chemicals from water and wastewater; it is also surprisingly effective in removing a variety of inorganic pollutants. Though the effective adsorption of inorganic constituents would not necessarily be predicted by the chemistry of activated carbon, low levels of these chemicals can be removed effectively, primarily due to physical adsorption mechanism. Applications for this process can be found in water and waste water engineering, metallurgy and analytical chemistry. It has shown to absorb a variety of metal and organic species in various processing wastewaters [Ng et al, 2002]. Adsorption process has been the favored process due to its economic and reliability aspect. Basically, this research project emphasis the removal of Cu^{2+} ion, as heavy metal ions, in wastewater by using the manmade palm oil shells activated carbon.

1.2 Problem Statement

1.2.1 Problem Identification

The production cost of the commercial activated carbon has increases. Thus, the interest is growing in the use of other low cost materials as a material for preparation of activated carbon. The adsorption capacity of activated carbon from palm oil shells suggests the process is potentially commercializable [Kim et al, 2001]. Furthermore, the usage of waste palm oil shells is much more economic due to its availability in Malaysia. Copper is a ubiquitous metal mostly in manufacturing wastewaters [Toles et al, 1996]. Being in the group of heavy ions, it can pose health hazards if the concentration exceeds the allowable limits. Metal contamination is a dangerous cause of wastewater pollution indeed Cu^{2+} ions are essential nutrients, but when people are exposed to Cu levels of above 1.3mg/l for short period of time, stomach and intestinal problems occur. Long term exposure to Cu^{2+} leads to kidney and liver damage [Molinari, 2003]. The allowable limits for trade effluent discharge to sewer/watercourse and controlled watercourse is presented in Table 1[National Environment Agency, 2002].

The most common applied chemical treatment method for controlling metal toxicants are precipitations as hydroxides, carbonates or sulphides, sorption (adsorption, ion exchange), membrane process, electrolytic recovery, liquid-liquid extraction and flotation. [Dorda, 2003]. The contaminant problems have raised health and environmental concern and needed to be overcome. The study covered the adsorption of the copper ion using the activated carbon used from the waste palm oil shells and it releventality.

Table 1: Table of Allowable Limits for Trade Effluent Discharge to Sewer, Watercourse and Controlled Watercourse [http://app.nea.gov.sg]

Items of Analysis	Sewer	Watercourse	Controlled Watercourse
	(Units of milligram per liter or otherwise stated)		
1. Temperature of discharge	45°C	45°C	45°C
2. Colour	-	Lovibond	Lovibond
3. pH value	6-9	6-9	6-9
4. BOD (5 days at 20°C)	400	50	20
5. COD	600	100	60
6. Total Suspended Solids	400	50	30
7. Total Dissolved Solids	3000	2000	1000
8. Chloride (chloride ion)	1000	500	200
9. Sulphate (SO_4)	1	0.2	0.2
10. Sulphide (sulphur)	1	0.2	0.2
11. Cynide (CN)	2	0.1	0.1
12. Grease and oil	60	10	5
13. Arsenic	5	1	0.05
14. Barium	10	5	5
15. Tin	10	10	5
16. Iron (Fe)	50	20	1
17. Beryllium	5	0.5	0.5
18. Boron	5	5	0.5
19. Manganese	10	5	0.5
20. Cadmium	1	0.1	0.01
21. Chromium	5	1	0.05
22. Copper	5	0.1	0.1
23. Lead	5	0.1	0.1
24. Mercury	0.5	0.05	0.001
25. Nickel	10	1	0.1
26. Selenium	10	0.5	0.01
27. Silver	5	0.1	0.1
28. Zinc	10	1	0.5
29. Metals in total	10	1	0.5
30. Chlorine (free)	-	1	1
31. Phosphate (PO_4)	-	5	2
32. Calcium (Ca)	-	200	150
33. Magnesium	-	200	150

1.2.2 Significant of the Study

The findings of the study can help the industry to realize the ability to convert waste to useful material. It also enhances the knowledge on the related area. The university would be the owner for all findings, design, patents and other intellectual property rights.

1.3 Objective and Scope of Study

The study has several purposes that are

- to produce activated carbon from waste palm oil shells by chemical activation using sodium hydroxide as the chemical activation agent
- to analysis the raw materials and activated carbon using ultimate analysis (C,H,N, S meter)
- to study the effect of carbonization temperature and chemical activation agent concentration during the production of activated carbon
- to study the efficiency of the activated carbon produced to adsorb Cu^{2+} ions. The adsorption characteristics includes the adsorption capacity at different pH, loading ratio and concentration

The scope of work for the study was to evaluate the suitability of waste palm oil shells to produce activated carbon by manipulating the operating parameters such as carbonization temperature and chemical activation agent concentration. Activated carbon produced was evaluated in term of their performance of to adsorb Cu^{2+} ions from synthetic wastewaters at various copper concentrations, copper solutions in various pH and various loading ratio. Finally, adsorption isotherm was fitted in Langmuir and Freundlich isotherm. The area and scope of project was narrowed down so that the project is feasible and could be completed within the allocated time frame.

1.3.1 Relevancy of the Study

The study gives some incites in evaluating the suitability of waste palm oil shells as activated carbon to adsorb metal ions in wastewaters. Recycling the abundant solid waste of palm oil shells is more economical than producing commercial ones. Thus, this give benefits to Malaysia since they are reliable and also environmental friendly.

1.3.2 Feasibility of the Research Project within the Scope and Time Frame

The Gantt chart represents the time allocated in fulfilling the research project. It helps the student to keep track research activity in order to complete the study in time. The study activities include the analysis, data collection, practical and laboratory work and also technical report writing. The Gantt chart is presented in the appendix as Appendix A.

CHAPTER 2

LITERATURE REVIEW AND THEORY

2.1 Activated Carbon

2.1.1 History of Activated Carbon

The use of carbon extends so far back into history that its origin is impossible to be documented. Charcoal was used for drinking water filtration by ancient Hindus in India and carbonized wood was used as a medical adsorbent and purifying agent by the Eqyptians as early as 1500D.C [www.cee.vt.edu].

Modern development and use has been documented more precisely. Activated carbon was first generated industrially at the first part of the twentieth century, when carbon activated from vegetable material was produced for use in sugar refining. Powdered activated carbon was first produced commercially in Europe in the early 19th century, using wood as a raw material. This carbon found widespread use in the sugar industry. In the United States, the first production of activated carbon used black ash as the source, after it was accidentally discovered that the ash was very effective in decolorizing liquids. Activated carbon has since been used extensively for this purpose in many industries. In particular it has been commonly used for the removal of organic dyes from textile wastewaters.

The first documented use of activated carbon in a large scale water treatment application was in 19th century England, where it was used to remove undesirable odors and tastes from drinking water. Use in the United States for similar purposes closely followed. In recent years, the use of activated carbon for the removal of priority organic pollutants has become very common. Today, hundreds of brands of activated carbon are manufactured for a large variety of purposes.

2.1.2 Raw Material

Activated carbon is one of the most widely employed adsorbents [Kim et al, 2001]. Activated carbon is produced from a wide variety of carbon rich raw materials, including wood, coal, peat, coconut shells, nut shells, bones and fruit stones. New materials are currently under investigation as source for activated carbon. Almost any organic matter with a large percentage of carbon could be theoretically being activated to enhance its sorptive characteristics. In practice, however, the best materials to be selected for activated carbon produced must have a minimum amount of organic material, long storage life, suitable hardness to maintain their properties under usage conditions, maybe obtained at low cost and obviously are capable of producing a high quality activated product when processed.

The use of a particular raw material as a source of activated carbon is limited by the supply of that material. Thus, wood (at 130000 tons/year) is by far the most common source of activated carbon, followed closely by coal (100000 tons); coconut shell (35000 tons) and peat (35000 tons). In practice, coal and agriculture by products or lignocelluloses materials are the two main sources for the production of commercial activated carbons [Ahmadpour et al, 1997]. The raw material from which a given activated carbon is produced often has a large effect on its porosity distribution and surface area. As a result, activated carbons produced from different raw materials may have much different adsorbent qualities. Table 2 sums up some of the differences between raw materials used. It should be noticed that nutshells, including coconut shells and pecan shells, produce activated carbons with high micropore volumes. Carbonaceous adsorbents have been found to be particularly useful due to their good kinetic properties, high adsorption capacities and relative ease of their regeneration

94]. These carbons are very adsorbent but quantities of these raw materials are much more limited than coal or wood.

Table 2: Differences between Raw Material Used [Hu et al, 1994]

Raw Material	Density(kg/L)	Texture of AC	Applications
Soft wood	0.4-0.5	Soft, large pore volume	Aqueous phase adsorption
Nutshells	1.4	Hard, large micropore	Vapor phase adsorption
Hard coal	1.5-1.8	Hard, large pore volume	Gas vapor adsorption
Lignite	1.00-1.35	Hard, small pore volume	Wastewater treatment

2.1.3 Characteristics of Activated Carbon

The effectiveness of activated carbon as an adsorbent is attributed to its unique properties, including "large surface area, a high degree of surface reactivity, universal adsorption effect and favorable pore size. Activated carbon is often characterized by its extremely large surface area. In fact the surface area per gram of material can range from 500 to 1400 square meters and values as high as 2500m^2/g have been reported. The complex internal surface area is usually divided into three components. Channels and pores with diameters less than 2nm are commonly known as micropores; these micropores generally contain the largest portion of the carbon's surface area. In general, microporosity in carbons is created by removal of the carbons atoms by an activation process [Castello, 2001]. On the other hand, pores with diameters between 2 and 50 nm are known as mesopores and pores with diameters greater than 50nm are defined as macropores

For comparison, a given type or sample of activated carbon is usually quantified based on four primary criteria: total surface area, carbon density, particle size distribution and adsorptive capacity. All of those factors influence adsorption rate and capacity.

- *Total surface area* is measured by the adsorption of nitrogen gas onto the carbon and is expressed in square meters of surface area per gram of carbon. Because the gas molecules used to measure adsorption are very small, it should be noted that this measurement of surface area may be misleading when considering the adsorptive capacity of a carbon for large organic macromolecules. Those types of compounds may have adsorption limited by pore size considerations. Porous carbons possess not only high surface area but also high mesoporosity [Hu, 2003]

- *Carbon density* is the weight of one milliliter of carbon in air. Bulk density is also sometimes used for carbon as it is for soil and is expressed in pounds per cubic foot or in kilograms per liter
- Particle sizes in carbons are measured using standard U.S sieve sizes, as for soil constituents. *Particles size distribution* is important in carbon systems because they influence handling of the activated carbon material. For example, in granular carbon, the particle size affects hydraulic loading and backwash rates for a filter. On the other hand, particle size is often important because of its effect on adsorption rates as well
- *Adsorption capacity* is characterized by the effectiveness of activated carbon in removing a given contaminant. For comparison, several standard compounds are used for these measurements. For example, the commonly used 'iodine number' describes the carbon's capacity to adsorb low molecular weight substances, while the molasses number characterizes a carbon capacity for more complex compounds

The structural properties of activated carbon are very important to its effectiveness as an adsorbent, through activated carbon's structure are not fully understood and are difficult to explain with text. In general, activated carbon is sometimes described as having a crumpled layered surface, in which flat sheets are broken and curved back upon themselves. This unique structure creates activated carbon's very large surface area. It can be more properly visualized with the attached images, which provide both electron microscope photos and conceptual diagrams of the surface structure [Castello, 2002]

2.2 Adsorption

2.2.1 Adsorbents for Adsorption Process

Many adsorbents have been developed for a wide range of separations. [Geankoplis, 1993]. Typically, the adsorbents are in the form of small pallets, beads or granules ranging from about 0.1mm to 12mm in size with the larger particles being used in packed beds. A particle of adsorbent has a very porous structure with many fine pores and pore volumes up to 50% of total particle volume. The adsorption often occurs as a monolayer on the surface of the fine pores. However, several layers sometimes occur. Physical adsorption or van der Waals adsorption usually occurs between the adsorbed molecules and the solid internal pore surface and is readily reversible.

The overall adsorption process consists of a series of steps in series. When the fluid is flowing past the particle in a fixed bed, the solute first diffuses from the bulk fluid to the gross exterior surface of the particle. Then the solute diffuses inside the pore to the surface of the pore. Finally, the solute is adsorbed on the surface. Hence the overall adsorption process is a series of steps. There are a number of commercial adsorbents and some of the main ones are described as below. All are characterized by very large pore surface areas of 100 to over 2000m^2/g.

a) *Activated carbon.* This is a microcrystalline material made by thermal composition of wood, vegetable shells, coal and etc and has surface areas of 300 to 1200m^2/g with average pore diameter of 10 to 60A. Organics are generally adsorbed by activated carbon
b) *Silica gel.* This adsorbent is made by acid treatment of sodium silicate solution and then dried. It has a surface of 600 to 800m^2/g and average pore diameters of 20 to 50A. It is primarily used to dehydrate gases and liquids and to fractionate hydrocarbons
c) *Activated alumina.* To prepare this material, hydrated aluminum oxide is activated by heating to drive off the water. It is used mainly to dry gases and liquids. Surface areas range from 200 to 500m^2/g, with average pore diameter of 20 to 140A

d) *Molecular sieve zeolites.* These zeolites are porous crystalline aluminosilicates that form an open crystal lattice containing precisely uniform pores. Hence, the uniform pore size is different from other types of adsorbents which have a range of pore sizes. Different zeolites have pore sizes from about 3 to 10A. Zeolites are used for drying, separation of hydrocarbons, mixtures and many the applications.
e) *Synthetic polymers or resins.* These are made by polymerizing two major types of monomers. Those made from aromatics such as styrene and divinylbenzene are used to adsorb nonpolar organics from aqueous solutions. Those made from acrylic esters are usable with more polar solutes in aqueous solutions

2.2.2 Adsorption Process

Adsorption process operates in most natural physical, biological and chemical systems. Its operation employs solids such as activated carbon and synthetic resins for industrial application and purification of wastewaters. Specifically, it is used to remove components present in low concentrations in nonadsorbing solvents or gases and to separate the components in gas or liquid mixtures by selective adsorption on solids. Certain components of a fluid phase, called solutes, are selectively transferred to insoluble rigid particles suspended in a column.

Some initial definitions are necessary for the presentation of the various processes involved in the removal of contaminants from water by sorption onto the solid phase. The general term sorption includes adsorption, the process by which a solute attached to a solid surface and absorption, the process by which the solute diffuses into a porous solid and clings to interior surfaces. When the attachment of the solute is accomplished by means of a chemical reaction with the solid, the process is called chemisorption. Cation exchange processes are basically chemical reactions between ions in solution and ions in an insoluble solid phase [Geankoplis, 1993]. Cation exchange is also included as an adsorption process, but this is usually considered to be a minor mechanism in activated carbon sorption processes. These distinctions between types of sorption are subtle, but they are useful in understanding the unusual nature of activated carbon.

Many materials can be used as sorbents, but the activated carbon is so effective primarily because of its sorbent properties. The total process of a solute diffusing through a carbon particle to attach to an inner surface is the most accurately referred to as absorption, though the actual attachment of the solute at the site is actually adsorption. For carbon the sorption process is considered primarily physical rather than chemical. It should be noted, however, that the term adsorption seems to be used rather freely to refer to sorption processes in general.

Of course, the rate at which sorption occurs can be very important when trying to remove contaminants from water. The rate of adsorption is defined as the rate at which substances are removed from the liquid phase (adsorbate) to the solid phase (adsorbent). The three main processes which control the adsorption rate: diffusion of the solute through the layer of fluid surrounding the adsorbent particle, diffusion of the solute across the surface of the adsorbent and adsorption of the solute onto the internal surfaces of the adsorbent pores.

For most purposes, the adsorption of the solute molecule at the site on the internal surface occurs almost instantaneously, so it has little effect on the rate of the overall reaction. The transfer of solute from the bulk liquid to the surface layer of fluid around a particle can occur rather slowly, but in most treatment systems, this is encouraged by the constant movement of fluid pas the surface [Seader, 1998]. On the other hand, the diffusion of the solute through or across the surface of the adsorbent may occur rather slowly and this diffusion limits the rate of the sorption. Because the rate of adsorption is usually limited by diffusion, it is influenced by the same variables which affect diffusion rate. The concentration gradient of the solute across the surface of the adsorbent has a large effect on the rate as does the temperature of the system.

2.2.3 Adsorption with Activated Carbon

The difficulty in accurately predicting adsorption in given system is difficult, even assuming that only one solute is present. Predicting adsorption onto a complex activated carbon surface from an aqueous solution with multiple solutes becomes exceedingly more difficult. Nonetheless, some general knowledge about adsorption theory, along with experience, has allowed us to develop some general rules about carbon adsorption. There are factors which are known to most influence adsorption, while indicating that the large number of factors makes prediction difficult for complex wastewaters. When considering these factors, two properties of the adsorption system are of interest: the adsorptive capacity of a given amount of carbon for a particular solute and the adsorption rate at which that solute is taken out of solution. Obviously, these system properties are affected by characteristics of both the carbon and the solute. The factors affecting adsorption capacity include the surface area of activated carbon, pore size of carbon, solubility of solute in aqueous solution, pH and temperature.

Because adsorption reactions are usually exothermic, high temperature would seem to inhibit or slow adsorption, but this is not usually found to be a factor in most systems. An explanation for this may be revealed by again considering the rate limiting factor for adsorption. In carbon, adsorption is limited primarily by the diffusion of solute into the carbon particle. Higher temperatures may impede adsorption at the adsorption site but they significantly speed up the pace of diffusion offsetting any negative temperature effect. The factors affecting adsorption rate include the size of activated carbon particle, concentration of solute in solution and temperature of solution

Because adsorption rate is limited by diffusion, variables that influence diffusion have a significant effect on adsorption rate. For example, a higher concentration gradient across the surface of the carbon particle will increase the rate of adsorption, though a high concentration of solute can eventually have a negative effect on adsorptive capacity. In practice, the primary carbon variable influencing adsorption rate is the size of the carbon particle. Smaller carbon particles have a greater ratio of surface area to volume, making them more accessible to diffusion from solution. Notably, the size of the particle has little effect on adsorptive capacity as expressed by total surface area, while it is well known that smaller particles of a given mass of carbon would have a greater surface area than larger particles, the huge internal surface area of carbon dominates the calculation so much that the particle size essentially has no effect on capacity. The production of activated carbon increases the cost which adds a burden to the consumer. Therefore, the methods needed to minimize the cost of activated carbon production. One major way to cut on such cost of activated carbon is by choosing a cheap available starting material. Another way to cut on the cost is by a good choice of the production methods. Moreover, by choosing a suitable starting material, its use may reduce solid waste pollution while reducing the cost of raw material for the synthesis of activated carbon production process [Lafi, 2000].

2.2.4 Adsorption Isotherm

Adsorption is usually modeled by isotherms which relate the relative concentrations of solute adsorbed to the solid and in solution. The most commonly used isotherm is the most familiar Freundlich isotherm [Seader, 1998], which characterized most adsorption processes rather well under conditions present in most water treatment systems. One problem with this isotherm however, is its failure to consider that there maybe be a limited amount of adsorption sites on the surface of the solid; the lack of further sites may prevent adsorption under conditions in which equilibrium is reached. The Langmuir isotherm was developed to represent this site limitation and does it a better job at describing adsorption under some conditions, particularly as the solid becomes saturated and solute molecules have trouble finding adsorption sites. Finally Redlich-Peterson isotherm, a more recent development, incorporates some refinements which make it a better model than either of the other two. Unfortunately, this isotherm is rarely used because it requires the use of several constants and one of the other isotherms usually approximates a particular adsorption system with a good enough degree of accuracy.

2.2.5 Langmuir Isotherm

The Langmuir equation is derived from simple mass action kinetics, assuming chemisorptions [Seader, 1998] Assume that the surface of the pores of the adsorbent is homogeneous ($\triangle H_{ads}$ = constant) and that the forces of interaction between adsorbed molecules are negligible. Let θ be the fraction if the surface covered by adsorbed molecules. Therefore $(1-\theta)$ is the fraction of the bare surface. Then the net rates of adsorption is the difference between the rates of adsorption and desorption:

$$\frac{dq}{dt} = k_a p(1-\theta) - k_d \theta \qquad [1]$$

At equilibrium, $\frac{dq}{dt} = 0$ and [1] reduces to

$$\theta = \frac{Kp}{1+Kp} \qquad [2]$$

where K is the adsorption equilibrium constant ($= \frac{k_a}{k_d}$). Here

$$\theta = \frac{q}{q_m} \qquad [3]$$

where q_m is the maximum loading corresponding to complete coverage of the surface by the gas. Thus, the Langmiur adsorption isotherm is restricted to a monomolecular layer. Combining [3] and [2], we obtain

$$q = \frac{Kq_m p}{1+Kp} \qquad [4]$$

At low pressure, if $Kp < 1$, [4] reduces to the linear Henry's law form, while at high pressures where $Kp > 1$, $q = q_m$. At intermediate pressures, [4] is a non linear in pressure. Although originally devised by Langmiur for chemisorption, [4] has been widely applied to physical adsorption data.

The quantities K and q_m 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

$$\frac{p}{q} = \frac{1}{q_m K} + \frac{p}{q_m} \qquad [5]$$

Using [5], the best straight line is drawn through a plot of points $\frac{p}{q}$ versus p, giving a slope of $\frac{1}{q_m}$ and an intercept of $\frac{1}{q_m K}$. If the theory is reasonable, K should change rapidly with temperature, but q_m should not because it is related through v_m to the specific surface area of the adsorbent, S. it should be noted that the Langmuir isotherm predicts an asymptotic limit for q at high pressure.

2.2.6 Freundlich Isotherm

The Freundlich isotherm equation, which is empirical, often approximates data for many physical adsorption systems and is particularly useful for liquids. The equation is also nonlinear in pressure

$$q = kp^{\frac{1}{n}} \qquad [1]$$

where k and n are temperature dependent constants. Generally, n lies in the range of 1 to 5. With n = 1, [1] reduces to Henry's equation. Experimental q-p isotherm data can be fitted to [1] by a nonlinear curve fitting computer program or by converting [1] to a linear form as follows and using a graphical method or a linear regression program

$$\log q = \log k + \left(\frac{1}{n}\right)\log p \qquad [2]$$

If the graphical method is employed, the data are plotted as log q versus log p. The best straight line through the data has a slope of $\frac{1}{n}$ and an intercept of log k. In general, k decreases with increasing temperature, while n increases with increasing temperature and approaches a value of 1 at high temperature. Equation [1] is derived by assuming a heterogeneous surface with a nonuniform distribution of heat of adsorption over the surface.

2.3 Contaminants

2.3.1 Removal of Heavy Metals by Activated Carbon Adsorption

The presence of heavy metals in the environment is of great concern because of their increased discharged, toxic nature and other adverse effects on receiving waters [Blocher, 2003]. The potential across of copper in industrial effluents include metal cleaning and plating baths, pulp, paper board mills, wood pulp production and the fertilizer industry etc. Since copper is widely used material, there are many actual or potential sources of copper pollution. It is toxic to aquatic organism even at very small concentrations in natural water. It is also a micronutrient in agriculture and can, therefore accumulate in surface waters. Copper may be found as a contaminant in food, especially shellfish, liver, mushrooms, nuts and chocolate. Briefly, any processing or products such as food, water or drink. Copper is essential to human life and health but like all heavy metals, is potentially toxic as well [Nuhoglu et al, 2003]. For example, the excessive intake of copper results in its accumulation in the liver and produces gastrointestinal problems and continued inhalation of copper containing sprays is linked with an increase in lung cancer among exposed workers.

Both anions and cations have been removed from waters with activated carbon. Researchers have found that carbon exhibits preferential adsorption for ionic species and an order of preference has been defined: H > Al > CA > Li > Na > K. for anions, the NO ion is preferred over the Cl ions. It is not surprising that the pH plays an important role in the sorption characteristics of these ions, because the low pH provides large quantities of the preferred H ion, which may take the space of other ions on potential adsorption sites.

Even without pH variations, inorganic compounds exhibit a wide range of adsorbability on carbon. For example, dissolved salts like potassium chloride and sodium sulfate are almost nonsorbable, while iodine is one of the most adsorbable substances known. Significant reductions in inorganics compounds are not expected in carbon adsorption systems. Others point out cases in which effective inorganic adsorption is accomplished. It should be noted that such adsorption is accomplished only at very low concentrations of these ions and compounds. For example, carbon drinking water filters are often used to bring lead concentrations down from the range of 100ppb to below the action level of 15ppb. Previous studies had been conducted on heavy metals uptake [Toles, 1997] and on copper (II) ion [Kim, 2001]

In general, it was found that carbon adsorption is not nearly as effective at removing metals and inorganics as it is at removing at organic compounds. This is primarily because metals often exist in solution either as ions or as hydrous ionic complexes. Based on previous discussions of adsorption chemistry, neither of these forms is effectively adsorbed by carbon. The following metals are often removed from industrial wastewaters via activated carbon adsorption. It is notable that most of these can be toxic at a fairly low concentrations and carbon cab accomplish the type of finishing treatment often necessary with waste effluents containing them. Metals commonly removed with activated carbon are cadmium, chromium, zinc, lead, copper, mercury, cynide and etc.

CHAPTER 3
METHODOLOGY/PROJECT WORK

3.1 Raw Material

3.1.1 Grinding and Sieving

The waste palm oil shells provided was obtained from a palm oil processing mill. The waste palm oil shells was exposed to sunlight for a few days before being pre-heated at 110°C for 24 hours in an oven. The pre-heated treatment was required to reduce the moisture content inside the shells. The shells were grinded using a mortar grinder and sieved to get the required particle size fraction of 1-2mm.

3.2 Production of Activated Carbon

3.2.1 Carbonization

The grinded shells were placed in a crucible to undergo pyrolysis for at 700°C for 3 hours using a furnace. The pyrolyzed shells was cooled at room temperature and placed in desiccators for 24 hours to prevent oxidation. The carbonization was repeated for carbonization temperature at 800°C and 900°C.

3.2.2 Chemical Activation

20g of carbonized shells was impregnated with 0.05M sodium hydroxide in an Erlenmeyer flask. The Erlenmeyer was shake using a shaker for 4 hours. The activated carbon was washed with 5% HCl solution until the pH was within the 6-8 range. Then,

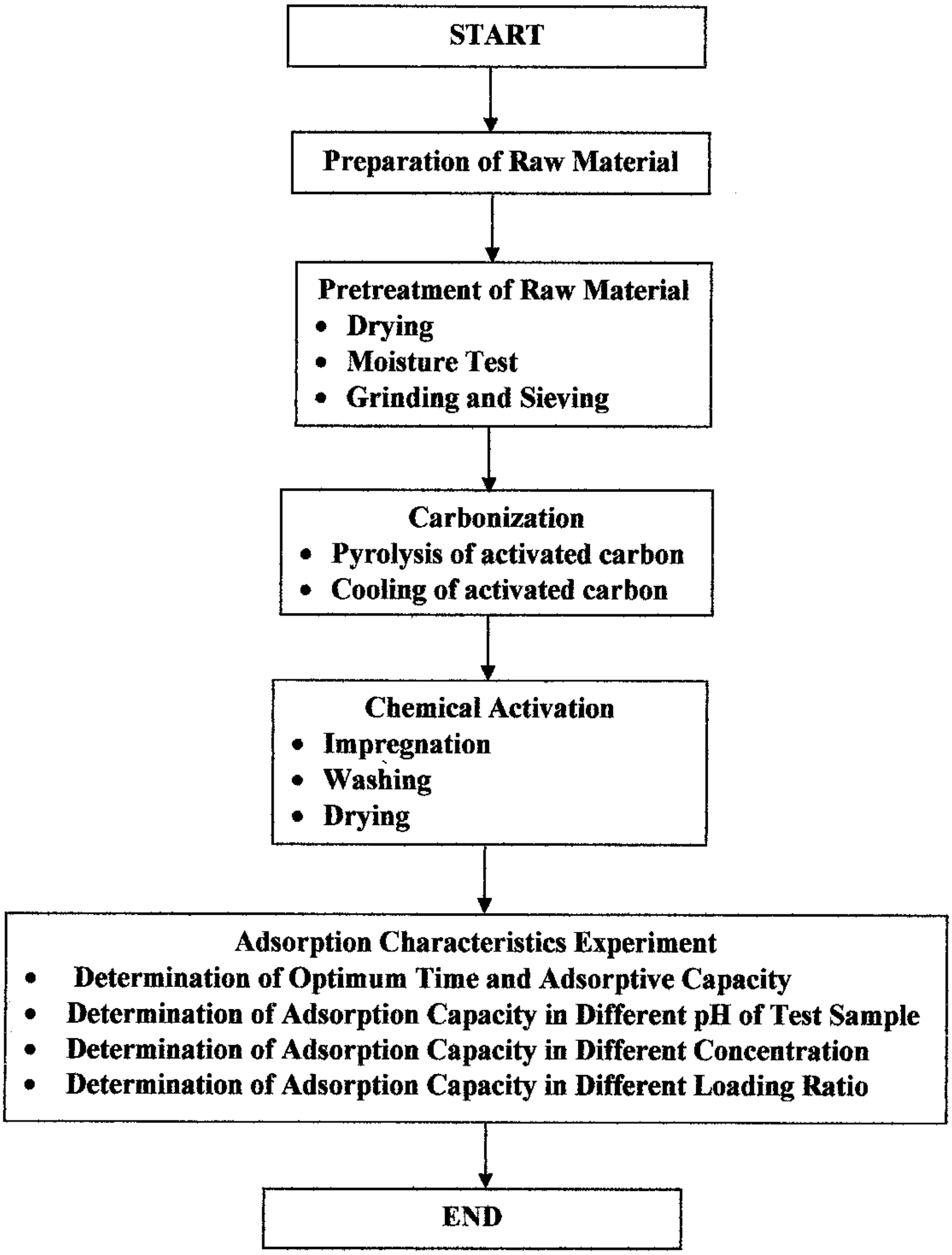

Figure 1: Process Flow for Preparation of Activated Carbon

it was washed with distilled water to remove chlorine and acid compounds. The activated carbon was dried at 110°C for 24 hours in an oven. The dried activated carbon was leave to cool to room temperature for 24 hours. The chemical activated was repeated for different sodium hydroxide concentration: 0.1M and 0.15M

3.2.3 C,H,N and S Analysis

Approximately 2.2mg of activated carbon was packed into the aluminium tin and sealed. It was combusted at 1000°C in a stream of oxygen. Using helium as a carrier gas, the oxygen was removed and the combustion products are reduced. The reduced gases was separated by gas chromatography and quantified with a thermal conductivity detector. The software program of the C,H,N and S analyzer was used for data collection and analyses.

3.3 Adsorption Testing

3.3.1 Determination of Adsorption Capacity at Various Copper Concentrations

0.5g of activated carbon was added to copper solution with 100ml of copper ion solution [50ppm] in 250ml conical flask. One control sample containing only water sample was also prepared. The samples were agitated for 24 hours. The samples were filtered through filter paper by neglecting the first 5ml of the filtrate to saturate the filter paper with synthetic waste water solution. The copper ion concentration is determined using the conductivity meter. The amount of copper ion adsorbed was calculated based on the difference between before and after adsorption process. The experiment was repeated for copper ion solution of 100ppm and 200ppm.

3.3.2 Determination of Adsorption Capacity at Various pH

0.5g of activated carbon was added to 100ml copper ion solution with different pH value in 250ml conical flask. One control sample containing only water sample was also prepared. The samples are agitated for 1 hour. The samples were filtered through filter paper by neglecting the first 5ml of the filtrate to saturate the filter paper with synthetic waste water solution. The copper ion concentration was determined using the conductivity meter. The amount of copper ion adsorbed was calculated based on the difference between before and after adsorption process. The experiment was done at pH3, pH7 and pH12.

3.3.3 Determination of Adsorption Capacity at Various Loading Ratio

0.5g of activated carbon was added to 100ml copper ion solution with in 250ml conical flask. One control sample containing only water sample was also prepared. The samples were agitated for 1 hour. The samples were filtered through filter paper by neglecting the first 5ml of the filtrate to saturate the filter paper with synthetic waste water solution. The copper ion concentration was determined using the conductivity meter. The amount of copper ion adsorbed was calculated based on the difference between before and after adsorption process. The experiment was repeated at 1.0g and 1.5g of activated carbon.

3.4 Tools Required

The study requires few equipment, apparatus and chemicals for laboratory work. Laboratory work was done under the supervision and assistance of research project supervisor and laboratory technician. All the tools were provided by Universiti Teknologi PETRONAS and can be presented in tables below:

Table 3: Chemicals/Materials Required

Chemicals/Materials	Quantity (volume, mass etc)
NaOH	12g in pallets form
$Cu(NO_3)_2.3H_2O$	500g in powder form
HCl	500g in powder form
Distilled water	As required
Palm oil shells	As required

Table 4: Equipment/Apparatus Required

Equipment	Quantity (units)
Conductivity Meter	1
C,H, N and S Meter	1
Furnace	1
Grinder/Mortar	1
Shaker	1
Desiccators	1
Pipette	1
Sieve	1
Measuring Cylinder	2
250ml Conical Flasks	2
500ml Conical Flasks	2
1000ml Conical Flasks	5
Crucible	10
Filter Papers	1 box

CHAPTER 4

RESULTS AND DISCUSSION

Nowadays, voluminous study is done on the production of activated carbon from various raw materials and its adsorption capacity on metal removal. The study utilizes the studies and the results and discussions of the findings are well presented in this section.

4.1 Characterization of Raw Material

The C,H,N and S was used to study the ultimate analysis of the raw material. It gave the chemical composition i.e carbon, hydrogen, nitrogen sulfur of raw palm oil shells The analytical results for C,H,N and S of raw palm oil shells are shown in the Figure 4.1

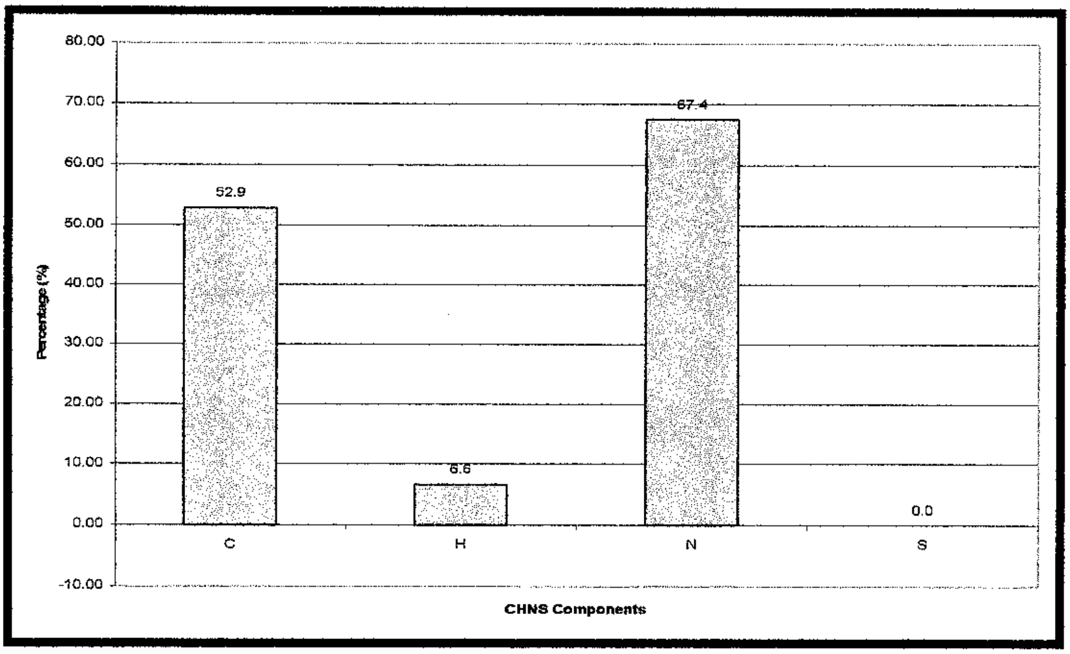

Figure 4.1: Carbon, Hydrogen, Nitrogen and Sulfur Analysis for Raw Palm Oil Shells

Table 4.1 Comparing Elemental Composition of Walnut Shells and Raw Palm Oil Shells (%)

Element	Walnut Shells [Kim et al, 2001]	Raw Palm Oil Shells
Carbon	46.6	52.9
Hydrogen	6.0	6.6
Nitrogen	0.7	67.0
Sulfur	-	-

Relatively, comparing Figure 4.1 and Table 4.1, the carbon, hydrogen and nitrogen content for raw palm oil shells is higher than the walnut shells [Kim et al, 2001]. But then, the sulfur content for walnut shells exceeds raw palm oil shells. From Jia, 2002, there is a commercially available coconut shell derived activated carbon was oxidized with nitric acid and both the original and oxidized activated carbons were treated with ammonia at 1073K to incorporate nitrogen functional groups into the carbon. An active carbon with very high nitrogen content (-9.4wt% daf) is prepared from a nitrogen rich precursor, polyacrylonitrile (PAN). These nitrogen rich had points of zero charge (pHpzc) similar to H type active carbons. From Knappe D, a result of his study showed that the adsorption capacity for a micro pollutant is maximized for adsorbents with several factors and this include the sum of oxygen and nitrogen contents should not exceed 2 to 3 mmol/g.

Oil palm shell or called *endocarp* is one of prospective precursor for the preparation of high quality activated carbon due to its high density, relatively high carbon content and low ash content compared to walnut shells. Instead of ultimate analysis, proximate analysis will give the important characteristics such as volatile matter, fixed carbon and total ash content. Proximate analysis for palm oil shells and char are represented in the Table 4.2 [Guo J, 2001]. The fixed carbon content for palm oil shells is relatively lower than char. Such carbon content is not sufficient for the palm oil shells to utilize as an adsorbent. Thus, carbonization process has enhances the fixed carbon content and rudimentary pore structure by eliminating the noncarbon species.

Table 4.2 Characteristics of Raw Oil Palm Shell and Resulting Char [Guo J, 2001]

Sample	Proximate Analysis (wt%)		
	Volatile Matter	Fixed Carbon	Ash
Palm oil shells	77.6	19.8	2.6
Char	30.6	63.4	6.0

4.2 Production of Activated Carbon

This study produced activated carbon from waste palm oil shells by carbonization and chemical activation process. The variation of activated carbon is presented in Table 4.3. The variations include the carbonization temperature and chemical activation agent concentration. The particle size for the activated carbon is fixed at 1-2mm. The raw material undergoes carbonization and followed by chemical activation with sodium hydroxide. The carbonization temperature was varies between 700°C, 800°C and 900°C. The chemical activation agent used was sodium hydroxide. In this case, the sodium hydroxide concentration was varies between 0.05M, 0.10M and 0.15M. The impregnated activated carbons are carbonaceous adsorbents which have chemicals finely distributed on their internal surface. The impregnation optimizes the existing properties of the activated carbon giving a synergism between the chemicals and the carbon, this facilitates the cost effective of certain impurities from gas streams which would be impossible otherwise.

Activated carbons are non- hazardous, processed, carbonaceous products, having a porous structure and a large internal surface area. These materials can adsorb a wide variety of substances i.e. they are able to attract molecules to their internal surface and therefore called adsorbents. The volume of pores of the activated carbons is generally greater than 0.2ml/g. The internal surface area is generally greater than $400m^2/g$. The width of the pores ranges from 0.3 to several thousand mm.

Table 4.3 Parameters Variation on Activated Carbon Produced

Sodium Hydroxide Concentration (M)	700°C	800°C	900°C
0.05	X	X	X
0.10	X	X	X
0.15	X	X	X

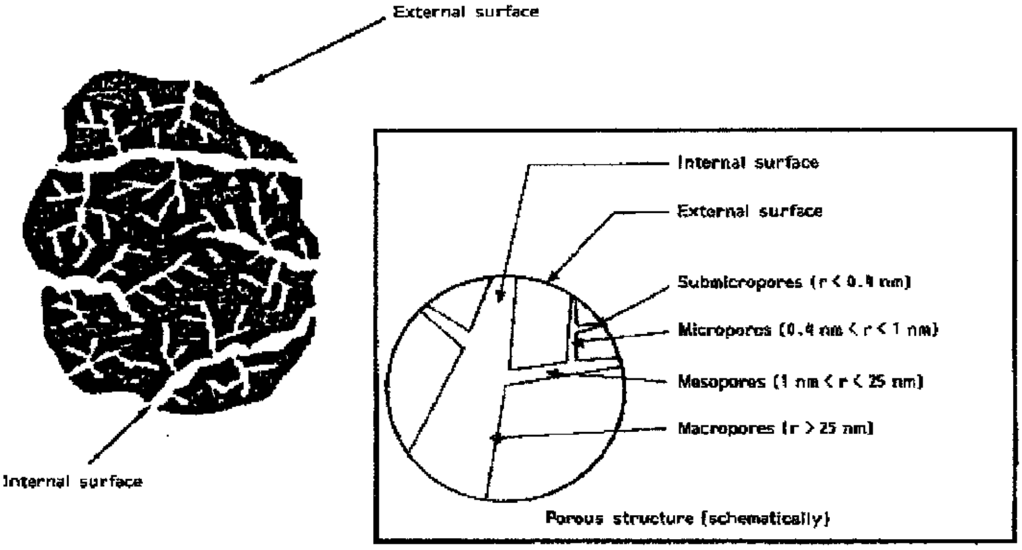

Figure 4.3 Schematic Activated Carbon Models

4.3 Adsorption Characteristics

The activated carbon is known for its effectiveness in removing organics chemicals from waster and waste water. It is also surprisingly effective in removing heavy metals. The presence of heavy metals in the environment is great concern because of their increased discharge, toxic nature and other adverse effects of receiving waters. The potential sources of copper in industrial effluents include metal cleaning and plating baths, pulp, paper board mills, wood pulp production and the fertilizer industry. Copper is toxic to aquatic organism even at very small concentrations in natural water. Thus, the study emphasizes the production of activated carbon and its ability to remove copper ion in the waste water. To estimate the applicability of produced activated carbon as an adsorbent for wastewater treatment, the adsorption test was performed using copper ion as the adsorbate.

4.4 Effects of Carbonization Temperature on the Adsorption Capacity

In general, carbonization and activation temperature are known to be very influential on the micropore structures of activation carbon, which determines the adsorption capacity [Kim, 2001]. For the purpose of examining the influence of the carbonization temperature on the adsorption capacity of activated carbon, the variation of carbonization temperature has been investigated for 24 hours adsorption time and at ambient temperature, which were observed to be the optimal activation conditions.

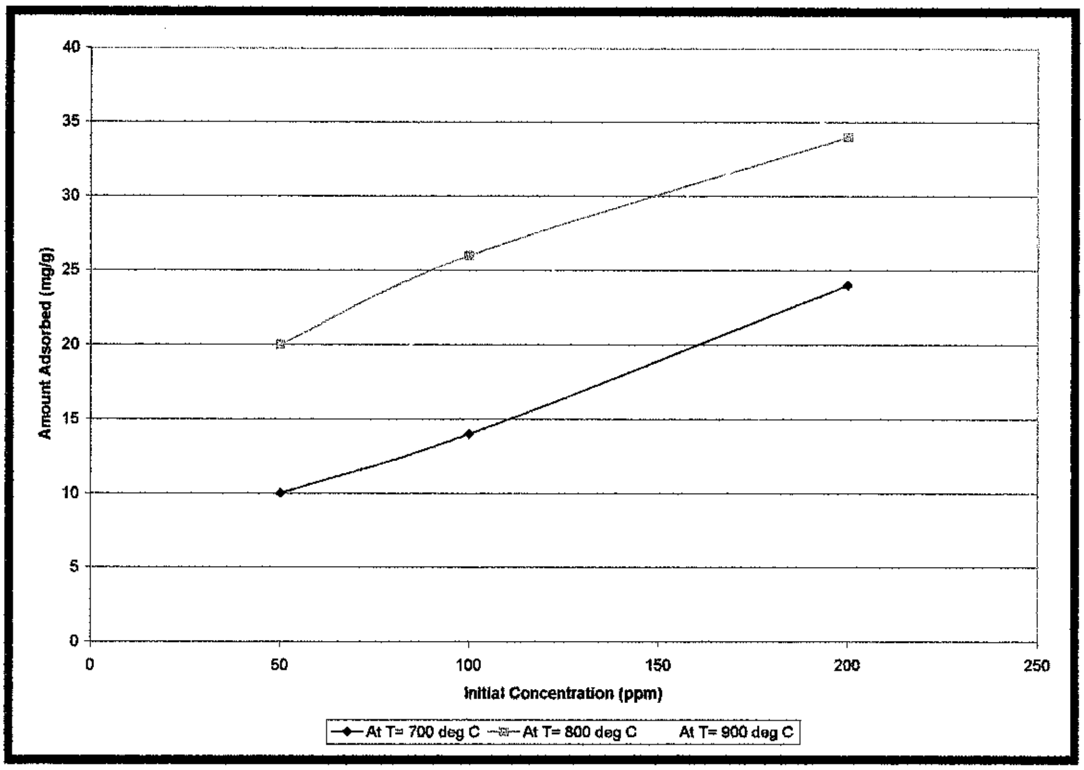

Figure 4.4 Effects of Carbonization Temperature on the Adsorption Capacity of Activated Carbon Produced (Sodium Hydroxide Concentration = 0.05M)

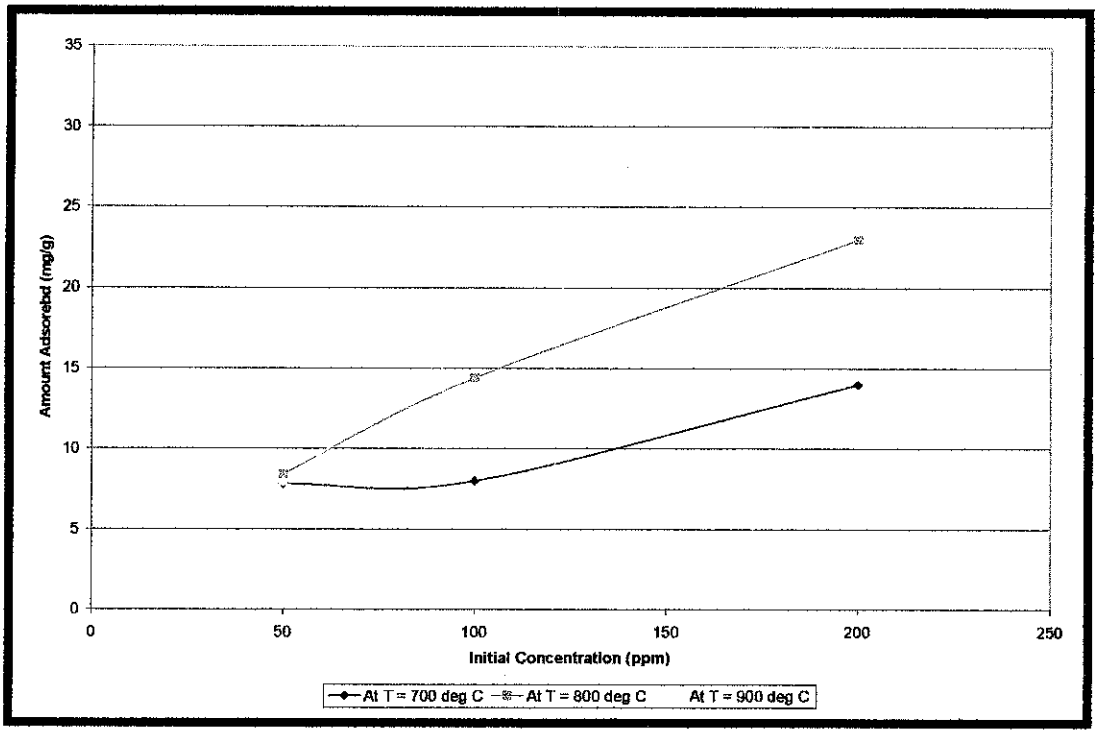

Figure 4.5 Effects of Carbonization Temperature on the Adsorption Capacity of Activated Carbon Produced (Sodium Hydroxide Concentration = 0.10M)

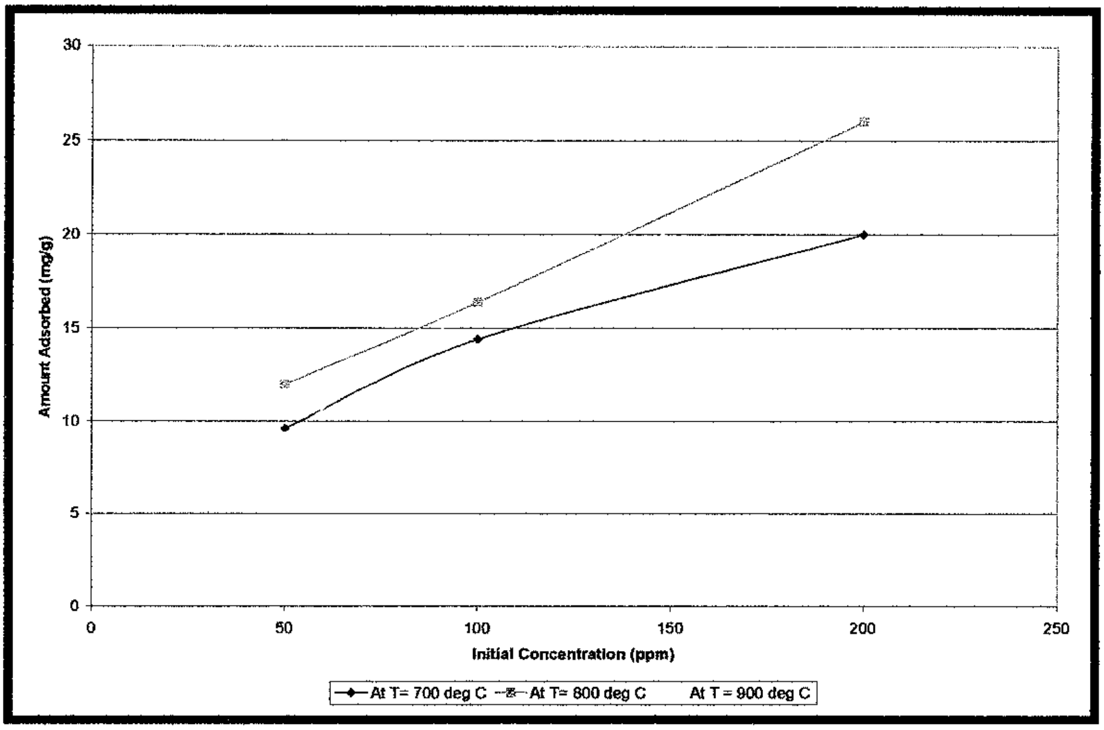

Figure 4.6 Effects of Carbonization Temperature on the Adsorption Capacity of Activated Carbon Produced (Sodium Hydroxide Concentration = 0.15M)

Carbonization temperature determined the effectiveness of palm oil shells as activated carbon. As carbonization temperature increases, the copper uptake in copper solutions increases and vice versa. Such pattern can be observed in Figure 4.4, Figure 4.5 and Figure 4.6. Figure 4.4 represents the activated carbon activated with 0.05M of sodium hydroxide. From the graph, the activated carbon carbonized at the carbonization temperature of 800°C gives the most copper uptakes compared to other carbonization temperature. The activated carbon activated with 0.15M of sodium hydroxide indicates the same result, refer Figure 4.6. Meanwhile, Figure 4.5 shows the activated carbon activated with 0.10M of sodium hydroxide and the most copper uptake is by the activated carbon produced at carbonization temperature of 900°C.

The solid and apparent densities and the porosity of the activated carbons prepared under various carbonization temperatures from waste palm oil shells are shown in Guo J, 2001. Increasing the carbonization temperature increased the solid density progressively and decreased the apparent densities, resulting the development of porosity. In general, activated carbons prepared from waste palm oil shells are highly porous with sufficiently high solid densities, thereby minimizing carbon losses during handling and conveying of these materials in industrial applications. The most important property of the activated carbon is its adsorptive capacity that is related to the specific pore surface area. Generally, the higher the pore surface area of the activated carbon, the larger is its adsorptive capacity. The temperature gives effect to BET and micropore surface areas of the activated carbon. The BET and micropore surface areas increased progressively with increasing carbonization temperature. 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. In Jim et al, 2001, it states that in general, carbonization and activation temperature are known to be very influential on the micropore structures of activated carbon which determines the adsorption capacities.

In addition, Lafi, 2000 studied the production of acorns and olive seeds. It is evident that activated carbon from oak produced at 800°C has the highest adsorption capacity and activated carbon produced at 400°C showed the lowest adsorption capacity. Hu, 2000 also studied the effect of heating temperature on the adsorbent produced. The temperature was varied from 500°C to 900°C. It came to the conclusion that high temperature favors the production of an adsorbent with a large adsorption capacity with a slightly increased micropore size. The samples treated at 700°C, 800°C and 900°C have high adsorption energy and their average pore sizes are about 0.52, 0.62 and 0.64nm. Castello, 2001 in paper on preparation of activated carbon with optimum pore sizes came with a conclusion that from 700°C to 850°C, the higher the pyrolysis temperature, the higher the BET surface area and micropore volume. The micropore size distribution becomes wider than ever.

At low temperatures, activation and carbonization is not sufficiently accomplished and elements such as hydrogen, oxygen, nitrogen and sulfur remain in large amount along with C after thermal treatment. Thus, as activation and carbonization temperature becomes larger, the yield of product is expected to decrease. The effect of activation temperature and its relation to fixed carbon content is also explained in Guo, 2001 and is presented in Table 4.3. As the carbonization temperature increases from 500°C to 900°C, the fixed carbon seems to increase due to combination release of volatile matters in a continual carbonizations process.

Table 4.4 Effects of Activation Temperature on the Proximate Analysis [Guo, 2001]

Activation Temperature (°C)	Proximate Analysis (wt%)		
	Volatile Matter	Fixed Carbon	Ash
500	22.6	71.5	5.9
600	13.8	79.6	6.6
700	7.2	86.6	6.2
800	3.4	88.1	8.5
900	1.0	89.5	9.5

4.5 Effects of Different Chemical Activation Agent Concentration on the Adsorption Capacity

Sodium hydroxide is cheaper and less corrosive than the typical activated agents often used and produces activated carbons with small mineral matter content [Lillo, 2000]. Chemical activations with hydroxides have recently been of great interest as it permits the preparation go activated carbons with a highly developed porosity. The study of reactions occurring during activation of activated carbon by sodium hydroxide has shown that chemical activation consists of a reaction between the carbon and the hydroxide. [Rodenas et al, 2003]. The reactions products are the metal carbonate, hydrogen and some metallic compound. From these reaction products, the proposed reactions

$$6NaOH + 2C \leftrightarrow 2Na + 3H_2 + 2Na_2CO_3$$

In this type of reaction (solid hydroxide) the reactivity of the solid has to be a key factor. It should be noted that the above reactions are global reactions that do not describe the detailed reaction mechanism. For the purpose of examining the influence of the concentration of chemical activation agent on the adsorption capacity of activated carbon, the variation of sodium hydroxide concentration has been investigated at 24 hours activation time and at ambient temperature, which were previously observed to be the optimal activation conditions [Kim, 2001].

Ahmadpour, 1997 indicates that the chemical to adsorbent (nutshells) ratio has been found to be the most important parameter in the carbonization of carbon precursor using the chemical activation technique. The adsorbent had been activated with potassium hydroxide, which can be a good reference to sodium hydroxide of this study, and zinc chloride. Adding chemical agents to the precursor decreases the weight loss of carbon products in the lower range of chemical ratio after which in increases in the potassium hydroxide series while it remains constant for zinc chloride activated samples. The influence of chemical ratio on surface area and micropore volume was investigated. It is seen that surface area and micropore volume are both increasing continuously with the chemical ratio. In zinc chloride, the micropore volume and area increase at high rate.

However, in the case of potassium hydroxide, the mechanism is different especially at high chemical ratio. The micropore creation mechanism is predominant even at high potassium hydroxide to nutshell ratio. Evans, 1998 also supported the facts that changing the potassium hydroxide to precursor sucrose char has effects on both the yield of product and the external surface area. Higher potassium hydroxide concentrations consistently produced a lower yield of product with a much larger external surface area.

Figure 4.7, Figure 4.8 and Figure 4.9 represented the results for amount of copper adsorbed for activated carbon produced at various sodium hydroxide concentrations. Activated carbon produced with 0.05M of sodium hydroxide concentration during chemical activation resulted better adsorption capacity compared to activated carbon produced with sodium hydroxide concentration of 0.10M and 0.15M. Figure 4.7 indicates the activated carbon produced with carbonization temperature of 700°C gives the most copper uptakes when activated with 0.05M of sodium hydroxide. The same results can be observed in Figure 4.8 and Figure 4.9. Arjunan, 2003 concludes that he amount of sodium hydroxide used during chemical activation process has strong effect on the copper uptake. Low calcium fly ash as a cementations material has an inherent drawback – its relatively low reactivity. Thus an external agent is required to accelerate the hydration reactions. His study describes a novel way of preparing highly active fly ash suspension using a number of chemical activators. The main chemical activators investigated included: hydroxides of calcium and sodium in various concentrations, sodium carbonate, sodium sulfate, and sodium chloride, nitrates of sodium, ammonium and calcium and binary mixtures of some of these compounds. These formulations have been used with both coarse and fine varieties of fly ash to determine the combined effect of mechanical and chemical activation. As a conclusion at various chemical components used for chemical activation, sodium hydroxide in low concentration produces better performance and activation effect can be enhanced if mechanical activation is combined with chemical activation.

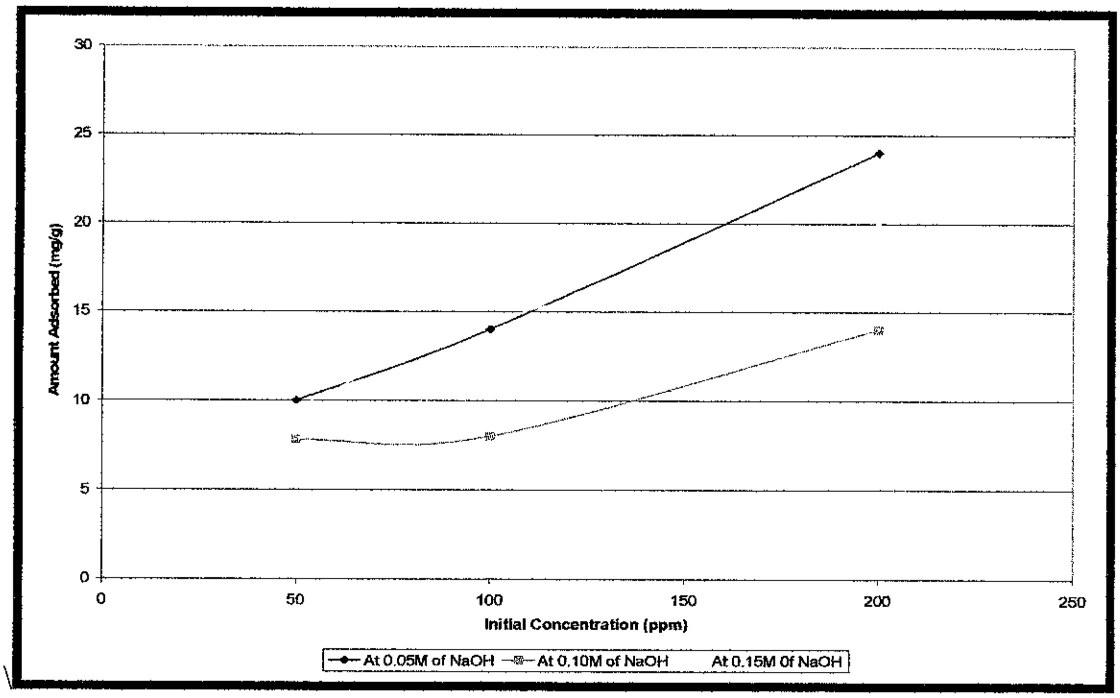

Figure 4.7 Effects of Sodium Hydroxide Concentration on the Adsorption Capacity of Activated Carbon Produced (Carbonization Temperature = 700°C)

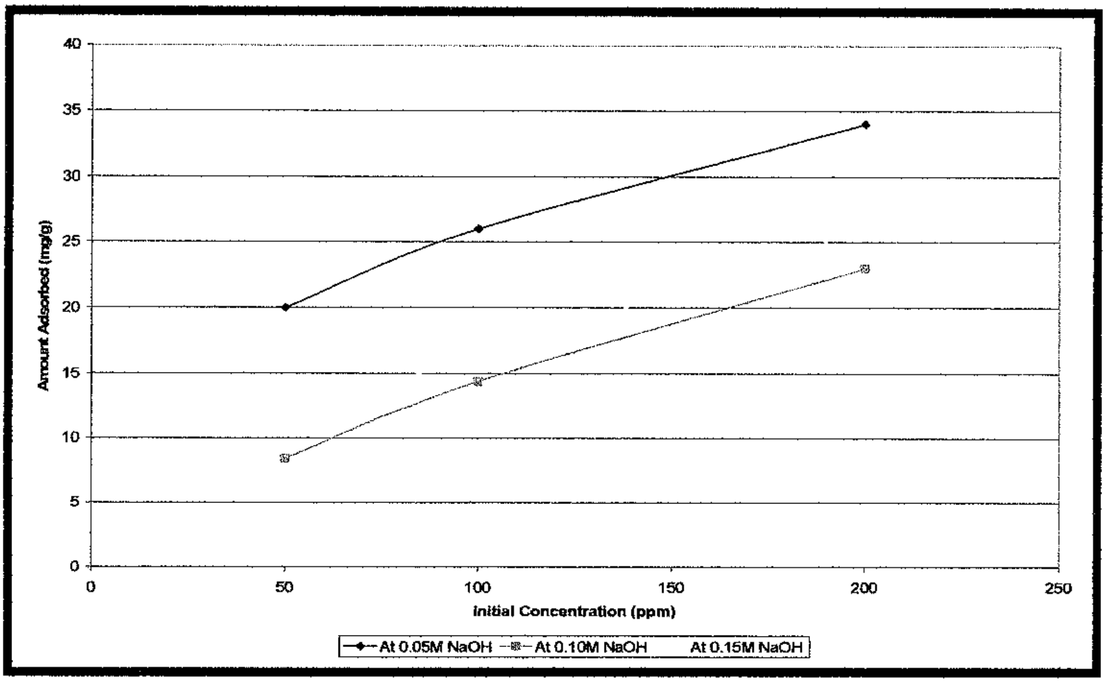

Figure 4.8 Effects of Sodium Hydroxide Concentration on the Adsorption Capacity of Activated Carbon Produced (Carbonization Temperature = 800°C)

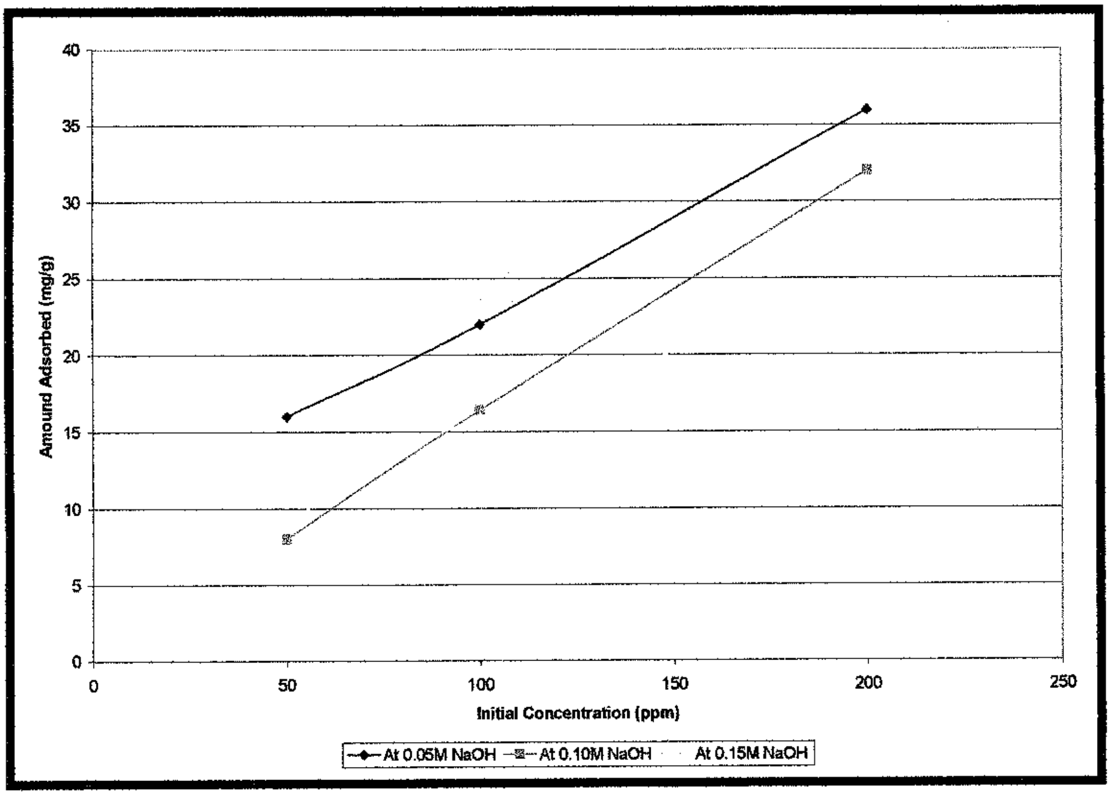

Figure 4.9 Effects of Sodium Hydroxide Concentration on the Adsorption Capacity of Activated Carbon Produced (Carbonization Temperature = 900°C)

4.6 Adsorption Capacity of Activated Carbon at Various Copper Concentrations

The adsorption of copper (II) ions of the experiment samples from aqueous solution of synthetic copper wastewater in the concentration range (50ppm to 200ppm). The pH of each solution was maintained at neutral conditions. It is seen that the adsorption isotherms are type I of the BET classifications showing initially a rapid adsorption tending to be asymptotic at higher concentrations. The uptake for copper ions is least in the case of activated carbon activated with 0.15M of sodium hydroxide than 0.05M of sodium hydroxide. At various copper concentration, the copper ion uptake increases as the copper ion concentrations increases. Activated carbon activated with 0.05M of sodium hydroxide gives good performance for having higher adsorption capacity. Also, as discussed before, higher carbonization temperature leads to better adsorption.

From Zhang et al, 2002, it agreed that the copper loading increases with increasing copper concentration. Regarding the influence of the initial concentration of copper ions, Antunes, 2003 stated that the equilibrium sorption capacity of the activated carbon increased with the increase in the initial copper concentration up to 1000mg/mL while the fraction of copper adsorbed presented the opposite trend. The difference between bulk and surface metal ions concentration is one of the driving forces to overcome the resistances to adsorption process. In the absence of mass transfer resistances, surface and bulk concentrations are identical, so the increase in initial concentration of copper ions will enhance the adsorption process. The equilibrium uptake is shown in Table 4.5.

Lafi, 2000, on the studies the production of activated carbon from acorns and olive seeds came out with a conclusion that the loading is seen to increase with increasing methylene blue concentration Goyal, 2001 presented the adsorption isotherm of copper ions of the four carbon samples from aqueous solution of cupric chloride in the concentration range of 20-1000mg/l. The uptake of copper ions is smaller in the case of fibrous carbons compared with granular carbons. However, for both fibrous and granular carbons, the copper uptakes increases with increasing solutions concentration

Table 4.5 Equilibrium Uptakes (q_e) and Fraction of Copper Removed (x_a, %) by Sargassum sp. At Different Temperatures and Initial Concentrations [Antunes, 2003]

C_0 (mg/mL)	298K		313K		328K	
	q_e(mg/g)	x_a, (%)	q_e(mg/g)	x_a, (%)	q_e(mg/g)	x_a, (%)
18.4	4.3	89.1	4.3	89.3	4.1	87.6
36.9	8.3	90.1	8.3	90.2	8.3	86.8
92.2	21.3	92.4	21.3	92.3	21.4	91.6
184	40.0	87.0	38.0	82.6	42.5	92.4
277	53.3	77.0	53.1	76.6	57.0	82.2
369	57.9	62.8	57.6	62.4	60.8	65.9

4.7 Adsorption Capacity of Activated Carbon at Various pH

The effect of pH of the solution on the adsorption of copper (II) ions on activated carbons was determined. The pH of the solution was controlled by the addition of hydrochloric acid and sodium hydroxide. The adsorption process was carried out at various pH i.e. acidic, neutral and basic. During the preparation of copper solutions at various pH, at higher pHs, the solution was generally more stable, but a green precipitate, presumably copper hydroxide, might appear if the pH was greater than about 11.5. [Zhang et al, 2002]. It is well known that the pH of the medium affects the solubility of metal ions, so pH is an important parameter on the adsorption of copper ions from aqueous solutions. The activated carbon presents a high content of ionizable groups after being activated with sodium hydroxide, which makes it at least in the theory, very liable to the increase in pH.

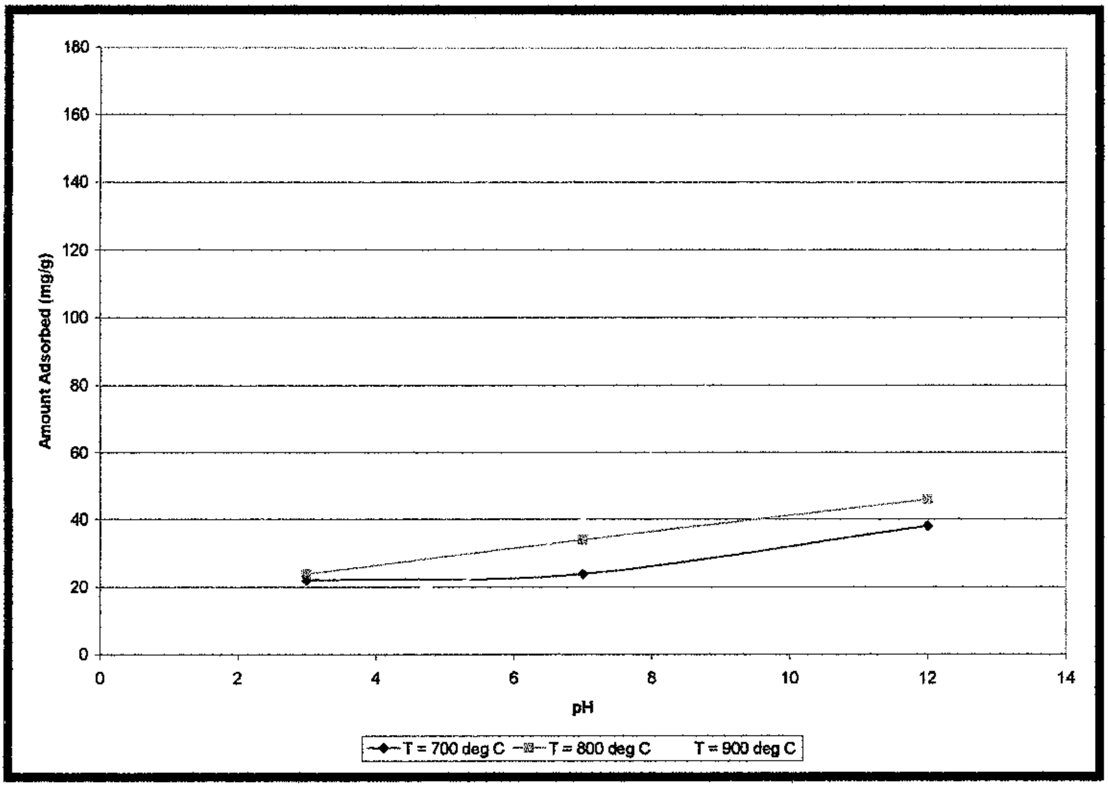

Figure 4.10 Effects of Various pH on the Adsorption Capacity of Activated Carbon Produced (Sodium Hydroxide Concentration = 0.05M)

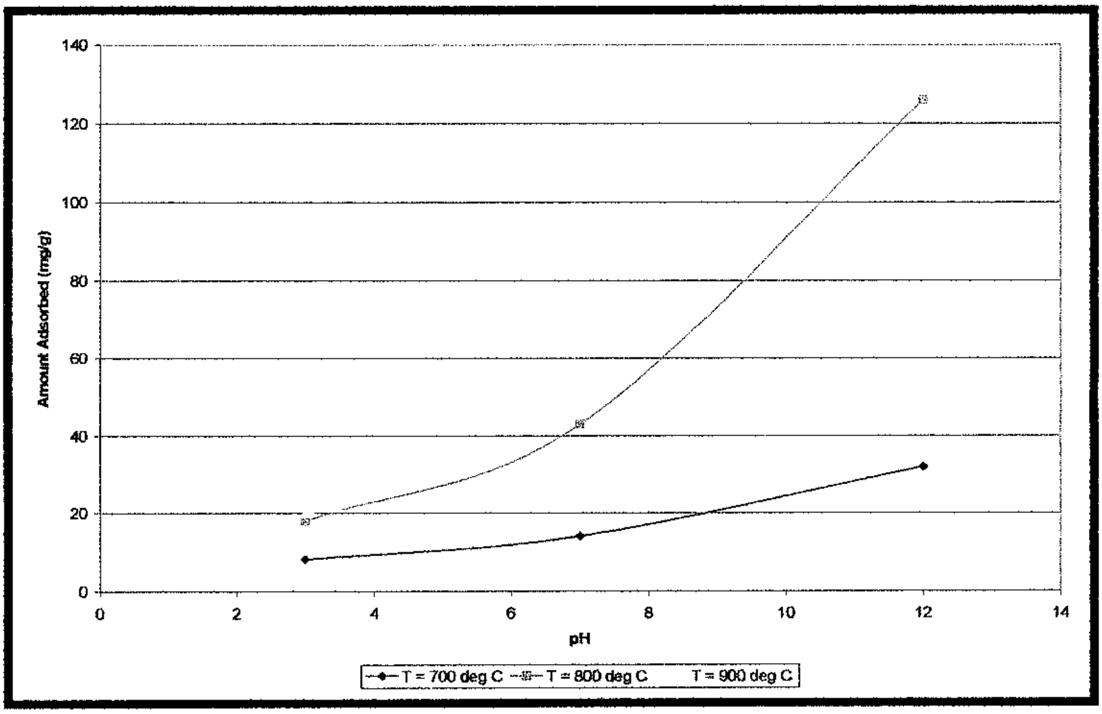

Figure 4.11 Effects of Various pH on the Adsorption Capacity of Activated Carbon Produced (Sodium Hydroxide Concentration = 0.10M)

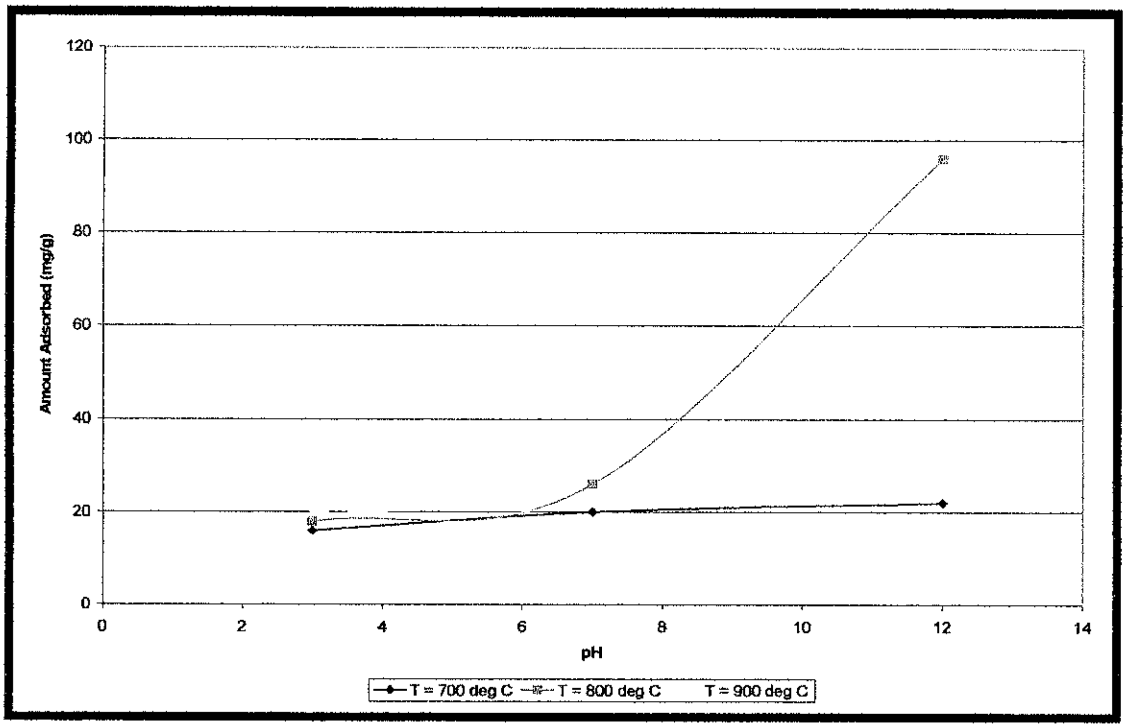

Figure 4.12 Effects of Various pH on the Adsorption Capacity of Activated Carbon Produced (Sodium Hydroxide Concentration = 0.15M)

Figure 4.10, Figure 4.11 and Figure 4.12 shows how the copper uptake depends on pH, and it increases with increasing pH. The activated carbon produced at carbonization temperature of 900°C and activated with sodium hydroxide concentrations of 0.05M gave the maximum adsorption capacity at pH12. From Figure 4.11 and Figure 4.12, the metal uptake is the best for activated carbon produced at carbonization temperature 800°C and activated with sodium hydroxide concentration of 0.10M and 0.15M at pH12. The maximum adsorption capacity was given for adsorption process at pH12 using the activated carbon produced at carbonization temperature of 900°C and activated with 0.05M of sodium hydroxide. The activated carbon is indicated as the superior adsorbent for this study.

The copper uptake increases with increase in pH. Loading is less dependent below pH12. It is well known that with the increase in pH, due to the decrease in the competition between protons and metal ions for surface sites, metal ion uptake by the activated carbon increases. It should further be noted that experiments must be carried out in a range of pH that metal ion removal can be associated only to the adsorption, and not to combination of adsorption and metal hydroxide precipitation [Rockstraaw, 2000].

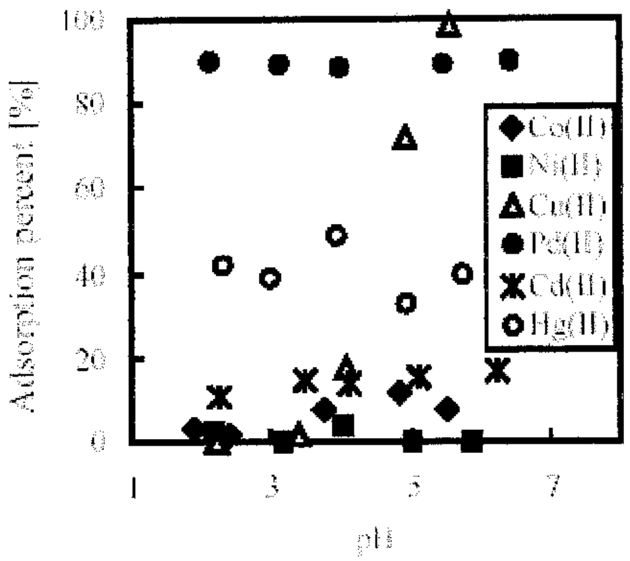

Figure 4.13 Effect of pH on the Adsorption Percent of Metal Ions on CUSI [Baba et al]

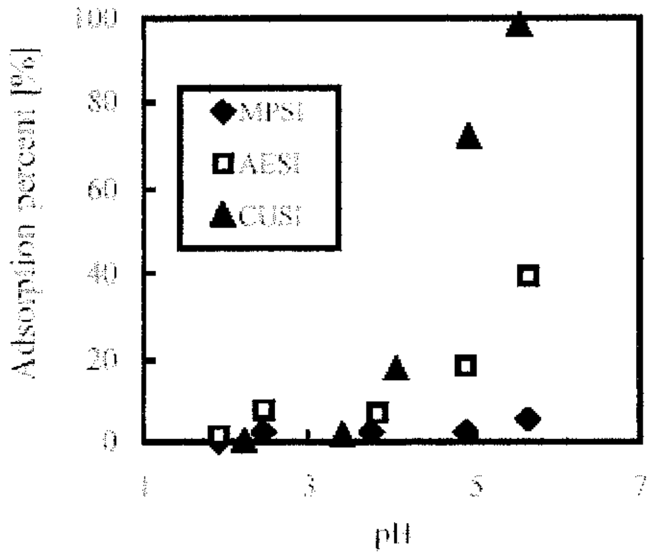

Figure 4.14 Effect of pH on the Adsorption Percent of Copper (II) on CUSI [Baba et al]

Copper ions adsorption doesn't favor lower pH ranges and low carbonization temperature. Figure 4.19 shows the plot of adsorption percentage of metal ions against equilibrium pH in the adsorption of Cu(II), Ni(II), Co(II), Hg(II) and Pd(II) on silica samples taken from Baba et al. It shows that adsorption of copper increases gradually with increasing pH. The adsorption is analogous to that observed in solvent extraction of cationic metal ions which acidic extractants including chelating extractants. It suggested that metal ions are adsorbed according to the cation change mechanism. Figure 4.14 shows the adsorption percentage of copper ion suggesting that hydrogen ion explicitly takes part in the adsorption reaction.

The influence of pH on the adsorption of bivalent and trivalent metal ions (Cd, Cr, Cu, Mn, Ni and Pb) is studied. As expected, the adsorption of metals decreases with decreasing pH because the aluminol and silanol groups are more protonated and hence they are less available to retain the investigated metals. This effect is strongly evident for Cu and also Pb and Cd. The reason of this behavior is that the surface complexation reactions are influenced influenced also by the electrostatic attractions between the surface charge and dissolved ions. The copper (II) behavior is probably due to the structure of its aquaion. In fact $[Cu(H_2O)_6]^{2+}$ has a tetragonal distortion due to the Jan Taller effect. The adsorption of copper is hindered by cation exchange mechanism. There factors contribute to a different pH effect on each metal as mentioned by Abollino.

4.8 Adsorption Capacity of Activated Carbon at Various Loading Ratio

Adsorption capacities are defined as the difference between initial and final copper ion concentration divided by the weight of activated carbon. Specific results on adsorption capacity for activated carbon at different carbonization temperatures and chemical agent concentration. Adsorption capacity is seen to increase with increasing loading ratio. It is evident that activated carbon produced at higher carbonization temperature has high adsorption capacity. Loading ratio is well known factors that affect the copper uptake in copper solutions. As the loading ratio increases, the copper uptake also increases. The pattern is well demonstrated in Figure 4.15, Figure 4.16 and Figure 4.17. From Figure 4.15, the activated carbon produced at carbonization temperature of 800°C and 900°C shows the increase in adsorption capacity, from loading ratio of 0.5g/100ml to 1.5g/100ml of activated carbon to copper solutions. Meanwhile, for Figure 4.16 and 4.17, the activated carbon produced at carbonization temperature of 800°C and activated with sodium hydroxide concentration of 0.10M and 0.15M respectively, is the best adsorbent at increasing loading ratio.

From Lam et al, 2003, it studies the amount of adsorbent to study its effect on the copper loading of the product. The copper concentration decreases as the amount of adsorbent increases, indicates the increase in adsorption capacity as the loading ratio increases. Lafi, 2000 indicates the adsorbent loading for oak, jift and commercial activated carbon. Oak, jift and commercial activated carbon has higher adsorption capacities at higher loading ratio. Zhang et al also study the effect of loading on gold and copper in adsorption process and same out with the same results.

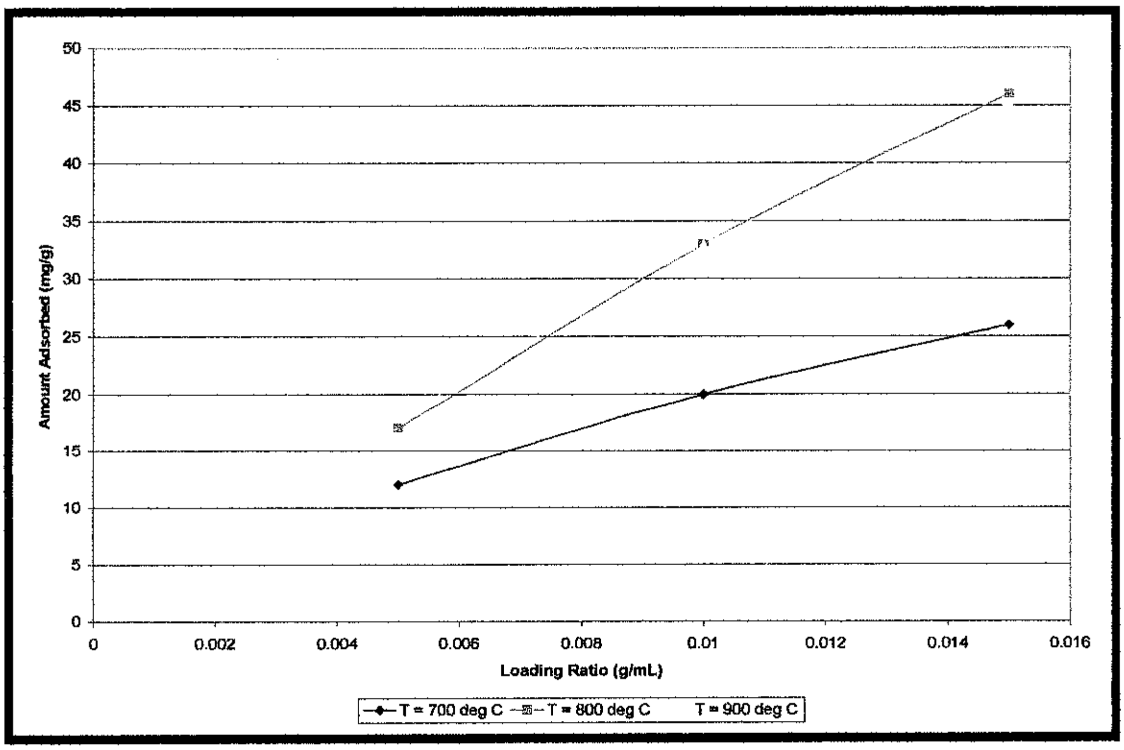

Figure 4.15 Effects of Various Loading Ratio on the Adsorption Capacity of Activated Carbon Produced (Sodium Hydroxide Concentration = 0.05M)

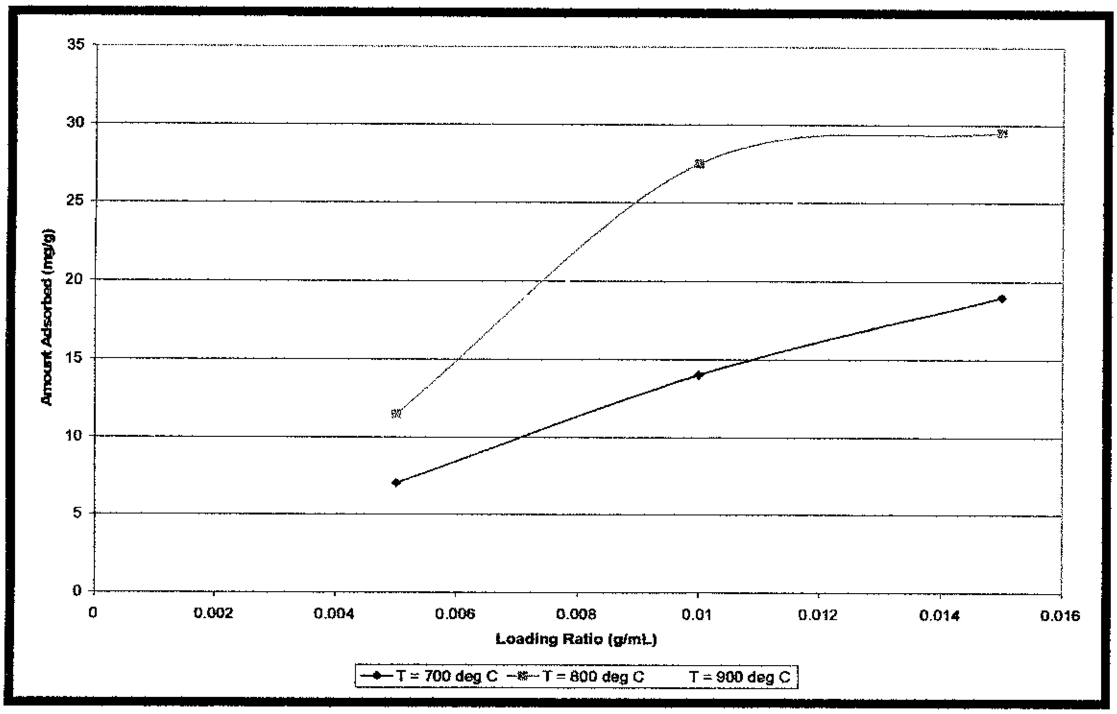

Figure 4.16 Effects of Various Loading Ratio on the Adsorption Capacity of Activated Carbon Produced (Sodium Hydroxide Concentration = 0.10M)

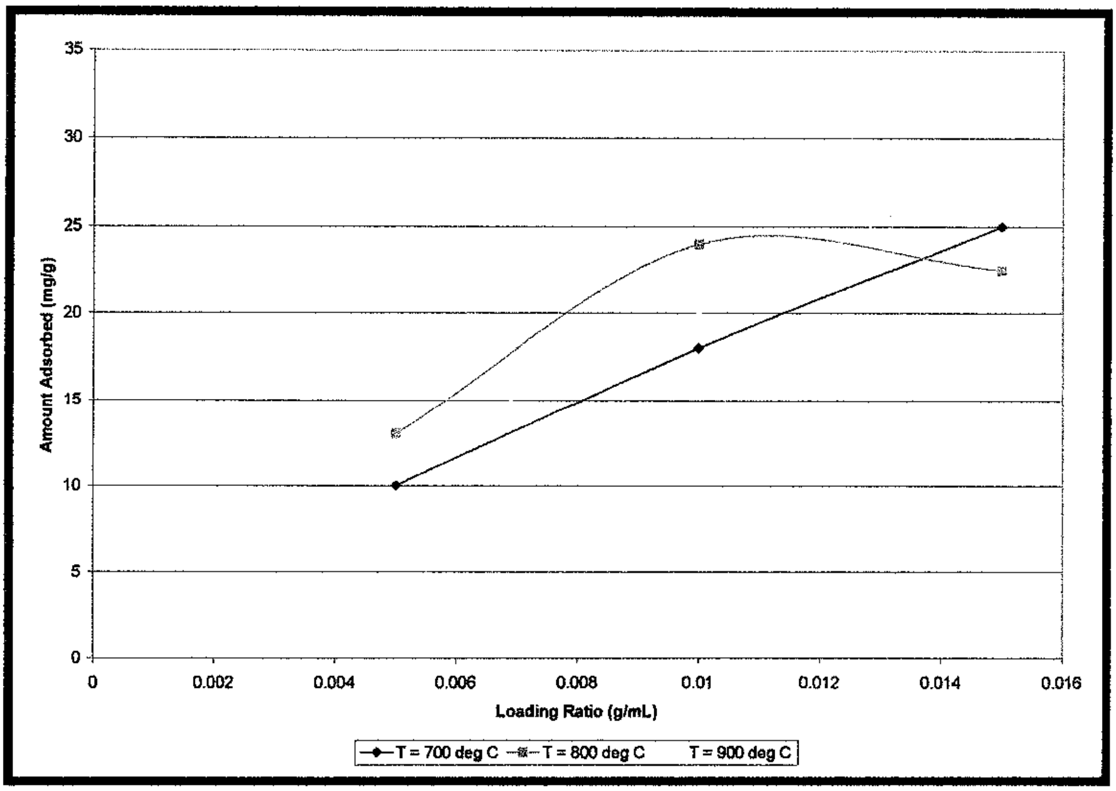

Figure 4.17 Effects of Various Loading Ratio on the Adsorption Capacity of Activated Carbon Produced (Sodium Hydroxide Concentration = 0.15M)

4.9 Study of Adsorption Isotherm

It is worth noting that a fair amount of information is necessary to correctly use one of these isotherms to correctly predict the adsorption in a given system. Modeling the equilibrium data is fundamental for the industrial applications of activated carbon since it gives the information for comparison among the activated carbon under different operational conditions, designing and optimizing operating procedures. To examine the relationship between sorbed (q_e) and aqueous concentrations (C_e) at equilibrium, sorption isotherm models are widely employed for fitting the data of which the Langmuir and Freundlich equations are the most widely used. In order to construct the adsorption isotherm, the activated carbon undergoing adsorption process at different copper concentration was chosen as the data. Such activated carbon was carbonized at various carbonization temperatures and activated at various sodium hydroxide concentrations. To get the equilibrium data, initial copper concentrations were varied while the weight in each sample was kept constant at 0.5g of activated carbon, 24 hours of equilibrium periods for sorption experiments were used to ensure equilibrium conditions [Antunes, 2003]

The Langmuir isotherm has a theoretical basis and is given by the following equation.

$$\frac{1}{q_e}=\frac{1}{Q_m}+\frac{1}{bQ_m}-\frac{1}{C_e}$$

where

q_e = amount (mg) of copper per gram of activated carbon adsorbed at equilibrium

C_e = concentration (mg/L) of copper in solution at equilibrium

Q_m(mg/g) and b$(mg/L)^{-1}$ = Langmuir constants. They represent the maximum adsorption capacity for the solid loading and the energy constant related to the heat of adsorption.

The constant Q_m and b are the intercept and slope of the linear plot of the experimental data of Langmuir graph ($1/q_e$ versus $1/C_e$), respectively

The Freundlich isotherm equation gives K and n constant and it must be determined experimentally. If a log-log plot of q versus c is made, the slope is the dimensionless exponent n. The dimensions K depend on the value of n. This equation is sometimes used to correlate data for hydrocarbon gases on activated carbon.

$$q_e = KC_e^{\frac{1}{n}}$$

Figure 4.18, Figure 4.19 and Figure 4.20 shows a linear relationship of 1/qe versus 1/Ce for the adsorption of copper ions on activated carbon produced, on Langmuir isotherm. From the graphs, the Langmuir constants were obtained as indicated in Table 4.7. Q_m indicates the maximum adsorption capacity for the solid loading. The maximum adsorption capacity was 909.0909mg/g for activated carbon carbonized at 900°C and activated with 0.10M of sodium hydroxide. Figure 4.21, Figure 4.22 and Figure 4.23 represents the Freundlich isotherm. The Table 4.8 represents Freundlich constants indicating the adsorption capacity and adsorption intensity, K and n, respectively.

Lafi, 2000 represents comparison of experimental data of activated carbons with the Freundlich and Langmuir equations. The adsorption fit with the Freundlich equation and the data can be categorized under such model. The results from this study are tested against the known adsorption models they best follow Freundlich equations.

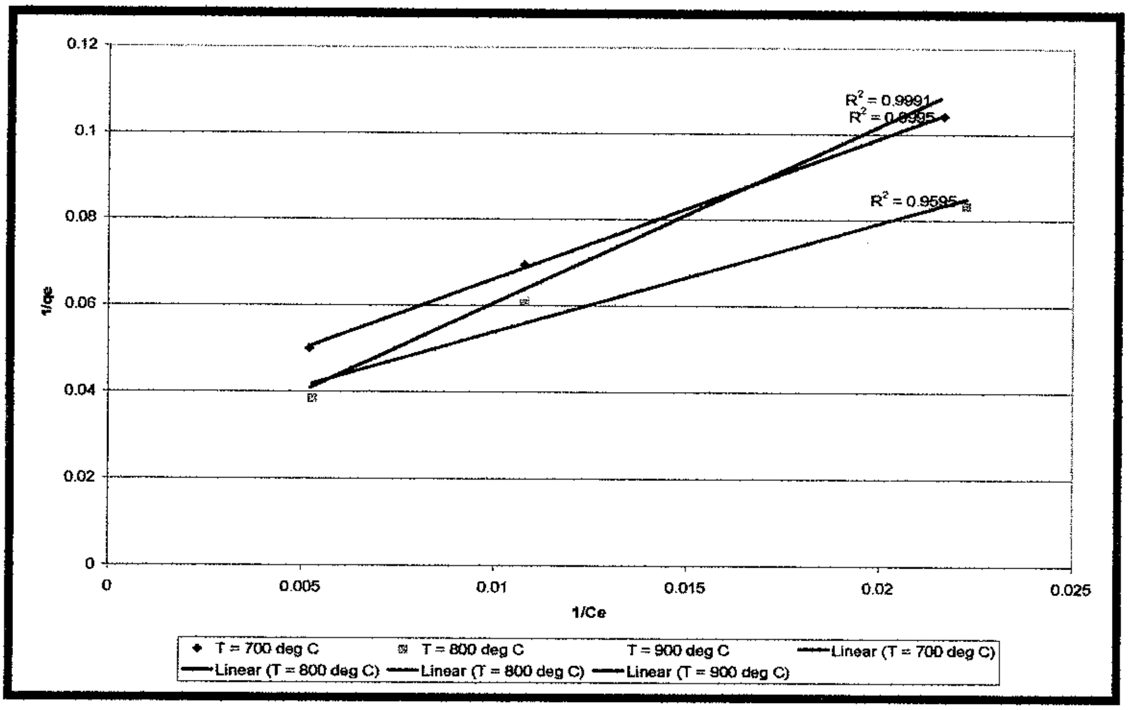

Figure 4.20 Langmuir Isotherm on the Adsorption Process for Activated Carbon Activated with 0.15M of Sodium Hydroxide

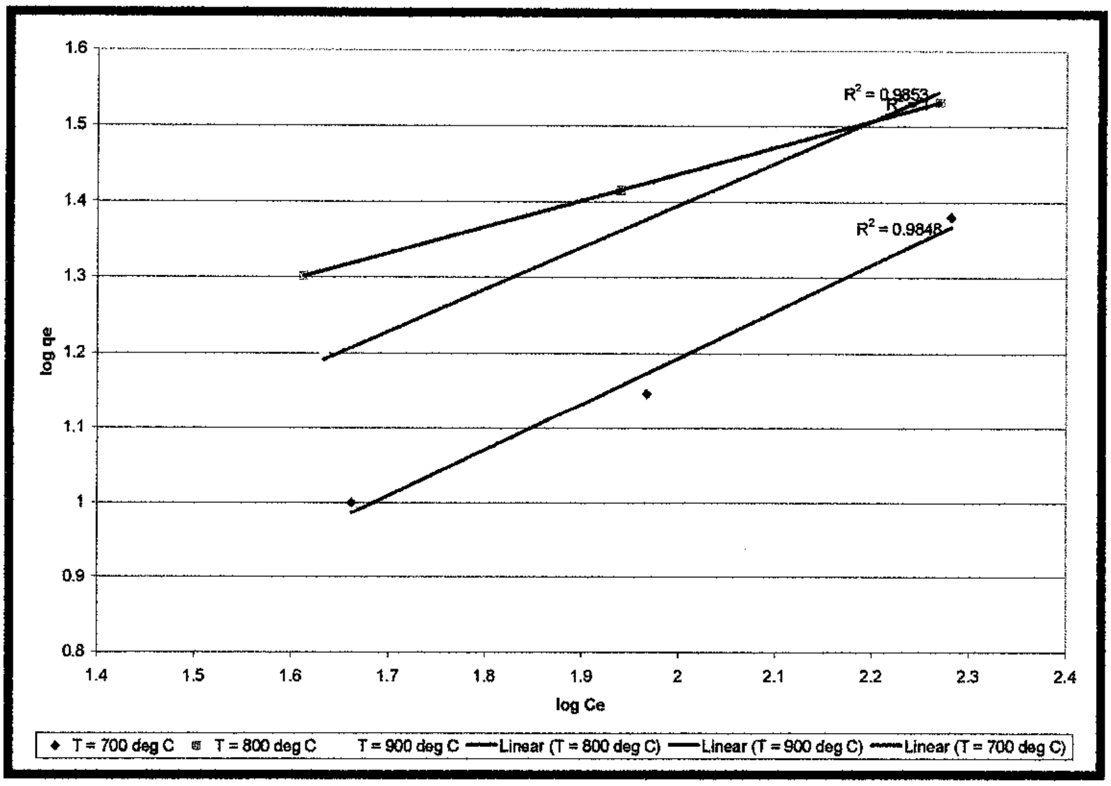

Figure 4.21 Freundlich Isotherm on the Adsorption Process for Activated Carbon Activated with 0.05M of Sodium Hydroxide

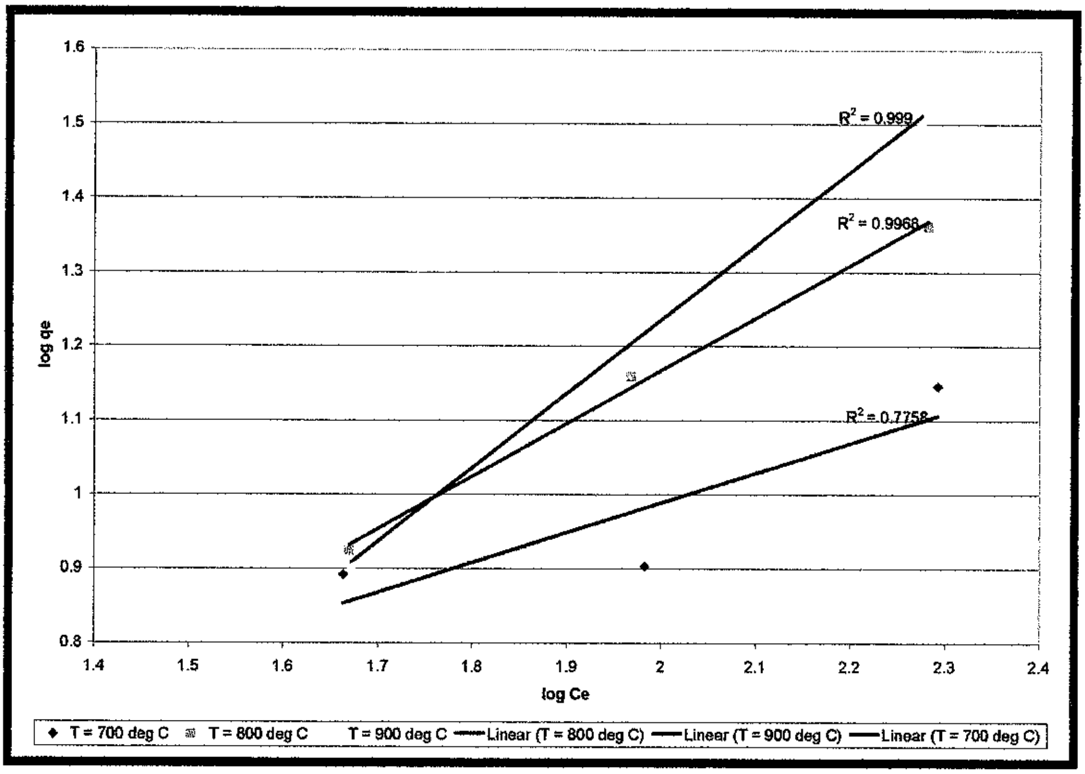

Figure 4.22 Freundlich Isotherm on the Adsorption Process for Activated Carbon Activated with 0.10M of Sodium Hydroxide

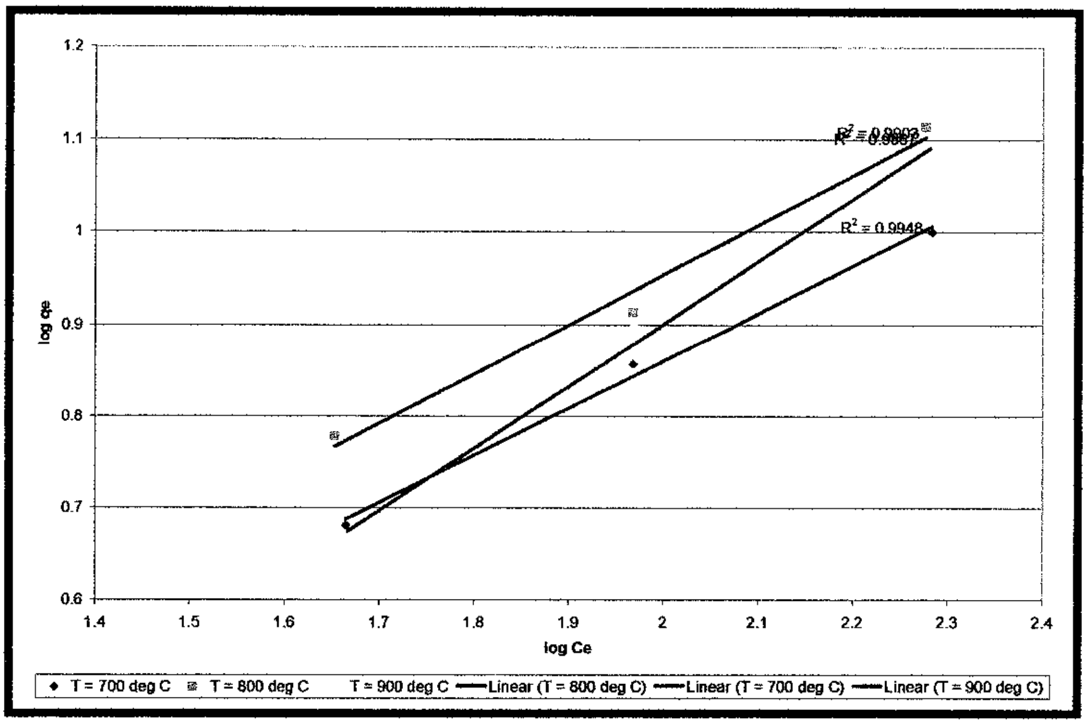

Figure 4.23 Freundlich Isotherm on the Adsorption Process for Activated Carbon Activated with 0.15M of Sodium Hydroxide

Table 4.7 Langmuir Constant for Adsorption of Copper Ions on Activated Carbon Produced at Various Carbonization Temperature and Chemical Activation Agent Concentration

Carbonization Temperature	Q_m (mg/g)	R^2
Chemical Activation with 0.05M of Sodium Hydroxide		
700°C	2.4564	0.9067
800°C	40.3225	0.9823
900°C	49.0196	0.9573
Chemical Activation with 0.10M of Sodium Hydroxide		
700°C	13.9276	0.6067
800°C	52.6318	1
900°C	909.0909	0.9992
Chemical Activation with 0.15M of Sodium Hydroxide		
700°C	29.9401	0.9995
800°C	35.0877	0.9595
900°C	51.8135	0.9991

Table 4.8 Freundlich Constant for Adsorption of Copper Ions on Activated Carbon Produced at Various Carbonization Temperature and Chemical Activation Agent Concentration

Carbonization Temperature	K	n	R^2
Chemical Activation with 0.05M of Sodium Hydroxide			
700°C	0.9169	0.6157	0.9848
800°C	5.4288	0.351	1
900°C	1.9213	0.5559	0.9853
Chemical Activation with 0.10M of Sodium Hydroxide			
700°C	1.5272	0.4024	0.7758
800°C	0.5490	0.7138	0.9968
900°C	0.1727	0.9995	0.999
Chemical Activation with 0.15M of Sodium Hydroxide			
700°C	1.3564	0.5147	0.9947
800°C	1.5118	0.5385	0.9903
900°C	0.7044	0.677	0.9902

CHAPTER 5
CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

Production of activated carbon by chemical activation has been attempted employing palm oil shells as the raw materials. The utilization of the produced activated carbon for heavy metal removal was proven workable. The objective of the study are to produce activated carbon from waste palm oil shells by carbonization and chemical activation using sodium hydroxide and to study the adsorption capacity various copper concentrations, pH and loading ratio. Carbonization temperature had significant effect on pore volume evolution. The higher the carbonization temperature, the greater the solid density and the lesser the apparent densities, resulting the development of porosity Thus, the activated carbon produced at carbonization temperature of 900°C indicates better adsorption capacity, 36mg/g. Chemical activation with sodium hydroxide concentration of 0.05M produces an activated carbon with better performance and activation effect. Lower sodium hydroxide concentrations consistently produced a higher yield of product with a much larger external surface area. The best condition for copper ions removal is at 200ppm of copper concentrations and pH12. The maximum adsorption is 168mg/g, given by activated carbon produced at the carbonization temperature of 900°C and sodium hydroxide concentration of 0.05M. The adsorption characteristics were represented in both Freundlich and Langmuir isotherm. However, Freundlich adsorption isotherm fits the adsorption characteristics of the activated carbon produced. As a conclusion, the best parameters have been obtained from this study to produce activated carbon from the waste of palm oil shells.

5.2 Recommendations

The study indicates the significance of using waste palm oil shells to produce activated carbon for wastewater treatment purposes. Thus, some recommendations have been proposed for future work:

i. To conduct the analysis on activated carbon using thermagravimetric analyzer (TGA), AUTOSORB-1, BET Surface Area and etc. From the equipment, we will be able to maintain the proximate analysis such as fixed carbon content and the surface area of the activated carbon.

ii. To vary more parameters on the preparation of activated carbon such as carbonization time, chemical activation temperature, various chemical activation agent, method of preparation (carbonization – chemical activation and vice versa) and etc

iii. To vary more parameters on the adsorption capacity such as the adsorption time, the and etc

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APPENDIX A

Gantt Chart

No	Detail/Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Selection of Project Topic	▨													
	-Propose topic														
	-Topic assigned to students														
2	Preliminary Research/Design Work		▨	▨											
	-Introduction														
	-Objective														
	-List of reference/literature														
	-Project planning														
3	Submission of Preliminary Report (Initial Proposal)			✓											
4	Project Work				▨	▨	▨	▨							
	-List of reference/literature														
	-Practical/laboratory work														
5	Submission of Progress Report								✓						
6	Project Work Continue								▨	▨	▨	▨			
	-Practical/laboratory work														
7	Submission of Dissertation Final Draft												✓		
8	Oral Presentation													✓	
9	Submission of Project Dissertation														✓

✓ Suggested milestone

APPENDIX B

Calibration Curve Obtained from Conductivity Meter

a) At Various Concentrations of Copper Solutions

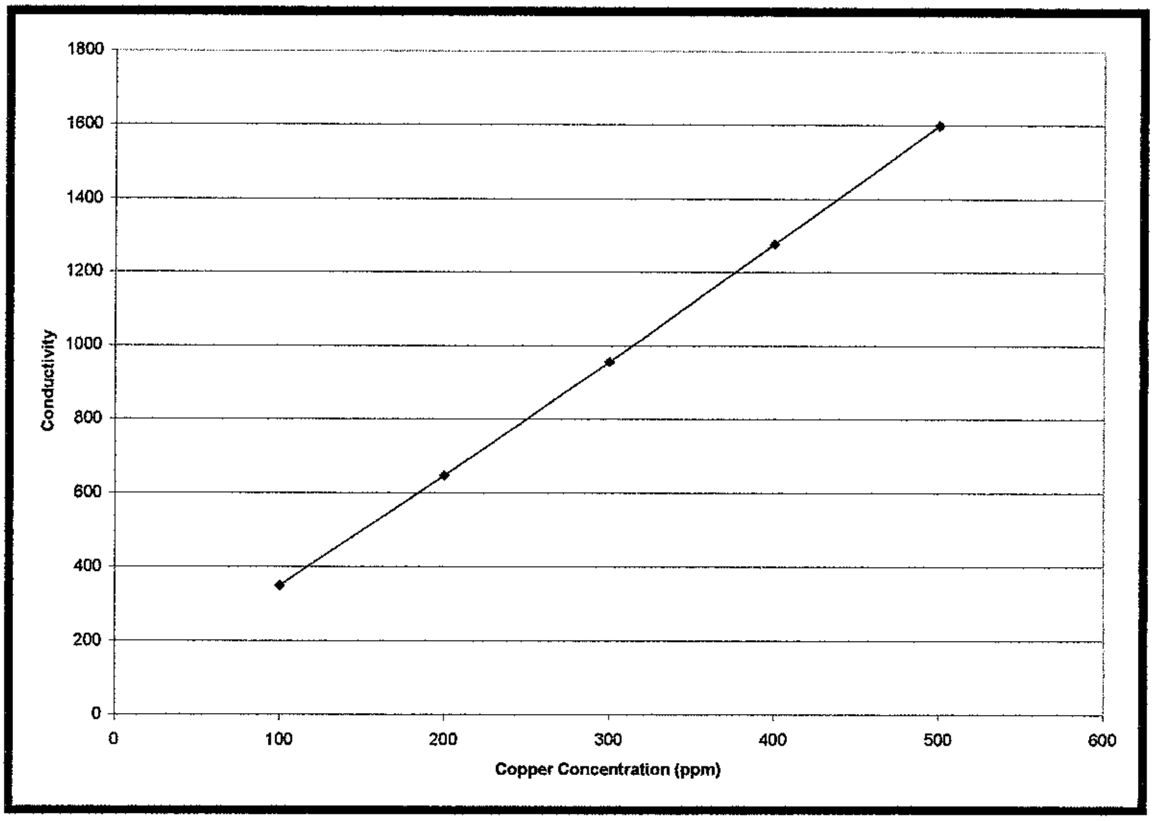


Figure B1: Calibration Curve at Various Concentrations for Copper Solutions

b) At pH 3 (acidic)

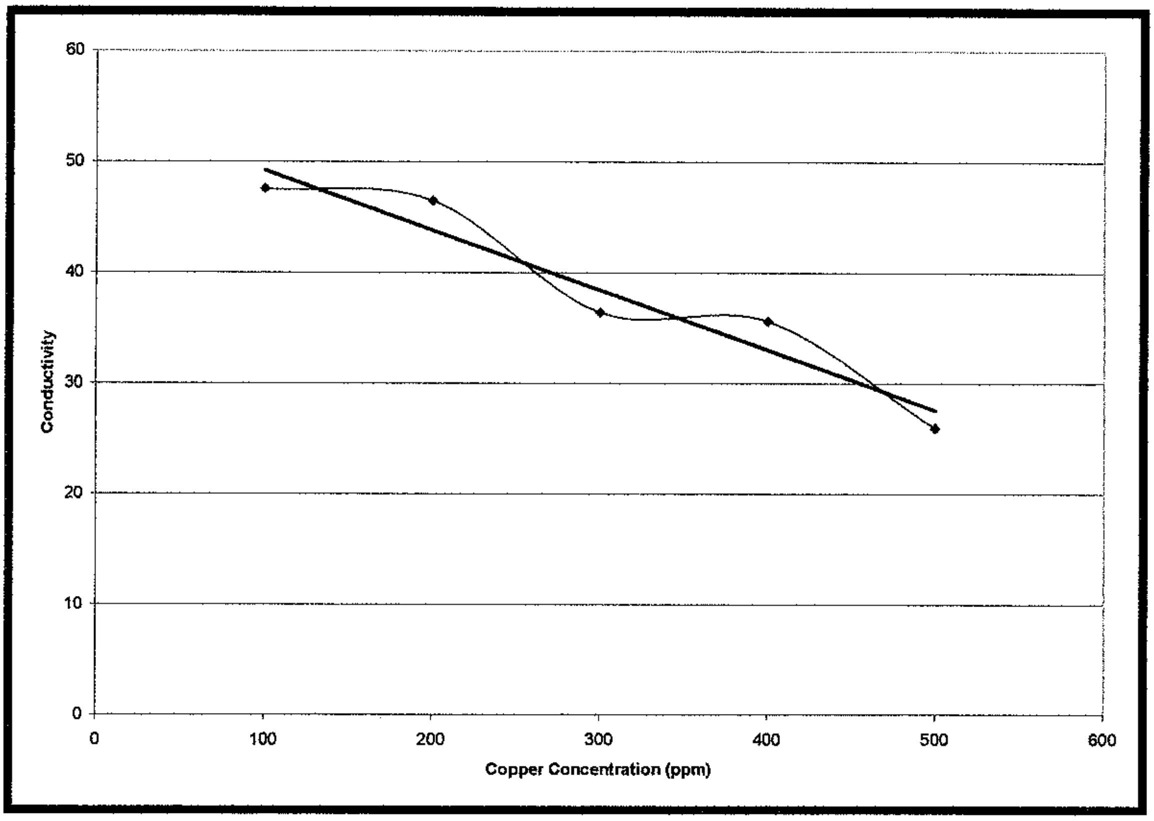


Figure B2: Calibration Curve at pH 3 (acidic) from Conductivity Meter

c) At pH 12 (basic)

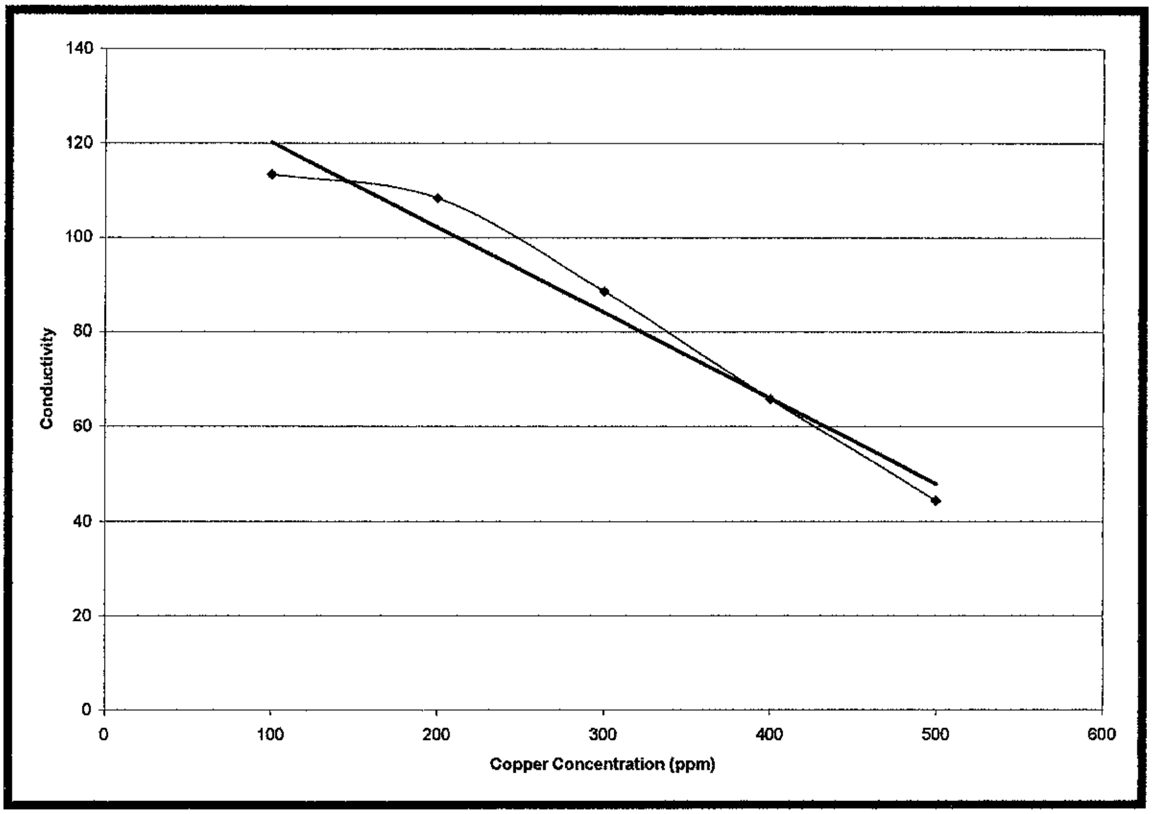


Figure B3: Calibration Curve at pH 12 (basic) from Conductivity Meter

APPENDIX C

Calculation in Preparing $Cu(NO_3)_3.3H_2O$ Solutions at Various Concentrations

$100\text{ppm} = 100\frac{\text{mg}}{\text{L}}$

Dalam 1L = 100mg Cu^{2+} ion

Dalam 1 mol $Cu(NO_3)_3.3H_2O$ [241.6g] = 64g Cu

For 50ppm

$\frac{50\text{ppm}}{64\text{g}} \times 241.6 = \underline{188.75\text{mg}}$

For 100ppm

$\frac{100\text{ppm}}{64\text{g}} \times 241.6 = \underline{377.5\text{mg}}$

For 200ppm

$\frac{200\text{ppm}}{64\text{g}} \times 241.6 = \underline{755\text{mg}}$

For 300ppm

$\frac{300\text{ppm}}{64\text{g}} \times 241.6 = \underline{1132.5\text{mg}}$

For 400ppm

$\frac{400\text{ppm}}{64\text{g}} \times 241.6 = \underline{1510\text{mg}}$

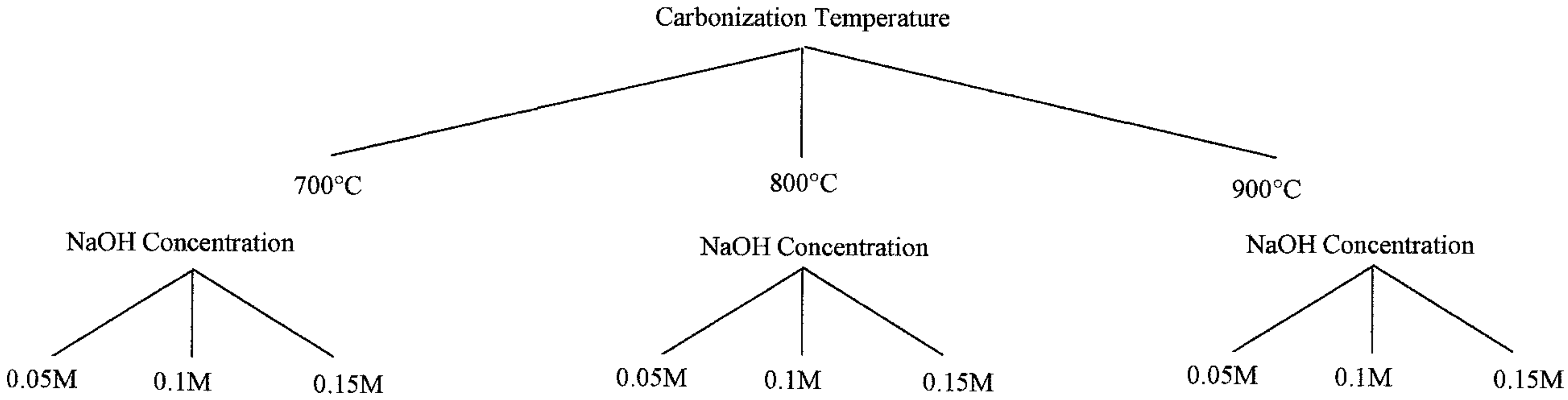
For 500ppm

$\frac{500\text{ppm}}{64\text{g}} \times 241.6 = \underline{1887.5\text{mg}}$

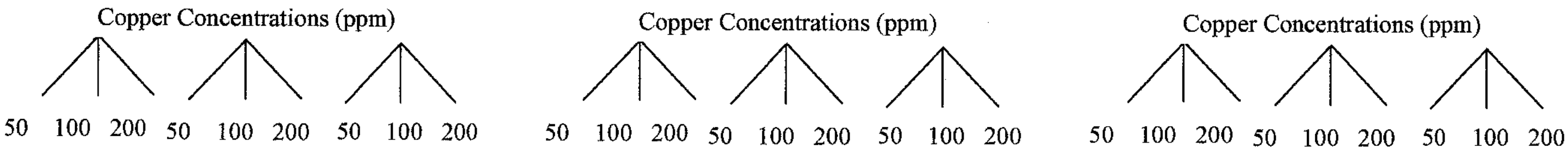
APPENDIX D

Sample Preparation Tree Diagram

A. Preparation of Activated Carbon



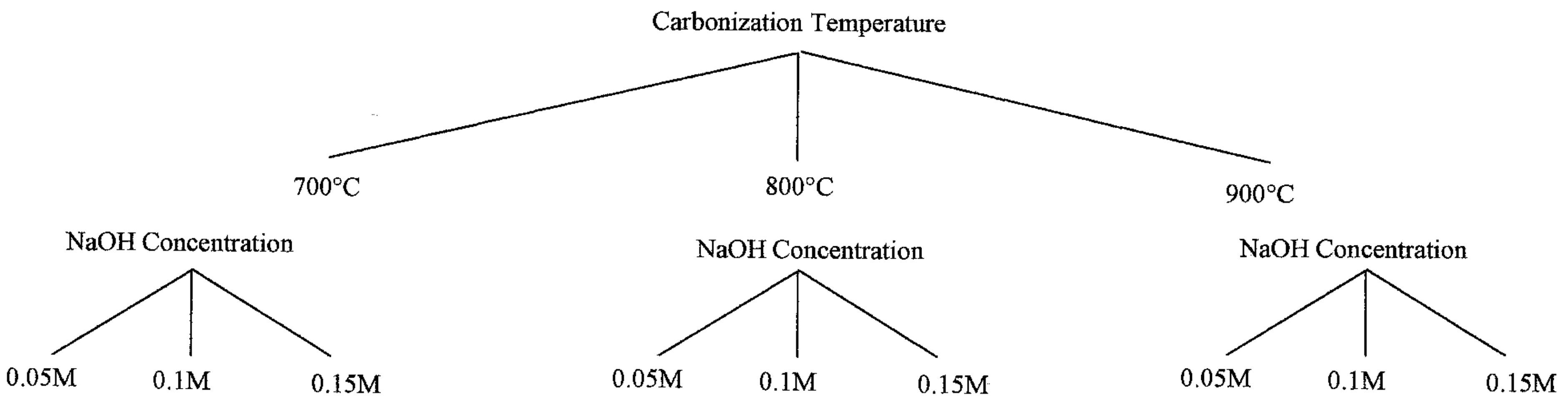
B. Adsorption Testing



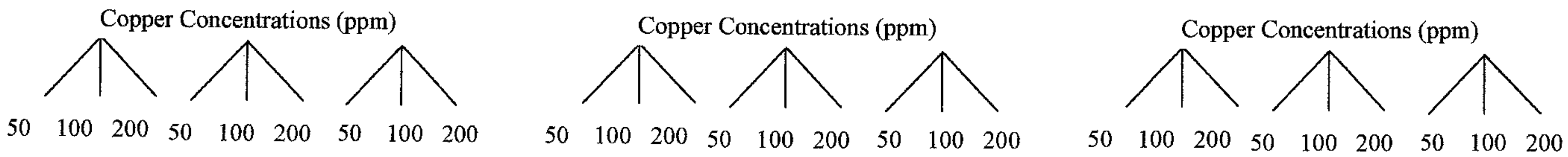
The copper concentrations that give the maximum adsorption capacity is going to be used for the adsorption capacity experiment on various pH and loading ratio

contd..

A. Preparation of Activated Carbon



B. Adsorption Testing



The copper concentrations that give the maximum adsorption capacity is going to be used for the adsorption capacity experiment on various pH and loading ratio

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