REMOVAL OF PHENOL FROM THE AQUEOUS SOLUTIONS BY ADSORPTION ONTO ACTIVATED CARBON DERIVED FROM KAPOK (CEIBA PENTANDRA) HULL

by

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

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CERTIFICATION OF APPROVAL

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Approved by,

____
(AP IR Abdul Aziz B Omar)

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
Sept 2012

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.

ABDUL RAHIM BIN ZAINI

ABSTRACT

Phenols are one of the most toxic industrial pollutants and even at low concentration it is reported to affect water quality and is harmful to human health. For that reason, much interest has been seen to produce material for treating effluent from industry using natural resources and comes from cheaper raw materials. The objective of this research is to contribute in the search for less expensive adsorbents and their utilization possibilities for agriculture waste by-products such as kapok hull, for the elimination of phenol from aqueous solution. Malaysian kapok hull (KH) can be processed as a precursor to produce activated carbon and has a potential to remove organic compounds such as phenol in wastewater. For this research, activated carbon prepared from Kapok hull using chemical activation (impregnated by 1M NaOH and thermally treated at 550°C) is applied. Isotherm studies were carried out to evaluate the effect of pH (2-10) and initial phenol concentration (25-200 mg/L). Field Emission Scanning Electron Microscope (FESEM) and FTIR are used to study the pore structure and functional groups obtained of the active carbons respectively whereas UV-Vis Spectrophotometer is used to determine the adsorption capacity of the activated carbon towards organic pollutant. As the concentration of adsorbate increases, adsorption capacity increases. The adsorbent exhibited good sorption potential at pH range of (3-7).

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ABBREVIATIONS AND NOMENCLATURES

RKH	Raw Kapok Hull
KHAC	Kapok Hull Activated Carbon
FSEM	Field Emission Scanning Electron Microscopy
FTIR	Fourier Transform Infrared Spectroscopy
NaOH	Sodium Hydroxide
HCl	Hydrochloric Acid
FBAU	Fixed Bed Activation Unit
US EPA	United States Environmental Protection Agency

CHAPTER 1

INTRODUCTION

1. 1 Background of study

Phenols exist in different concentrations in wastewater disposed from many industrial processes due to the rapid development of chemical, petrochemical and oil refining industries over the past several decades. Many industrial wastes contain phenolic compounds are difficult or impossible to be removed by conventional biological treatment process (Ibrahim et al., 2010). In the past several decades, extensive research has been conducted to develop innovative and promising adsorbent materials to deal with treatment problem of contaminate industrial effluents (Castilla et al., 2008)

Phenols are major pollutants of industrial processes including petrochemical industry, oil refining, coal refineries, phenol manufacturing, coke conversion, pharmaceutical, resin manufacturing plants and etc (Ibrahim et al., 2010). It is one of the most toxic pollutants, and even at low concentrations it is reported to have significance not only in aquatic ecosystems but also in the human body. Phenolics constitute the 11th of the 126 chemicals which have been designated as priority pollutants by the United States Environmental Protection Agency (Nayak et al., 2007).

Despite the availability of various abatement technologies for phenolic derivatives from wastewater, the adsorption process using activated carbon still remains the best due to their extended surface area, microporous structure, high adsorption capacity, and high degree of surface reactivity (Ahmaruzzaman & Gayatri, 2010). However, the use of commercial activated carbon based on relatively expensive starting material (coal and petroleum pitch) is not appropriate for most pollution control applications (Hameed, 2011). This has prompted a growing research interest for developing more suitable, efficient, cheap and easily accessible types of adsorbents, particularly from the waste materials.

From the earlier studies, it was revealed that activated carbon prepared from hulls of *C. pentandra* has good capacity for the adsorption of Copper and Cadmium (Rao, 2008). Shabudeen et al. (2006) reported that carbon prepared from waste Kapok hull was found to be cost effective in removing Rhodamine dye-B from aqueous solution. Referring to the potential of this activated carbon, the study of activated carbon prepared from C. pentandra hulls for the removal of phenol in aqueous solution is being studied. The present work focuses on producing activated carbon derived from kapok hull by employing the chemical treatment method using Sodium Hydroxide (NaOH). In this work, the suitability of the activated carbon for phenol adsorption is being studied.

1.2 Problem Statement

In recent years, interest has been focused on the removal of phenols from aqueous solution. Traditionally, biological treatment, activated carbon adsorption, solvent extraction, chemical oxidation and electrochemical methods are the most widely used methods for removing phenol and phenolic compound from wastewater (Ra, 2008). Despite the availability of the above mentioned processes for the removal of organic pollutants, the adsorption process still remains the best because of its simple design and easy operation (Ahmaruzzaman & Gayatri, 2010). The treatment of wastewater by adsorption with activated carbon is considered to be an effective method for the removal of phenol from waste solution because of its large surface area, micro porous nature, high adsorption capacity, high purity and easy availability (Hameed, 2011).

In spite of this advantage, it suffers from few advantages .Adsorption process is quite expensive due to the high cost of the activated carbon and its regeneration process produces additional effluent and results in considerable loss (10-15%) of the adsorbent (Jadhav & Vanjara, 2004). This has prompted a growing research interest in the production of low-cost alternatives to activated carbon. Taking these criteria into consideration, many researchers have investigated the adsorptive properties of unconventional adsorbents from locally agriculture wastes.

1.3 Objectives

The objectives of this project are:

1. To investigate the potential of kapok hull activated carbon (KHAC), an agriculture waste by-product, for the removal of phenol from aqueous system.

1.4 Scope of Study

This scope of research focuses on ability of activated kapok hull to remove phenol from an aqueous solution in batch process. To achieve these, a study will be carrying out with the following objective:

A. Development of activated carbon as adsorbent material from kapok hull by using chemical activation process and carbonization.
B. Perform surface characterization study on adsorbent material before and after treatment.
C. Experimental study on the effect of initial concentration and initial pH of the phenol solution to the adsorption capacity.
D. Develop the mathematical description of the adsorption equilibrium using Langmuir and Freundlich isotherm

CHAPTER 2

LITERATURE REVIEW

2.1 Organic Pollution in Wastewater

Ground and surface water contamination by organic pollutants from a variety of different activities, including industrial and agricultural sectors, becoming high concern by the authorities. Phenol is one of the most toxic industrial pollutants and even at low concentration it is reported to effect water quality and is harmful to human health. The content of phenols in industrial wastewater is usually in the range of 0.1-6800 mg/L (Busca, 2008). The World Organization Health (WHO) recommend the permissible concentration of phenol contents in portable waters is up to 0.1 µg/L and the US environmental Protection Agencies (USEPA) regulations calls for lowering phenol content in wastewater to less than 1 mg/L (Banat et al., 2000) .In Malaysia, the guidelines limit for phenol concentration to 0.001 mg/L in wastewater set by Malaysia Environmental Quality Act, 1974 for Standard A (0.001 mg/L) or standard B (1 mg/L) (DOE, 1974). Hence, the treatment of wastewater containing phenol is necessity.

2.2 Current and Past Technology in Phenol Removal from wastewater

Many technologies have been investigated for removing of phenolic compounds in wastewater. The conventional methods for phenol removal from water and wastewater include extraction, steam distillation, bacterial and chemical techniques, oxidation with ozon/hydrogen peroxide (Naas et al., 2010)), electrochemical oxidation (Poclaro and Palmas, 1997), reverse osmosis (Goncharuk et al., 2002) and photo catalytic (Koyama et al, 1994). However, in water treatment the most widely used method is adsorption onto the surface of activated carbons (Estevanho et al., 2006; Tomaszewska et al., 2004; Jung et al., 2001). Many researchers have shown that activated carbon is an effective adsorbent for organic compounds, specifically for phenolic compounds due to their extended area, microporous structure, high adsorption capacity and high degree of surface reactivity. Thought the use of commercial activated carbon is a well known adsorbent, the high cost and the need for a costly regeneration system of this type of adsorbent limits its use in developing countries.

In recent years, special attention has been focused on the use of natural adsorbents as an alternative to replace the conventional adsorbents. Hence, it is growing need to derive the activated carbon from cheaper and locally available material. Nowadays, the use of agricultural wastes as an absorbent material or a basic material to produce activated carbon is deemed the best option. This is because agricultural wastes are easily accessible, available at a low cost and are renewable. More importantly, it is sustainable.

Generally, the starting materials for the production of activated carbons are those with high carbon but low inorganic contents, e.g. wood, lignite, peat and coal (Gonzalez, 2004). Agriculture products have high carbon content and lower non organic content which make them good basic materials for the preparation of activated carbon. Many reports have appeared on the development of activated carbon from cheaper and readily available materials including activated carbon prepared from bagasse (Juang et.al, 2002), rubber seed coat (Rengaraj et.al, 2002), oil palm fibber (Tan et al. ,2007) and coconut husk (Tan, 2008) . So far, the research on producing the activated carbon from Kapok hulls for the removal of phenol has not been done.

2.3 Activated carbon

Activated carbon is a very porous material made from *carbonaceous* material which mean that any organic material with a high carbon content (Rafatullah et al., 2010). Activated carbon materials are effective in removing pollutants (both gaseous and liquid). The advantage of activated carbon materials as adsorbents is that the treated effluent is of high quality, the design of the process is simple, and the operation of the process developed or adopted is easy (Aly, 2010). There are two methods to prepare activated carbon which are physical and chemical activation. Apart from this method, chemical activation is preferable compared to physical activation because chemical activation is using lower temperature and shorter treatment time.

Figure 1 shows the *Ceiba petandra* (L.) Gaertn or locally known as kekabu or Kapok, which is cultivated in Southeast Asia, Malaysia, Sri Lanka, other parts of East asia and Africa (Abdullah , 2009). Kapok is a fast growing tree and becomes productive within 4-5 years. Yields increase for about 8 years and its economical lifespan is about 60 years (Ecocrop, 2011). In Malaysia, Kapok is among the indigenous crops and cotton obtained from the fruits has been used primarily as a core material for the beds and pillows while the trees are planted traditionally in village houses. The plants (rook, bark, gum and leaf) have high medicinal application except hulls. However, hulls obtained from the fruits are of no economic importance and are considered and agriculture waste. Kapok hulls may have potential as inexpensive sorbents, simple regeneration and easy in availability. (Rao et al. 2006) .A number of researchers has been reported using Kapok hulls as raw materials to produce activated carbon.

Figure 1: Hulls of kapok is the outermost layer of fruits

Earlier investigations on kapok hull were carried for the treatment of copper and cadmium containing wastewater (Rao et al, 2008). Kapok hull also has been employed for the removal of organic pollutans of dyes categories such as basic dyes (Shabudeen, 2006). However, to the best of knowledge, kapok hull has never been utilized for the removal of phenolic compounds from wastewater.

2.4 Adsorption

The analysis and fitting of isotherm model data to different isotherm models is a vital step in determining suitable model that can be used to describe the adsorption process. There are a few types of isotherm existing but the most commonly used ones are Langmuir and Freundlich isotherm. The Langmuir and Freundlich isotherm models are used to describe the relationship between the amount of phenol adsorbed and its equilibrium concentrations in solutions.

The Langmuir Adsoprtion Isotherm describes quantitatively the buildup of a layer molecule on an adsorbent surface as a function of the concentration of the adsorbed material in the liquid in which it is in contact. In a modified form, it can also describe a bi-layer deposition. The shape of the isotherm (assuming the (x) axis represents the concentration of adsorbing material in the contacting liquid) is a gradual positive curve that flattens to a constant value.

It is defined as:

$$q_e = \frac{abC_e}{1 + bC_e} \qquad Equation\ 1$$

Where q_e = mass of adsorbate adsorbed per unit mass of adsorbent, mg adsorbate / g activated carbon

a, b = empirical constant

C_e = equilibrium concentration of adsorbate in solution after Adsorption, mg/L

The constants in the Langmuir isotherm can be determined by plotting $\frac{1}{q_e} versus\ s \frac{1}{C_e}$ and making use of equation 3 rewritten as:

$$\frac{1}{q_e} = \frac{1}{Q_o} + \frac{1}{bQ_oC_e} \qquad Equation\ 2$$

Dimensionless constant R_L can be represented as :

$$R_L = \frac{1}{1 + bC_o}$$

where b (L/mg) refers to Langmuir constant and C_o is the initial concentration of the adsorbate (mg/L). R_L specify the adsorption isotherm either unfavourable $(R_L > 1)$, Linear $(R_L = 1)$, favorable $(0 < R_L < 1)$ or irreversible $(R_L = 0)$.

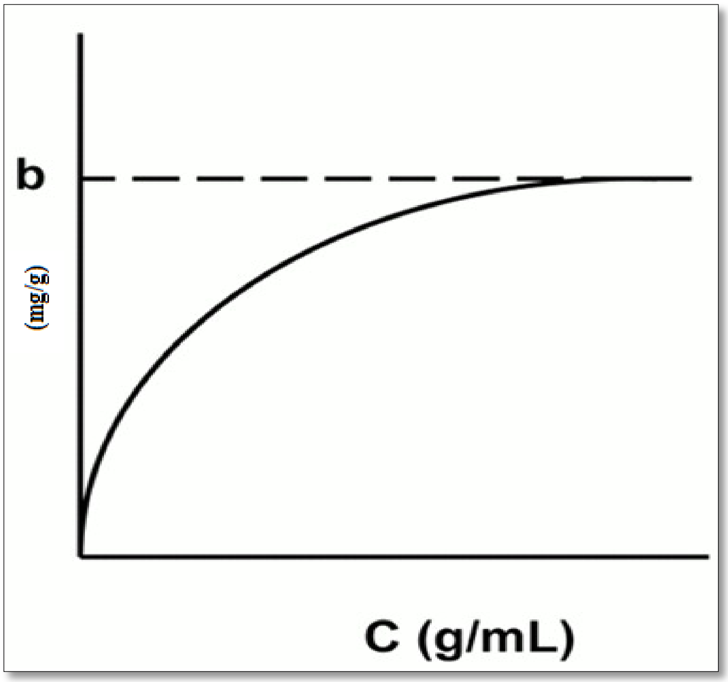


Figure 2: Langmuir Isotherm curve

The Freundlich Isotherm is an equation which states that the volume of gas adsorbed on a surface at a given temperature is proportional to the pressure of the gas raised to a constant power (McGraw-Hill Dictionary of Scientific & Technical Terms, 2003). It often represents an initial surface adsorption followed by a condensation effect resulting from extremely strong solute-solute interaction.

It is defined as:

$$q_e = K_f C_e^{\frac{1}{n}} \qquad Equation\ 3$$

Where q_e = mass of adsorbate adsorbed per unit mass of adsorbent,
mg adsorbate/g of activated carbon
K_f = Freundlich capacity factor,
$(\text{mg adsorbate/g activated carbon})(\text{L water /mg adsorbate})^{\frac{1}{N}}$
C_e = Equilbrium concentration of adsorbate in solution after adsorption mg/L
1/N = Freundlich Intensity Parameter

The constant in the Freundlich isotherm can be determined by plotting $\log q_e\ versus\ \log C_e$ and the equation 1 is rewritten as:

$$\log(q_e) = logK_f + \frac{1}{n}\log C_e$$

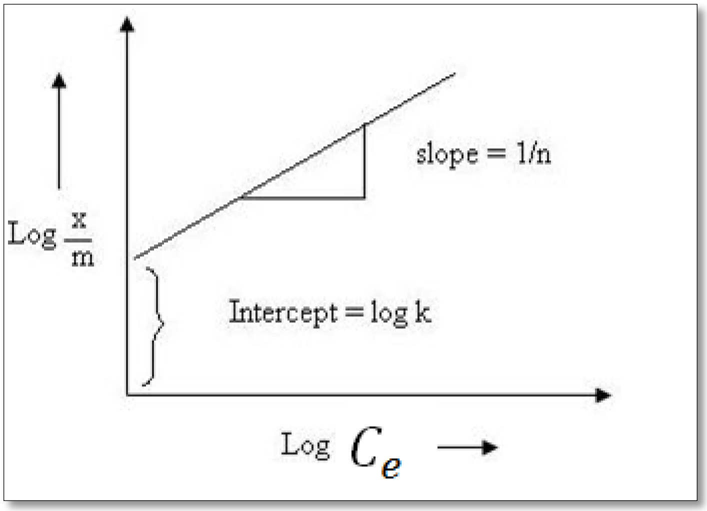


Figure 3: Freundlich Isotherm curve

CHAPTER 3

METHODOLOGY

3.1 Research Methodology

The research experimental works consists of two parts where the first part, is to prepare the kapok hull activated carbon (KHAC), and the second part it is used in the experiment for determining the adsorption capacity.

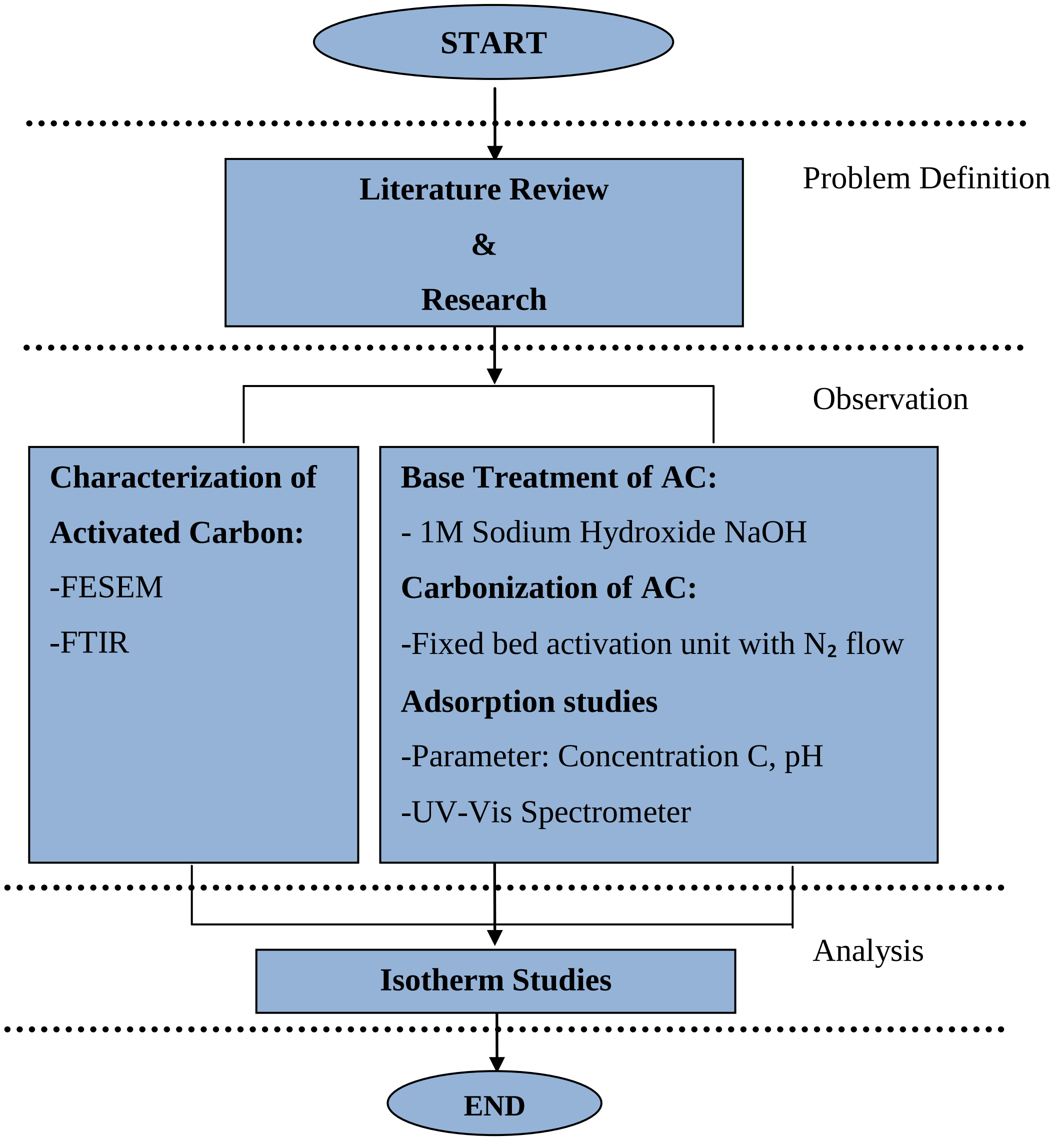


Figure 4 : Research Methodology

3.2 Experimental Procedure

3.2.1 Equipment and Chemicals

All reagents used were of analytical grade. The equipment & chemicals required for conducting experiment are shown in Table 1.

Table 1 : List of chemicals and equipment

Chemicals	**Description**
Phenol (R&M Chemicals)	Pollutant (Adsorbate)
Sodium Hydroxide (R&M Chemicals)	Used to modify the activated carbon and adjusting pH
Hydrochloric acid (Fisher)	Adjusting pH
Equipment	**Function**
Oven (Mermaid)	To dry activated carbon during modification process
Fixed Bed Activation Unit	To activate the activated carbon after being treated with Sodium Hydroxide.
Water Bath Shaker	Used for the adsorption experiment
UV-Vis Spectrometer (Shimadzu UV-3600)	To determine the initial and final concentration of phenol.

3.2.2 Preparation of Activated Carbon

The kapok hulls were collected from the local fields of Bota Kanan village, Perak, Malaysia. The hulls were cut into small pieces, washed several times with distilled water, dried in sunlight, and then undergo 60ºC for 24 hours in hot air oven. The purpose of washing and drying is to remove all the volatile components as moisture content in it.

The cleaned kapok hulls were passed through grinding and sieve at 1mm for further pretreatment. The dried material is subjected for base treatment using 1 M NaOH solution (ratio 1:10) for 24 hours at room temperature. After completed, the resulting sample was repeatedly washed to neutralize the pH and to remove the excess base with distilled water until virtually colorless. This effort was done to avoid possible interference of the soluble portion or color components in absorbance readings on the UV-visible spectrophotometer (Gayatri, 2010).

Subsequently, the sample was kept in hot air oven for 12 hours at 110°C. Then, the sample was taken in the Fixed Bed Activation unit and the temperature was gradually raised to 550°C under nitrogen flow of 150cm^3/min (Shabudeen, 2006). The sample was held for an hour before cooling to room temperature. Once it reached room temperature, air is introduced. The sample is noted as KHAC. It has been shown that lignocellulosic materials are favored for activation by chemical processes especially using NaOH as the chemical reagent, and since the proven composition of kapok hull has a cellulosic component, NaOH has been used as the activating agent (Freites et al., 2007).

3.2.3 Adsorption studies

The phenol used for adsorption study was procured from R&M Chemical and was 99.5% pure. Distilled water is used for the dilution of solution. The adsorption of phenol on activated carbon was determined by batch method, which is simple and easy to perform. Furthermore, it permits convenient evaluation of parameters that influence the adsorption process. The effect of initial adsorbate concentration and solution pH were investigated. In batch method, solutions of phenol (200 ml) with different initial concentration (25-200 mg/L) were added into 250 mL conical flasks. A fixed amount of the adsorbent (0.2 g) was added to phenol solutions and each sample was kept in water bath shaker of 120 rpm at 30 ±1ºC for 24h to reach equilibrium of the solid solution mixture. The pH of the solutions was not adjusted.

A similar procedure was followed for another set of conical flasks containing the same phenol without activated carbon to be use as a blank for the calibration curve purpose. The flasks were then removed from the shaker and the final concentration of phenol in the solution was analyzed using a double beam UV-vis spectrophotometer (Shimadzu, Japan) at 270 nm wavelength. The samples were filtered prior to analysis in order to minimize interference of the carbon fines with the analysis.

On the other hand, the adsorption of phenol by the KHAC was studied over a pH range of 3-10 at 30ºC and the studies were carried out for 24h. Initial concentration of phenol was 200 mg/L and the adsorbent dose was kept at 0.2 g. Hydrochloric acid (HCl) and sodium hydroxide (NaOH) were used to adjust the artificial wastewater pH by adding a few drops of diluted 0.1N HCL or 0.1N NaOH. The pH was measured by using pH meter.

3.3 Characterization

3.3.1 Field Emission Scanning Electron Microscopy (FESEM)

The raw and activated kapok hull (KH) was characterized in term of morphological characteristics and composition of activated carbon using Field Emission Scanning Electron Microscopy (FESEM) shown in figure 5. Then, a model FESEM SUPRATM 55VP operated at 5 kV was used for recording the images of the kapok hull. Under FESEM, the pore development can be easily observed due to the combination of higher magnification, larger depth of focus and great resolution.

Figure 5: Field Emission Scanning Electron Microscopy (FSEM)

3.3.2 Fourier Transform Infrared Spectroscopy (FTIR)

The samples were also analyzed using Fourier Transform Infrared Spectroscopy (FTIR model 8400S) shown in figure 6, which determines the functional groups present in the adsorbents. FTIR is used to obtain an infrared spectrum of adsorption. The kapok hull sample was put in a sample holder and infrared spectrum was recorded at the wavelength of 4000 to 400 cm^{-1}. FTIR is used to determine what surface functional groups are available in the sample tested. Characterization of sample is essential to give the information regarding to the structure and the presence of functional groups in a molecule interest. It reveals information on molecular vibrations that cause a change in the dipole moment of molecules.

Figure 6 : Fourier Transform Infrared Spectrophotometer

3.3.3 Ultraviolet-Visible (UV-Vis) spectroscopy

The concentration on phenol samples was evaluated using the UV-Vis spectrometric (shown in figure 7) to obtain the final concentration where the sample is estimated by measuring the residual concentration of phenol in the solution. The residual concentration of phenol over time by the kapok hull activated carbon adsorption reaction was analyzed using a double beam UV-vis spectrophotometer (Shimadzu, Japan) at 270 nm wavelength. The maximum absorbance, λ *max* was determined from the recorded spectra.

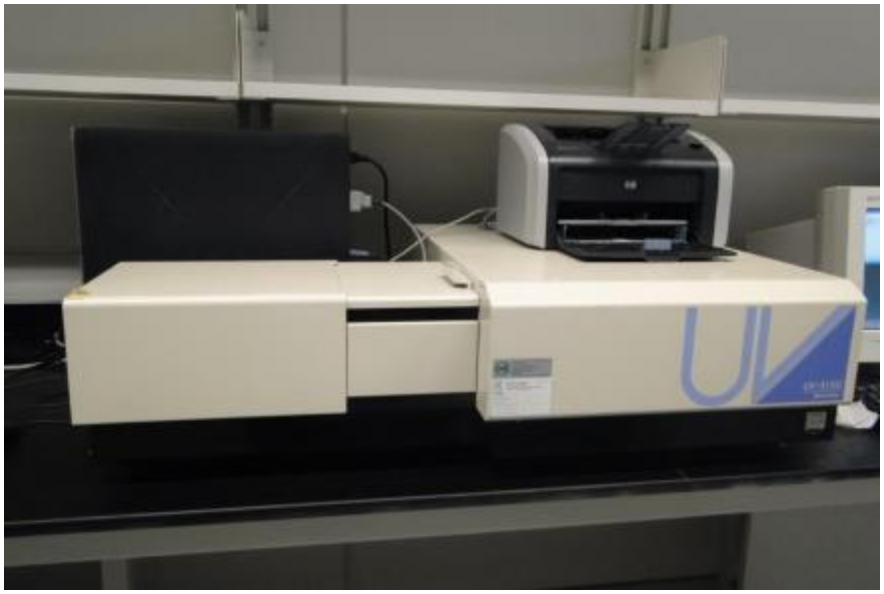


Figure 7 : UV-vis Spectrophotometer

3.4 Project Activities

Figure 8 : Raw Kapok Hull

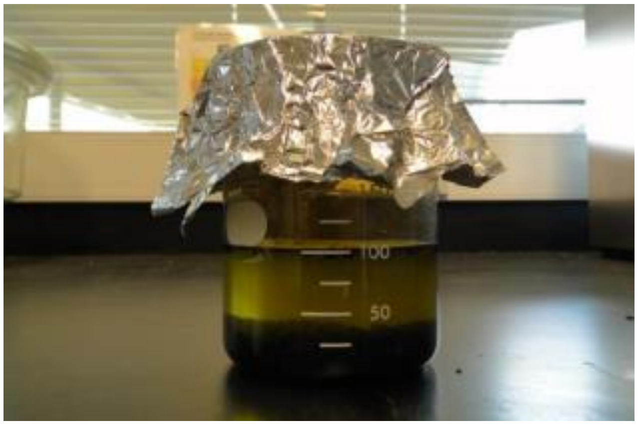


Figure 9 **:** Chemical activation with NaOH

Figure 10 : Oxidize kapok hull to undergo carbonization

Figure 11 : Oven

Figure 12 : Fixed Bed Activation Unit

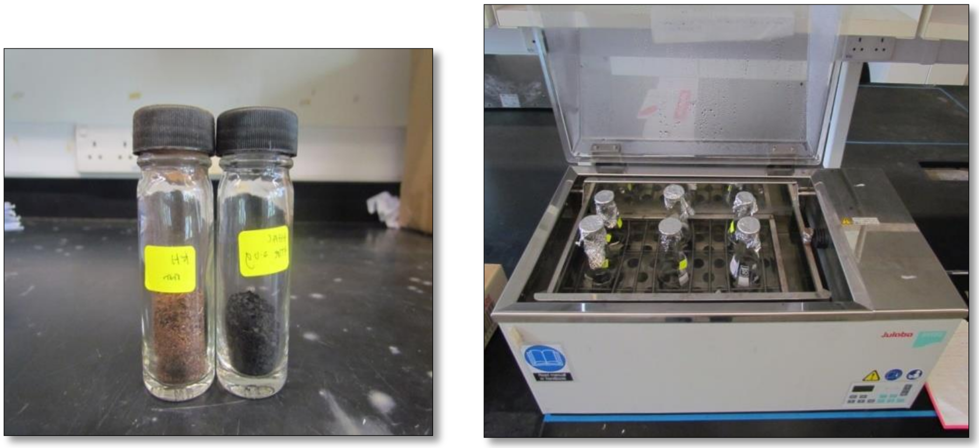


Figure 13 : Kapok Hull Activated Carbon and adsorption study inside water bath shaker

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Yield of Activated Carbon

Activation process efficiency is represented by the yield of activation of an AC. According to Mohammadi (2010), yield of AC is the amount of activated carbon at the end of activation process. Table 2 shows the results of percentage weight loss for activated carbon during carbonization at 550ºC in a fixed bed activation unit. Four crucibles containing 10g of impregnated kapok hull were carbonized by using fixed bed activation unit. The kapok hull samples before carbonization and the final product (after chemical activation) were weighed using an electronic weighing balance after drying to determine the final product yield. Activation yield from this research was calculated by using equation 4. It can be seen that the percentage of AC obtained at a fixed time during carbonization decreased with increase in temperature. This is due to the fact that as the temperature increases, the degree pyrolysis increases and more of the non carbonaceous volatile materials are removed from the rest of the char. In the other words, this is caused by the released of volatilization of raw material components and loss of moisture (Chandra et al., 2009).

$$\% \, Weight\ Loss = \frac{Initial\ weight - Final\ Weight}{Initial\ Weight} * 100 \qquad \text{Equation 4}$$

Table 2: Percentage of activation yield at 550ºC for 2 hours

Sample No	Initial Weight (g)	Final Weight (g)	Percentage of Weight Loss (%)
1	10	4.4	56
2	10	4.6	54
3	10	4.6	54
4	10	4.7	57

4.2 Characteristics of the Adsorbent

4.2.1 Fourier Transform Infrared Spectroscopy

The infrared (IR) spectrum of phenol loaded adsorbent is shown in figure 14. The absorption at 3404 cm^{-1} indicates the corresponding to the overlapping of free hydroxyl of -OH and N-H (amino) group (Chen et al., 2002). The bands appearing at 1388 and 1535 cm^{-1} are ascribed to the formation of oxygen functional groups like a highly conjugated C=O stretching in carboxylic groups, and carboxylate moieties, respectively (Jia et al., 2000). The additional peaks at 1457 and 1118 cm^{-1} confirmed the presence of-C-O and –C-N linkages respectively (Krishnan et al., 2003). Due to the adsorption of phenol on the surface of KHAC, some prominent peak due to H-bonded -O-H stretch, C=O and C-O stretch of esters may be held responsible for the adsorption of phenol on the KHAC surface.

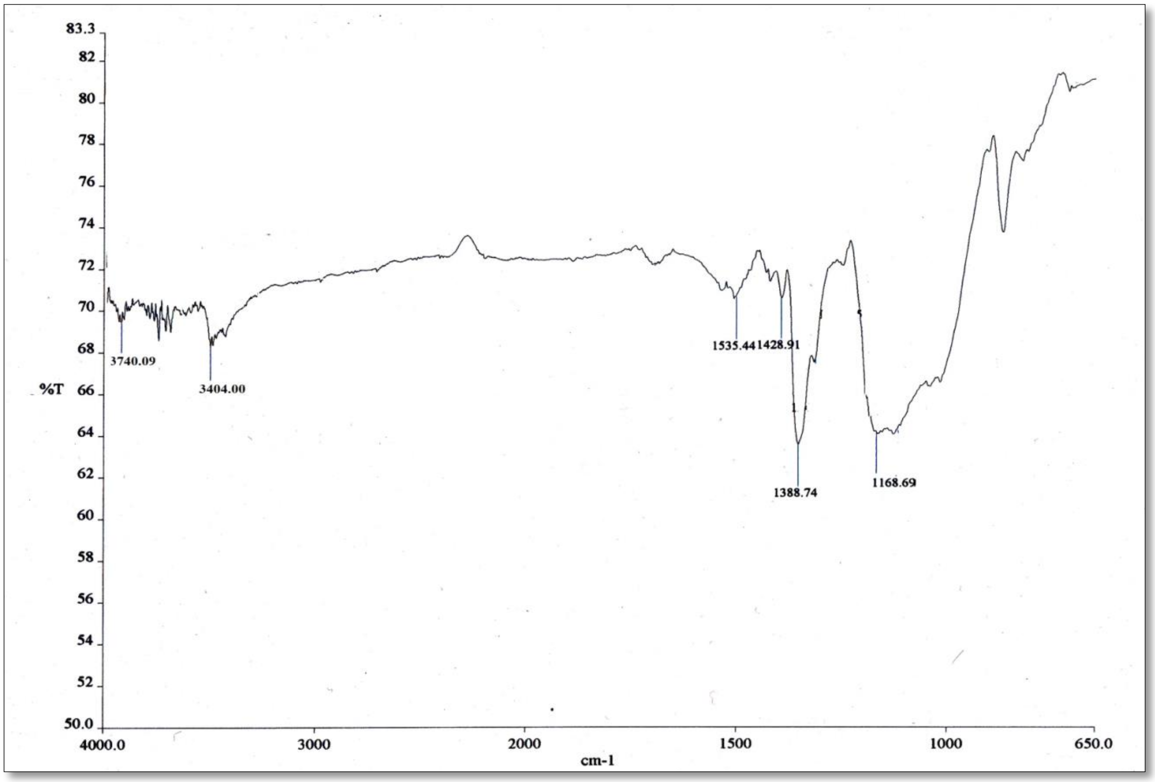
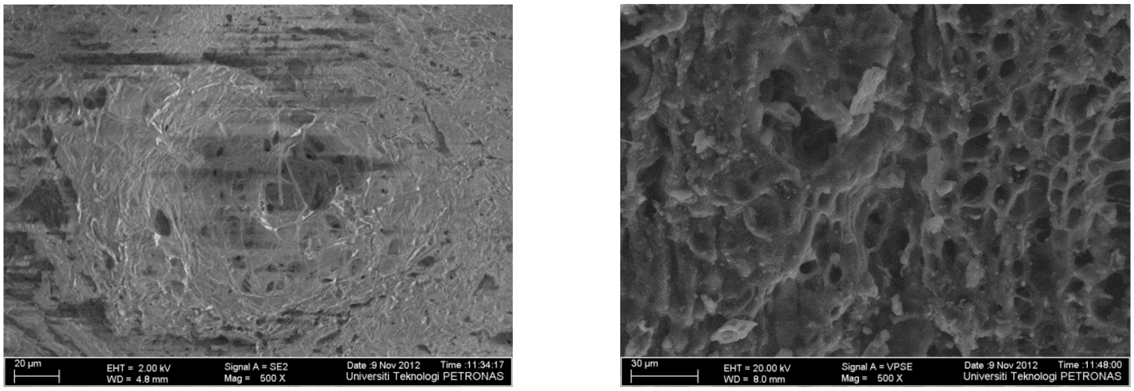


Figure 14 : FTIR Spectrum of *Ceiba pentandra* hull

4.2.2 Field Emission Scanning Electron Microscopy (FESEM)



(a) **(b)**

Figure 15: FESEM Photograph at 500x of (a) raw KH (b) KHAC

The morphological characteristic of raw kapok hull and modified kapok hull was observed by using Field emission electron microscope (FSEM). Figure 15 shows the surface texture and porosity of sample before and after chemical activation respectively. From the FSEM analysis, it was found that there were holes and cave type opening on the surface of the adsorbent, which would have more surface area available for adsorption (Ozacar and Sengi, 2005). The morphology of treated kapok hull (550ºC with 1M NaOH), showed that the surface was highly porous compared to the raw kapok hull (Fig. 15a) because the structure of RKH was destroyed by heat and converted to very small particles with large surface area. The porosity also increased compared to the raw kapok hull, because the base removed the inorganic compounds such as carbonate from the surface of adsorbent.

4.3 Adsorption Study

4.3.1 Calibration Curve

The ultraviolet (UV) region scanned is normally ranged from 200 to 400 nm and the visible portion is from 400 to 800 nm. The calibration curve was constructed to determine the adsorption performance and the phenol (adsorbent) was prepared at different concentrations. For each solution, the absorbance at the wavelength of strongest absorption (in this case 270 nm) using the same container for each one was measured. Then, calibration curve was able to plot in a graph of that absorbance against concentration. Table 3 below shows the concentrations of phenol vs. absorbance of each sample.

Table 3: Experimental Data for Calibration Curve

Phenol Concentration (ppm)	**Absorbance of each sample**
25	0.452
50	0.993
80	1.687
150	2.376
200	3.184

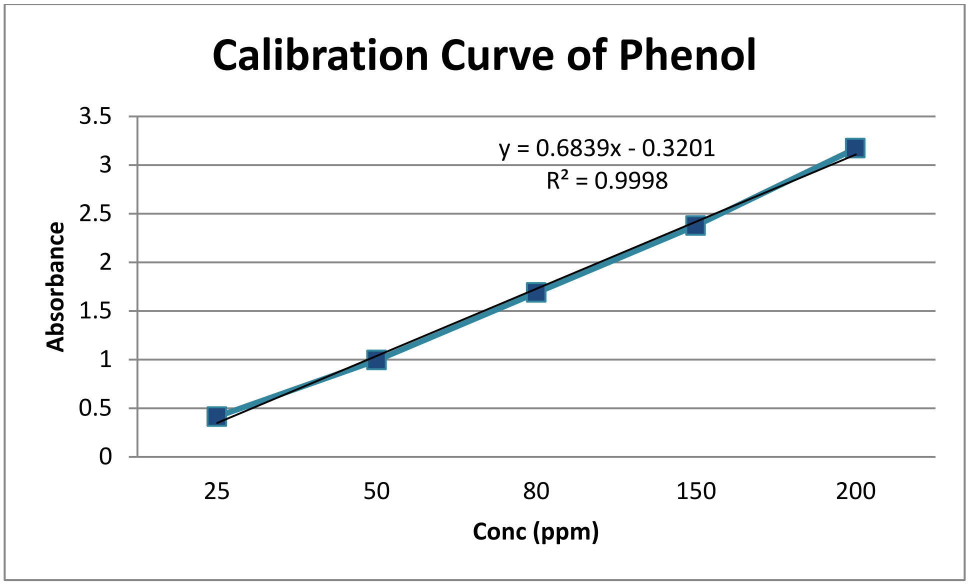


Figure 16: Calibration Curve of Phenol

From the graph in figure 14, the value of R^2, which indicates the deviation of the data points collected if compared to the straight line plotted is 0.9998. This mean the adsorbate solution prepared is suitable to be used throughout the whole experiment since the value of R^2 is near to 1.

4.3.2 Effect of contact time and initial concentration on phenol adsorption

Table 4 shows the initial and final concentration of phenol during adsorption experiment. The effect of agitation time on the extent of adsorption of phenol at various initial concentrations is shown in figure 4. Experimental studies were carried out with varying initial concentration of phenol ranging from 25 to 200 mg/l using 0.2 g/l of adsorbent dose and the pH of the solution was not adjusted. The amount of adsorption at equilibrium, q_e (mg/g) and the percent adsorption (%) was computed using the relation (Gayatri, 2010):

$$q_e = \frac{(C_o - C_e)V}{W} \qquad Equation\ 4$$

where C_o and C_e (mg/L) are the liquid-phase concentrations of phenol at initial and equilibrium, respectively. V(L) is the volume of the solution, and W (g) is the mass of dry adsorbent used. The effect of C_o on the extent of adsorption on KHAC as a function of time is shown in Fig. 4.

Table 4: Initial and Final Concentration of Phenol

Time (h)	**Initial Concentration (mg/L)**				
	25	**50**	**80**	**150**	**200**
1	17.431	31.361	60.222	109.907	108.803
2	15.265	28.402	46.934	86.574	105.19
3	9.943	24.941	42.603	80.401	101.273
4	8.722	21.889	40.603	77.69	99.024
5	7.532	20.353	39.23	74.633	98.313
24	7.311	17.494	32.654	71.835	94.883

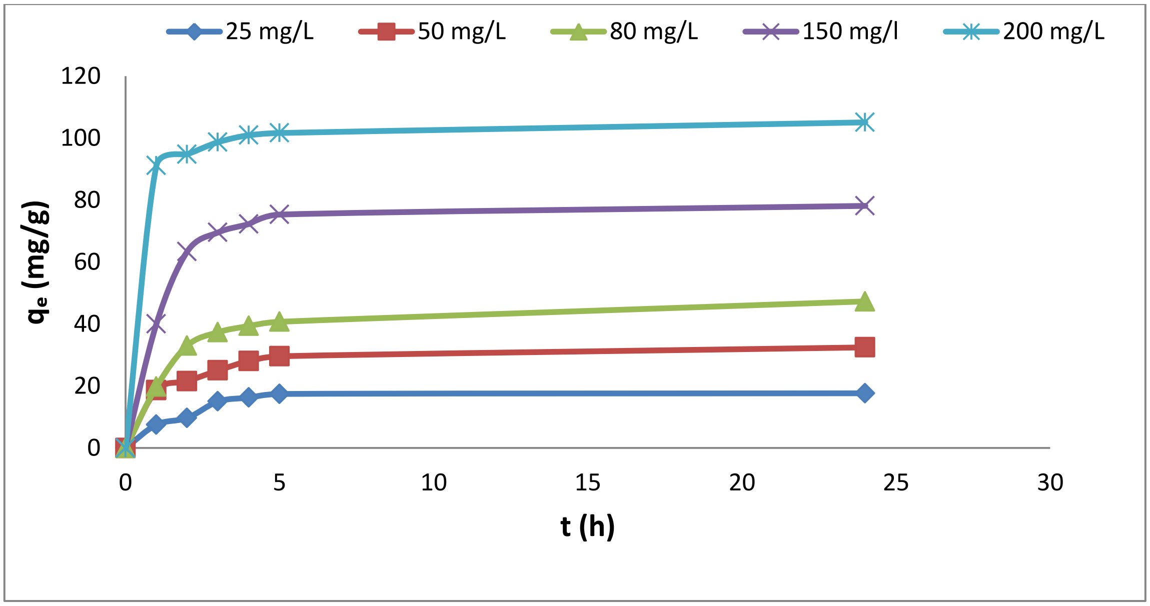


Figure 17: The variation of adsorption uptake with time at various initial concentrations

Table 5: Amount of phenol adsorbed per unit weight of KHAC

t (h)	**q_e (mg/g)**				
	25ppm	**50 ppm**	**80 ppm**	**150 ppm**	**200 ppm**
0	0	0	0	0	0
1	17.569	18.639	19.778	40.093	91.197
2	19.735	21.598	33.066	63.426	94.81
3	21.057	25.059	37.397	69.599	98.727
4	23.278	28.111	39.397	72.31	100.976
5	23.468	29.647	40.77	75.367	101.687
24	23.689	32.506	47.346	78.165	105.117

From this research, it is found that amount of phenol adsorbed, increases with increase in time and after a time interval of 5 h, it remains more or less constant. It is very clear from the results that the agitation time required for maximum uptake of phenol by activated carbon was dependant on the initial phenol concentration. The saturation curves rise sharply in the initial stages, indicating that there are plenty of readily accessible sites. Eventually, a plateau is reached in all curves indicating that the adsorbent is saturated at this level.

It can be seen from figure 17 that the contact time needed for phenol solutions with initial concentrations 25-200 mg/L to reach equilibrium was 5h. Almost, no remarkable improvement was observed after longer contact time. After this equilibrium period, the amount of solute adsorbed did not change significantly with time, indicating that this time is sufficient to attain equilibrium for the maximum removal of phenol from aqueous solution by kapok hull activated carbon. So, the optimum contact time was selected as 5h for further experiments. This data is important because equilibrium time is one of the parameters for economical plant application (Fan and Anderson, 2005). It was also seen that an increase in initial phenol concentration resulted in increase phenol uptake. This is in agreement with the finding that the rate of uptake of adsorbate is found to increase non-linearly with increasing concentration of solute (Jhadav & Vanjara, 2004). The removal curves are single, smooth and continuous, indicating the formation of monolayer coverage of the phenol molecules onto the outer surface of the adsorbent.

At any time the amount of phenol adsorbed per unit weight of adsorbed increased with increasing C_o. The C_o provides the necessary driving force to overcome the resistances to the mass transfer of phenol between the aqueous and the solid phases. The increase in C_o of phenol enhances the adsorption uptake of phenol (Jadhav et al, 2004).

4.3.3 Effect of solution pH on phenol adsorption

The pH of the aqueous solution is an important controlling parameter in the adsorption process. The pH was varied from 2.0 to 8.0 using different initial solution pH values by addition of 1N H_2SO_4 or 1N NaOH solution and the adsorbent was kept at 0.20 g. All the phenol reaction was conducted at an initial concentration of 200 mg/L at 30ºC.

Fig. 18 below shows that the phenol removal was maximum and unaffected when the initial ph of the phenol solution was in the range of 3-8 and thereafter it drops suddenly which decreases gradually with an increase in pH of the solution. A similar trend of pH effect was observed for the adsorption of phenol on activated carbon-commercial grade and laboratory grade (Srivastava et al., 2006). It is clear from Fig. 18 that the extent of adsorption is higher in acidic solution than in basic solution. The % adsorption of phenol decreases with an increase in alkalinity of the medium.

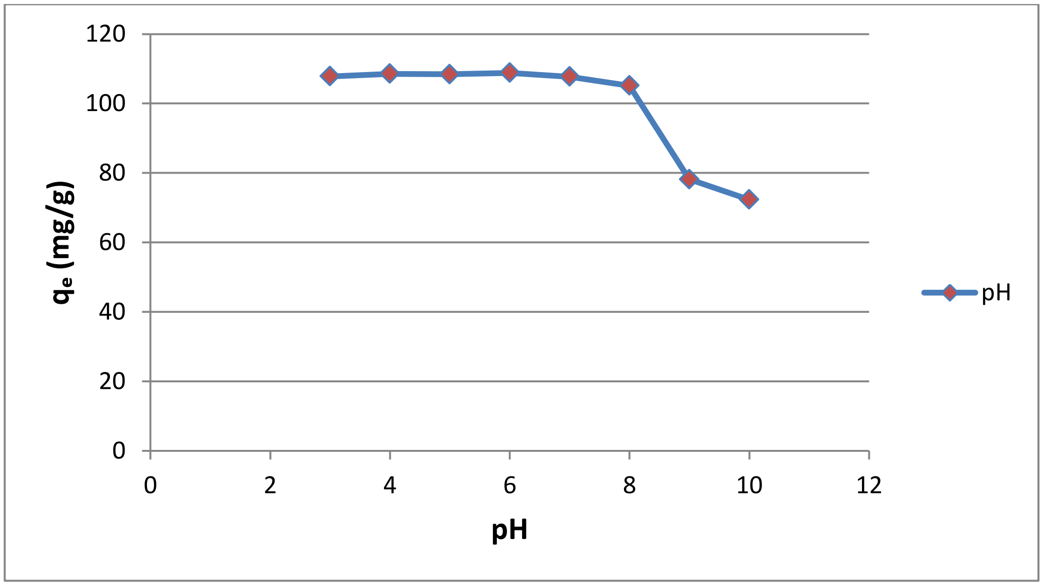


Figure 18: Effect of solution pH on adsorption of phenol onto KHAC

Generally, solution pH affects the surface charge of adsorbent and degree of ionization of the adsorbate (Aksu, 2003). Phenol as a weak acid compound with pKa≈9.89 is dissociated at pH>pK_a. At low solution pH, the adsorption affinity of KHAC toward phenol is high. This is due to existence of phenol in molecular form at low pH conditions. In contrast, as the solution pH increases, the concentration of the anionic form phenol and negative charge of KHAC increases. Therefore, the adsorption decrease at high pH values due to ionization of adsorbate molecules. The reason could be also due to the electrostatic repulsions between the negative surface charge and the phenolate-phenolate anions in solution (Castilla, 2004). While at acidic pH, the percentage removal was higher because phenol was undissociated and the dispersion interaction predominated.

4.3.4 Adsorption isotherm

Adsorption isotherm is basically important to describe how solutes interact with adsorbents, and is critical in optimizing the use of adsorbents. In addition, the analysis of the isotherm data is important to develop an equation which accurately represents the results and could be used for designing purposes. Adsorption isotherms of phenol on KHAC were obtained by stirring the various concentrations of phenol (25-200 mg/L) with 0.1 g of adsorbent. The Langmuir and Freundlich isotherm model along with regression coefficients were used to describe the relationship between the amount of phenol adsorbed and its equilibrium concentration in solutions. The adsorption isotherm thus obtained, are shown in Figs. 19 and 20 for Langmuir isotherm and Freundlich isotherm respectively.

It is seen from the linearity of plots in Figs 19 & 20 that adsorption of phenol on KHAC follow both Langmuir and Freundlich isotherm models with regression constant greater than 0.90. The values of Langmuir and Freundlich constants are listed in table 6.

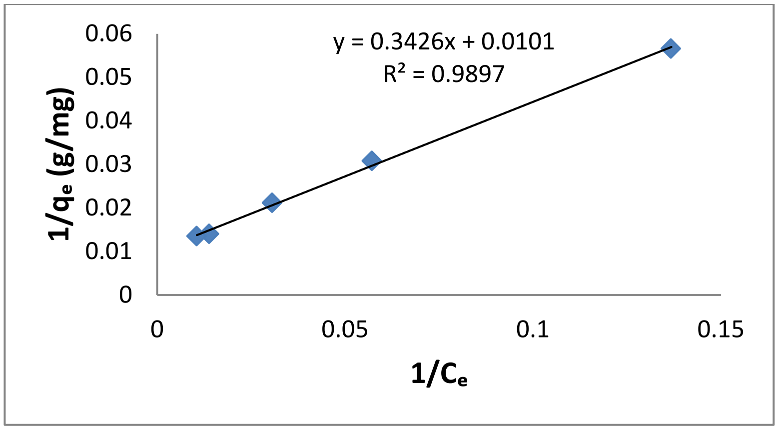


Figure 19 : Langmuir adsorption isotherm of phenol onto KHAC at 30ºC

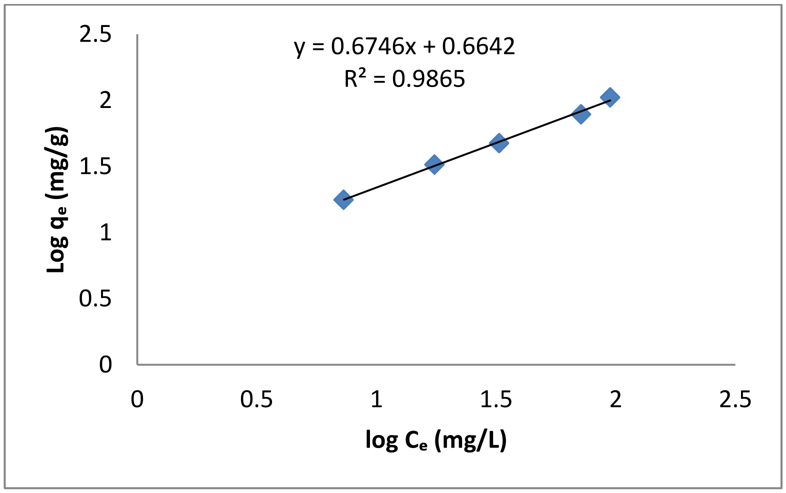


Figure 20 : Freundlich adsorption isotherm for phenol onto KHAC at 30ºC

Table 6 : Isotherm constants for adsorption of phenol onto KHAC at 30ºC

Isotherms	Parameters
Langmuir	
Q_o (mg/g)	91.95
b (L/mg)	0.023
R^2	0.9897
Freundlich	
K_f (mg/g(L/mg)$^{1/n}$)	4.615
N	1.482
R^2	0.9865

Since the value of ($R^2=0.9897$) nearer to 1 indicates that the respective equation better fits the experimental data. The experimental data yielded excellent fits within the following isotherms order: Langmuir>Freundlich, based on its R^2 values. All the evaluated equilibrium models gave good fit to the experimental data, it can be concluded that the Langmuir is the best models describing adsorption of phenolic compounds on the kapok hull activated carbon. This indicates the coverage of monolayer of phenol solution onto KHAC surface. The Langmuir isotherm model is valid for monolayer adsorption on the surface containing a finite number of identical sites even on adjacent sites. The model refers to homogeneous adsorption, with no transmigration in the plane of the surface (Vijayarghavan, 2006). In term of dimensionless separation factor, the separation factor R_L was found to be 0.179 and this again confirmed that the Langmuir isotherm was favorable under conditions used in this research.

The comparison of maximum monolayer adsorption capacities of different adsorbents obtained from different sources are listed in Table 7 along with the values obtained in the present study. Several authors have reported Freundlich and Langmuir constants for adsorption of phenol on various adsorbents. The Freundlich and Langmuir constants values obtained in some of these works, although under different environmental conditions, are compared with the values obtained in the present work in Table 7. It may be seen that the isotherm parameters differ widely in their values for activated carbons of different origins. Hence one should be cautious while using these values in design of adsorption isotherm.

Table 7 : Comparison of adsorption capacities of various adsorbents for phenol

Adsorbent	**Q_o (mg/g)**	**Reference**
Organo modified bentonited	333	(Basri et.al, 2009)
Granular Activated Carbon	165.80	(Kumar et al. 2007)
Bagasse fly ash	23.832	(Srivastava et al., 2006)
Data Seed Carbon	138.88	(Mane et.al, 2005)
CS/CA blended beads	156	(Kumar et.al, 2008)
A.*leucocephala* bark powder	94.33	(Min et al., 2011)
Kapok hull	91.95	Present study

CONCLUSION

The activated carbon prepared from agriculture waste can be effectively used as cost effective adsorbent for the removal of phenol from aqueous solutions. A maximum adsorption capacity of 91.95 mg/g was exhibited by KHAC. The solution pH played a significant role influencing the capacity of an adsorbent towards phenol molecules. The obtained results showed that the kapok hull activated carbon possessed a high adsorption capacity to remove phenol. The Langmuir model fits the experimental data very well indicating monolayer coverage of phenol molecules at the outer surface of kapok hulls. All the above results suggested that *Ceiba Pentandra* hull is an effective and alternative biosorbent, but also it is highly efficient for removal of phenol compound from aqueous medium in terms of high adsorption capacity, economically viable and locally available especially for the treatment of wastewaters in Malaysia.

RECOMMENDATION

There are a few recommendations proposed to improve this project. The BET and porosity analysis shall be done for strong evidence about the increasing of surface area and porosity of activated carbon after impregnation with NaOH. Besides that, the effect of other parameters such as carbon dosage, activation temperature, and chemical treatment shall be investigated to determine the optimum condition to prepare for excellent activated carbon. Detailed economic analysis would be required in any evaluation of these adsorbents. Perhaps in the further research, a comparison study on different method to develop the surface of activated carbon can be done. Finally it is recommended to run the adsorption study using different pollutant, both the organic compound and heavy metal ion to confirm whether it is applicable to be used for other contaminants.

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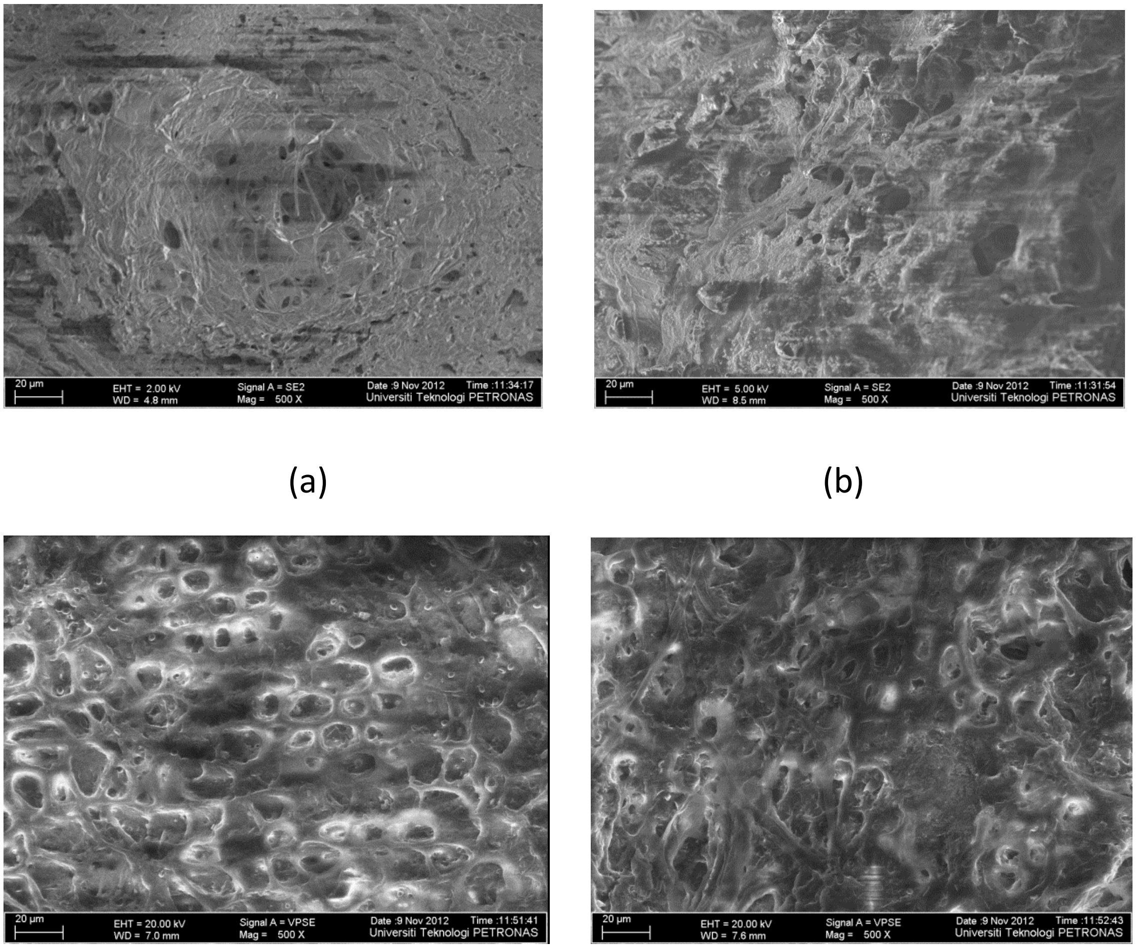
APPENDICES



(a) (b)

(c) (d)

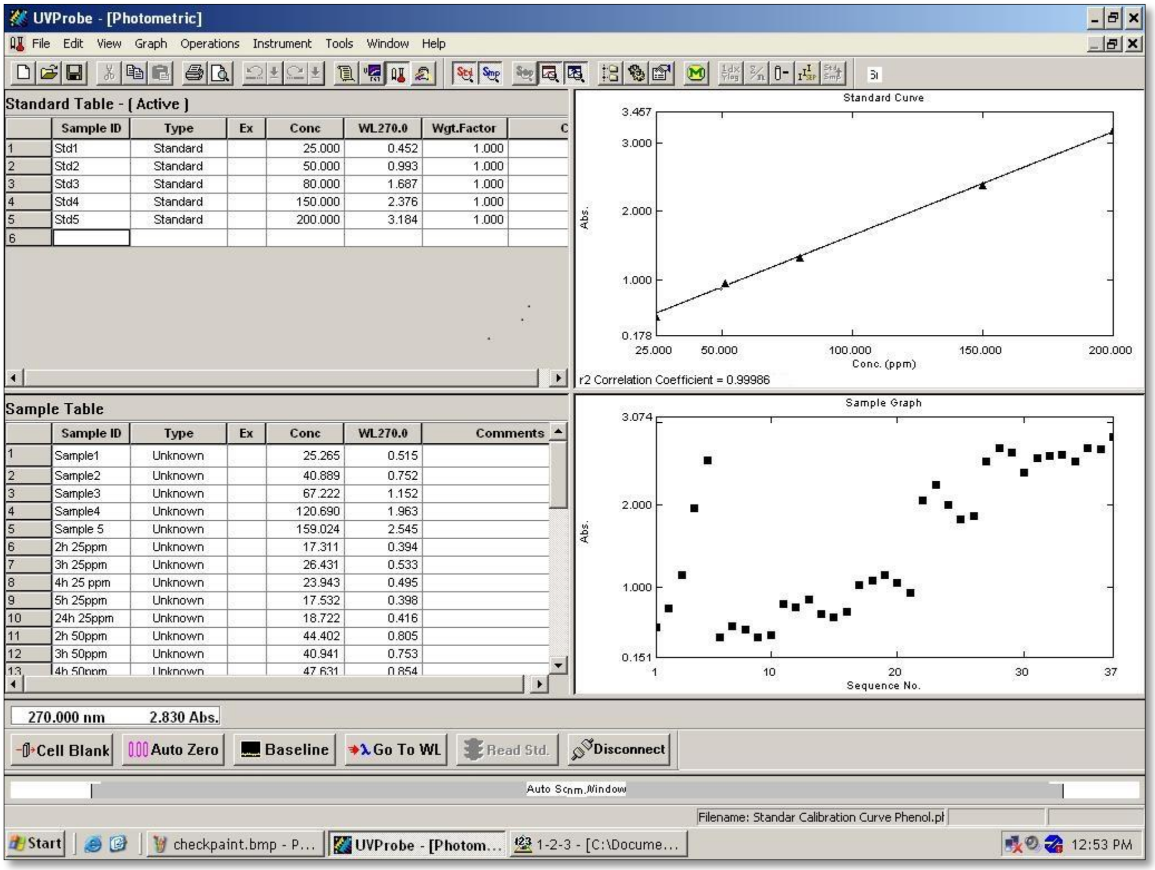
FESEM at 500x magnifying (a) raw KH (b) KH activated carbon

q_e (mg/g)	**pH**
107.814	3
108.526	4
108.413	5
108.803	6
107.695	7
105.117	8
78.165	9
72.31	10

Adsorption capacity for different pH value

Initial Concentration, Co mg/L	**Ce**	**qe**	**1/qe**	**1/Ce**	**log qe**	**log Ce**
25	7.311	17.689	0.13678	0.04	0.86398	1.39794
50	17.494	32.506	0.05716	0.02	1.24289	1.69897
80	32.654	47.346	0.03062	0.0125	1.51394	1.90309
150	71.835	78.165	0.01392	0.00667	1.85634	2.17609
200	94.883	105.117	0.01054	0.005	1.97719	2.30103

Adsorption isotherm plot values



Standard Table - (Active)

	Sample ID	Type	Ex	Conc	WL270.0	Wgt.Factor	C
1	Std1	Standard		25.000	0.452	1.000	
2	Std2	Standard		50.000	0.993	1.000	
3	Std3	Standard		80.000	1.687	1.000	
4	Std4	Standard		150.000	2.376	1.000	
5	Std5	Standard		200.000	3.184	1.000	
6							

r2 Correlation Coefficient = 0.99986

Sample Table

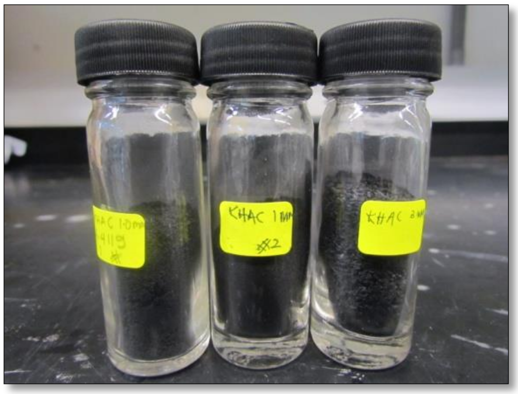
	Sample ID	Type	Ex	Conc	WL270.0	Comments
1	Sample1	Unknown		25.265	0.515	
2	Sample2	Unknown		40.889	0.752	
3	Sample3	Unknown		67.222	1.152	
4	Sample4	Unknown		120.690	1.963	
5	Sample 5	Unknown		159.024	2.545	
6	2h 25ppm	Unknown		17.311	0.394	
7	3h 25ppm	Unknown		26.431	0.533	
8	4h 25 ppm	Unknown		23.943	0.495	
9	5h 25ppm	Unknown		17.532	0.398	
10	24h 25ppm	Unknown		18.722	0.416	
11	2h 50ppm	Unknown		44.402	0.805	
12	3h 50ppm	Unknown		40.941	0.753	
13	4h 50ppm	Unknown		47.631	0.854	

270.000 nm 2.830 Abs.

Filename: Standar Calibration Curve Phenol.pl

Calibration curve of phenol using UV-Vis Spectrophotometer

(a)



(b)

Ceiba Pentandra hulls (a) raw KH (b) treated with 1M NAOH (550C, 2h)