

**ADSORPTION OF P-NITROPHENOL USING  
PALM KERNEL SHELL ACTIVATED CARBON:  
SHALLOW BED TECHNIQUE**

by

**Zaifadzmeen Zakiah Bt Zaini**

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

UNIVERSITI TEKNOLOGI PETRONAS  
TRONOH, PERAK  
DECEMBER 2011

**CERTIFICATION OF APPROVAL**

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Approved by,



(Dr. Nurlidia Mansor)

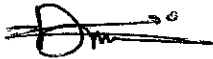
UNIVERSITI TEKNOLOGI PETRONAS

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DECEMBER 2011

## **CERTIFICATION OF ORIGINALITY**

This is to certify that I am accountable 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.



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**ZAIFADZMEEN ZAKIAH BT ZAINI**

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## ABSTRACT

This report discusses the research that has been done in order to understand the adsorption of p-nitro-phenol (PNP) by using activated carbon as adsorbent in shallow bed technique method.

Adsorption is still one of the preferred methods to remove phenolic compound in wastewater to this end. Palm Kernel Shell (PKS) Activated Carbon will be used as the adsorbent in the experiment. Their adsorptive properties are due to their high surface area, a microporous structure and high degree of surface reactivity. Granular type of activated carbon is usually used in fixed bed adsorption process because of ease of operation and no carbon loss.

PNP is considered very hazardous. It induces methemoglobin formation. Inhalation or ingestion of PNP may cause headache, drowsiness, nausea and cyanosis. Contact with the eyes may cause irritation. Respiratory effects, an increase in methemoglobin, effects on the liver and corneal opacity were reported in studies of acute exposure to PNP by U.S. EPA 1994. Thus, the choice to study the removal of PNP using PKS activated carbon adsorption is essential. Safety precautions before conducting the experiment are also taken into consideration.

In a shallow bed column, the bed length is very thin and is operated at adequate high flow rate. The advantage of shallow bed system is that the adsorption rate can be obtained directly, without having to depend on material balance because the mass transfer resistance at the fluid-to-solid film surrounding adsorbent particles in this shallow bed column can be negligible. The PNP concentration will vary only slightly across the bed length. The amount of PNP adsorbed each time can be obtained by sampling the effluent at short interval. Spectroscopic method will be used for the result analysis.

# CHAPTER 1: INTRODUCTION

## 1.1 Background

Basically, phenolic compound present in wastewater are considered to be very hazardous. It may threaten people's health and causes environmental pollution if released into the aquatic environment by agriculture pesticides, cosmetic industry, petroleum industry, mining industry and many more [1]. This is because, phenolic compound in water emit bad odour and flavour and are very poisonous to aquatic life, plants and human as a product of accumulation. Besides, ingestion of phenols in concentration of 10 to 240mg/L for a continuous time will cause irritation in the mouth, dark urine, vision problem, reproductive defect and might lead to cancer if combined with other chemicals [2].

While p-nitrophenol (PNP) may induces methemoglobin formation. Inhalation or ingestion of PNP may cause headache, drowsiness, nausea and cyanosis. Contact with the eyes may cause irritation. Respiratory effects, an increase in methemoglobin, effects on the liver and corneal opacity were reported in studies of acute exposure to PNP [3]. Thus, emission of phenolic compound especially PNP to the environment has become a major public concern. The government has realized the importance and therefore made regulation standards for phenol emission towards the environment. In line to that, Malaysia local authorities has decided that streams should be limited to 0.001mg/L phenol to protect human health from the possible harmful effects of exposure to phenol via drinking water and contaminated water plants and animals [4]. To comply with these regulations and improve reputation, industries have to remove phenol contents in their effluent.

The biological degradation process are commonly used for domestic and industrial wastewater however, they cannot treat phenolic wastewater at high concentrations successfully. Therefore, many new treatment technologies are still constantly researched and developed. Research efforts include chemical oxidation, solvent extraction and adsorption. Although many different adsorbents were tried to remove PNP from wastewater, activated carbon was still the most widely used adsorbent to this end [5].



## **1.2 Problem Statement**

The use of activated carbon as an adsorbent for industrial wastewater treatment is capital-intensive and has several other problems such as regeneration of activated carbon, intraparticle resistance in adsorption processes in practice and high cost of manufacture. Many researches tried to minimize the effect of liquid film resistance when determining the effective intraparticle diffusivity in order to design a fixed bed reactor for adsorption process. Thus, this study proposed Shallow Bed technique to determine adsorption capacity, diffusivity and liquid mass transfer coefficient of Palm Kernel Shell activated carbon for P-nitrophenol removal.

## **1.3 Objectives**

The main objective of this study is to evaluate and obtain the adsorption capacity ( $q$ ), diffusivity ( $D_s$ ) and liquid mass transfer coefficient ( $k_F$ ) of Palm Kernel Shell activated carbon (PKS AC) for p-nitrophenol (PNP) removal with Shallow Bed technique in order to optimize adsorption process in reactor.

## **1.4 Scope of Study**

The study of p-nitro-phenol (PNP) removal will be conducted based on column process using shallow bed adsorption technique. The amount of PNP adsorbed each time can be obtained by sampling the effluent at short interval. Spectroscopic method will be used for the result analysis. The Palm Kernel Shell activated carbon manufactured by KD Technology Sdn. Bhd. Malaysia will be used as the adsorbent.

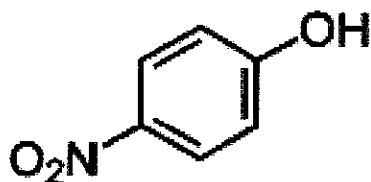
## **1.5 Feasibility of the Project**

In a shallow bed column, bed length is very thin. This reduces diffusion resistance at fluid solid film. Therefore, adsorption rate can be obtained directly without having to depend on the material balance. Experimental work can be done in short interval.

## CHAPTER 2: LITERATURE REVIEW

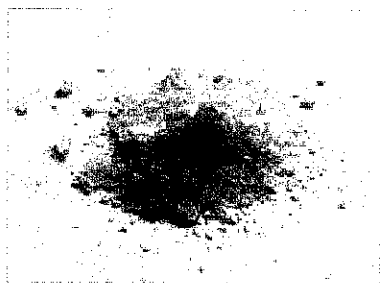
### 2.1 P-nitrophenol (PNP)

P-nitrophenol also called 4-nitro-phenol or 4-hydroxynitrobenzene is a phenolic compound that has a nitro group at the opposite position of hydroxyl group on the benzene ring.



**Figure 2.1.1** *Structural Formula of PNP [6]*

The pure PNP forms yellow crystals at room temperature and gradually turn red upon irradiation of sunlight. In solution, PNP alone appears pale yellow whereas its phenol salts tend to develop a bright yellow colour. The physicochemical properties are given in Table 2.1.1.



**Figure 2.1.2** *Pure PNP forms yellow crystals*

**Table 2.1.1** *Physicochemical properties of PNP [7]*

Molecular mass (g/mol)	139.11
Melting Point (°C)	113-114
Boiling Point (°C)	279
Vapour Pressure (kPa)	$3.2 \times 10^6$
Water solubility (g/L)	12.4 (20°C)
Dissociate constant (pKa)	7.08 (21.5°C)
Ultra violet Spectrum	Max $\leq 290\text{nm}$

While handling PNP, several safety precautions must be considered. PNP can be absorbed into the body by inhalation, through the skin and into the mouth by ingestion. The inhalation risk increase as a harmful concentration of airborne particles can be reach quickly when dispersed. PNP is irritating the eyes, the skin and respiratory tract in short term exposure. It will produce yellow staining on the skin. PNP may causes effects on the blood to, resulting in formation of methemoglobin which causes headache, drowsiness, nausea and cyanosis. The effects of long term or repeated exposure may result skin sensitization. Thus wearing respirator and clean gloves during handling PNP in the experiment is a must [3].

The types of hazard and exposure of PNP, its symptoms, prevention steps and first aid/fire fighting equipment may be summarized in Table 2.1.2 as shown below.

**Table 2.1.2 PNP Hazard/Exposure, Symptoms, Prevention and First Aid/Fire Fighting [8]**

Hazard/Exposure	Symptoms	Prevention	First Aid/Fire Fighting
Fire	Combustible. Gives off irritating or toxic fumes	NO open flames.	Powder, water spray, foam, carbon dioxide.
Explosion	Finely dispersed particles form explosive mixtures in air.	Prevent deposition of dust; closed system, dust explosion-proof electrical equipment	In case of fire: keep drums, etc., cool by spraying with water.
Inhalation	Blue lips or finger nails. Blue skin. Cough. Burning sensation. Confusion. Convulsions. Dizziness. Headache. Nausea. Sore throat. Unconsciousness. Weakness.	Local exhaust or breathing protection.	Fresh air, rest. Refer for medical attention.
Skin	May be absorbed. Redness	Protective gloves. Protective clothing.	Remove contaminated clothes. Rinse and then wash skin with water and soap. Refer for medical attention.
Eyes	Redness. Pain.	Safety goggles, face shield or eye protection in combination with breathing protection.	First rinse with plenty of water for several minutes then takes to a doctor.
Ingestion	Abdominal pain. Sore throat. Vomiting	Do not eat, drink, or smoke during work.	Rinse mouth. Rest. Refer for medical attention.

Phenolic compounds are usually present in wastewater generated from the paint, solvent, petrochemical, coal conversion, pharmaceutical, plastic, iron-steel and paper and pulp industries [9].

Several methods are currently used for the removal of phenol and its derivatives from wastewater, e.g. microbial degradation [10], chemical oxidation [11], incineration [12], solvent extraction [13] and irradiation [14]. However, by far the most frequently used technology is adsorption by a solid phase.

## 2.2 Adsorption Process

Adsorption is the physical and/or chemical process in which a substance is accumulated at an interface between phases. For the purpose of wastewater treatment, adsorption from solution occurs when impurities in the water accumulate at solid-liquid interface. The substance which is being removed from the liquid phase to the interface is called as adsorbate and solid phase in the process is known to be adsorbent [15]. Dissolved species may participate directly in air-water exchange (air-stripping method) while sorbed species may settle with solids [16].

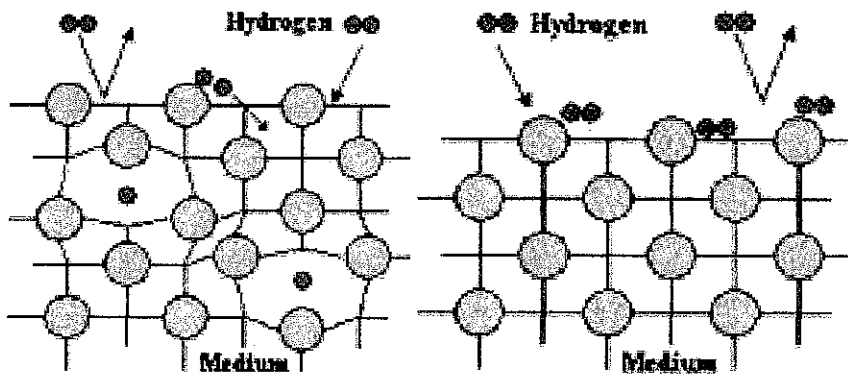


Figure 2.2.1 Chemisorption and Physisorption [17]

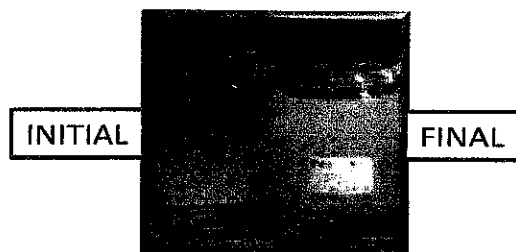
Physical adsorption (physisorption) is non-specific and is due to the operation of weak forces between molecules. In this process, the adsorbed molecules is not affixed to a particular site on the solid surface, it is free to move over the surface. The physical interaction among molecules, based on electrostatic forces, include dipole-dipole interactions, dispersion interactions and hydrogen bonding. When there is a net separation of positive and negative charges within molecules, it is said to have a dipole moment. Molecules such as  $H_2O$  and  $N_2$

have permanent dipoles because of the configuration of atoms and electrons within them. Hydrogen bonding is a special case of dipole-dipole interaction and hydrogen atom in a molecule has a partial positive charge. Positively charged hydrogen atom attracts an atom on another molecule which has a partial negative charge. When two neutral molecules which have no permanent dipoles approach each other, a weak polarization is included because of interactions between the molecules, known as the dispersion interaction [15].

Chemical adsorption (chemisorption) is also based on electrostatic forces, but much stronger forces act a major role in this process [18]. In chemisorption, the attraction between adsorbent and adsorbate is covalent or electrostatic chemical bonds between atoms, with shorter bond length and higher bond energy. The enthalpy of chemisorptions is very much greater than physisorption, and typical values are in the region of 200kJ/mol, whereas the value for

Adsorption is still one of the preferred methods to remove phenolic compound in wastewater to this end because it appears more technically and economically feasible for treatment operations. The advantages of adsorption over other technologies are that no additional sludge is produced compared to activated sludge treatment, additional reagents to overcome high alkalinity are not needed and the pH of discharged wastewater is unaffected [19]. The simplicity of equipment needed in adsorption process leads to relatively inexpensive fabrication is also one of the important key. Adsorption provides great environmental significance whereby it can effectively remove pollutants from both aqueous and gaseous stream. Recovery and reuse of the removed pollutant become possible under certain condition [20].

In this research, pure PNP in water produces bright yellow solution. When adsorption occurs, the colour of wastewater becomes pale yellow and finally clearer.



**Figure 2.2.2** *PNP adsorption with PKS AC*

### 2.3 Phenolic Compound Adsorption on Different Substrate Surfaces

Banat et al. [21] investigated the adsorption behaviours of phenol on bentonite in aqueous system systems and found the effective parameters on process. These parameters were contact time, pH and initial phenol concentration. Time to reach equilibrium for the adsorption of phenol was 6 hours, which was an indication of fast adsorption process. The efficiency of adsorption on bentonite increased with an increase in initial phenol concentration. On the other hand, the percentage of phenol adsorbed to bentonite was decreased when the initial phenol concentration increased. Adsorptive capacity of bentonite for phenol was limited to 1mg/g. The adsorption desorption isotherm (Langmuir and Freundlich) which were found to be good fitting for the equilibrium data.

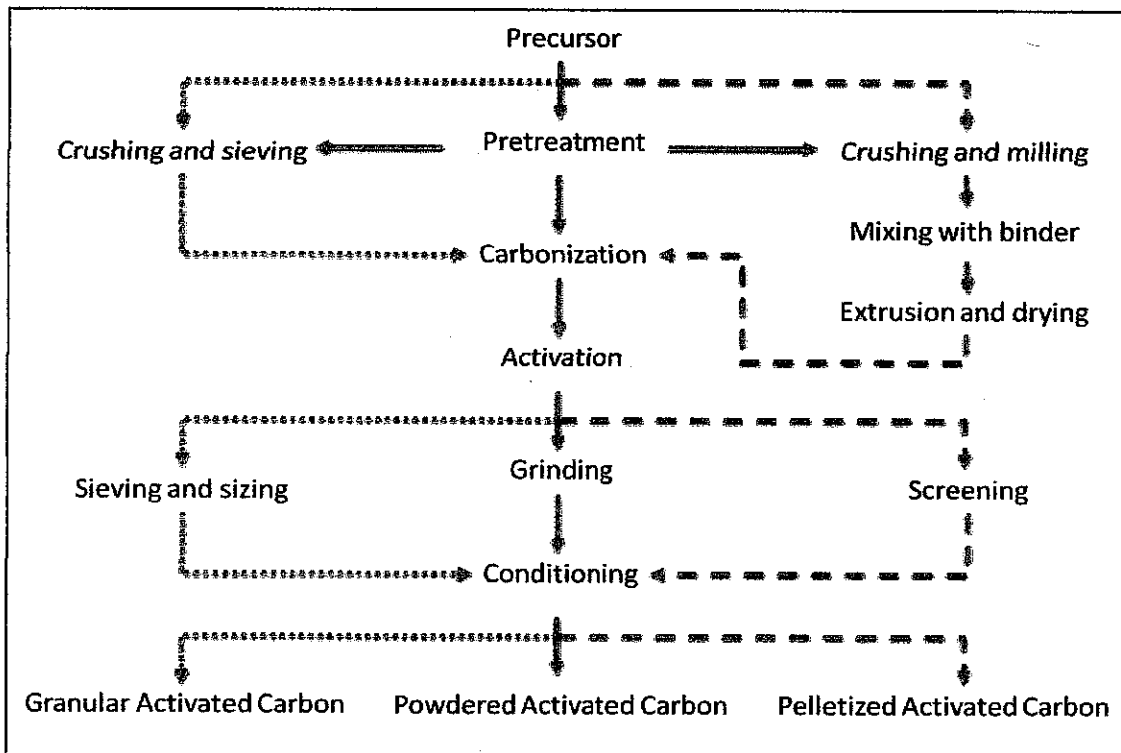
Roostai et al. [22] studied phenol with adsorption using different adsorbents such as silica gel, activated carbon, activated alumina and various zeolite structures. Adsorption followed first order reversible kinetic according to the models of Freundlich and Langmuir. Silica gel and activated alumina had no significant phenol adsorption but Zeolite-Y had the fastest adsorption kinetics according to this investigation. Activated carbon reached its limiting capacity during the adsorption of phenol, but very long contact time. Ten days period was needed to reach equilibrium.

Rengaraj et al. [23] used an agriculture waste rubber seed coat activated carbon to adsorb phenol. Adsorption of phenol on activated carbon follows first order reversible kinetics. It is possible to reach 96% removal efficiency after 24hours of contact time for initial phenol concentration of 25mg/l and carbon dosage of 0.2g/100ml. (30m<sup>2</sup> available surface areas for phenol solution).

In this research, PKS AC is used with high surface area, 1088m<sup>2</sup>/g. The adsorption capacity can reach more than 252mg/g which indicates highly adsorptive adsorbent. By using Shallow Bed technique, contact time can be reduced to less than one hour.

## 2.4 Activated Carbon

Activated carbon is produced by passing carbonaceous material through a heating mechanism at high temperature against counter current of air, steam, carbon dioxide, chlorine or flue gases. Sometimes chemical agents such as zinc chloride may be added. This activation increase power of carbon to absorb organic matters and distinguishes activated carbon from charcoal. The activation removes hydrocarbon which might interfere with the adsorption of organic matter. Activated carbon is very porous and has many carbon atoms with free valencies. It is available in granular as well as powder form. Granular activated carbons typically have surface area of 500–1400 m<sup>2</sup>/g. High surface area is the prime consideration in adsorption process [24].



**Figure 2.4** General flow sheet for thermal (physical) activation [25]

Activated carbon is widely chosen in adsorption because of its high adsorptive capacity and versatility expanded the application to numerous industrial waste streams such as paint, solvent, petrochemical, coal conversion, pharmaceutical, plastic, iron-steel and paper and pulp industries [9][20].

As mentioned in Chapter 1, Palm Kernel Shell activated carbon will be used in this experiment as the adsorbent. Table 2.4 below will summarize the product specification.

**Table 2.4 Product Specification PKS Activated Carbon**

Parameter	Value
Manufacturer	KD Technology Sdn. Bhd. Malaysia
Iodine Number	950 – 1150 mg/g
Surface Area	1088m <sup>2</sup> /g
Butane Activity	20 -30 %
CCL <sub>4</sub> Activity	55-77 %
Ball Pan Hardness	88 – 96 %
Ash Content	5% max
Apparent Density	0.42 – 0.52 g/cc
Moisture	5% max
pH Value	9-11
Particle Size Distribution	90% min
Size	Mesh 8x12 (1.7 – 2.4mm)
Material Density	1.7097 g/cm <sup>3</sup>
Bulk Density	0.4691 g/cm <sup>3</sup>

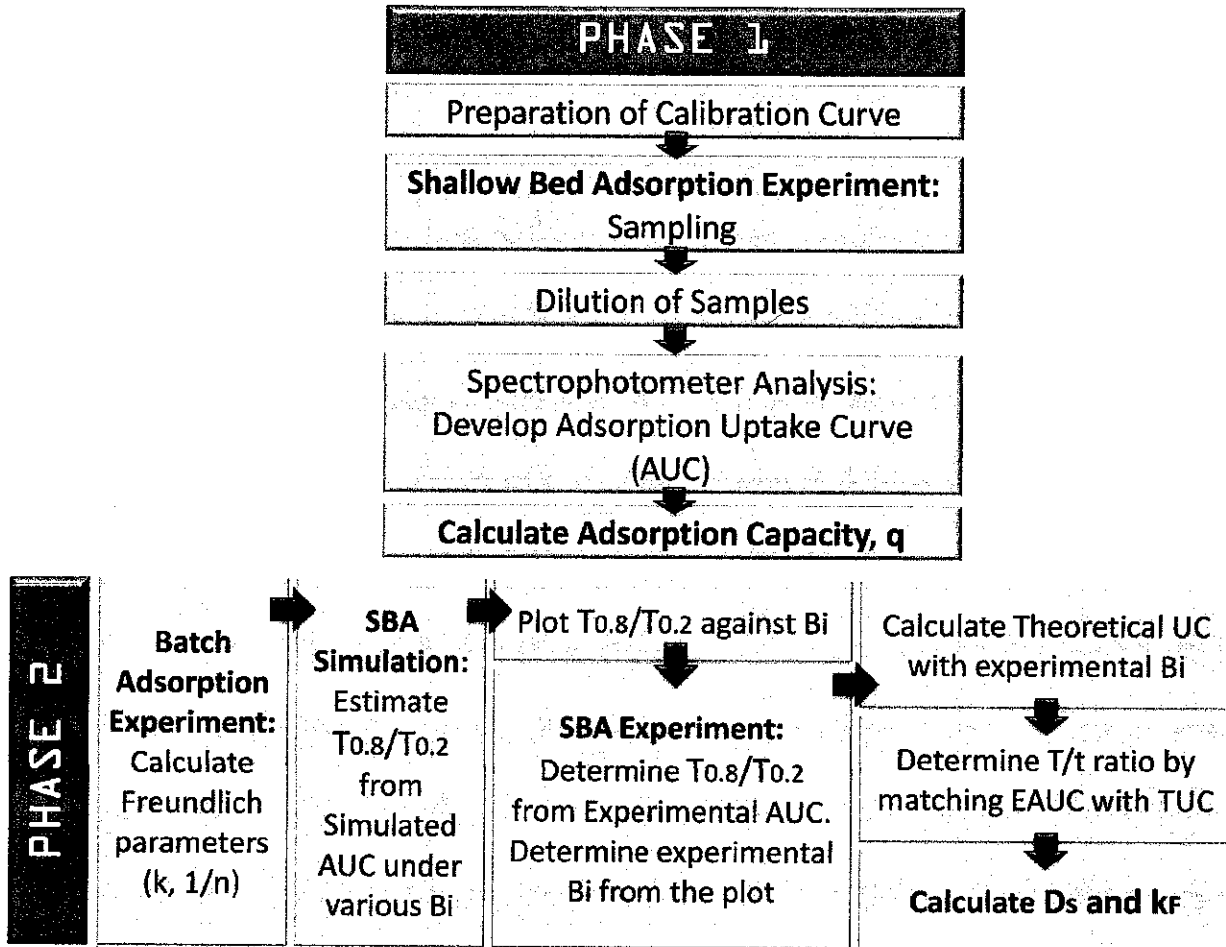
### 2.3 Shallow Bed Technique

In shallow bed reactor, bed length is very thin, 1.18cm. Under high fluid velocity, effluent concentration is equal to influent concentration. Hence PNP concentration at fluid-solid interface is the same as fluid running through spaces among particles. This reduces diffusion resistance at fluid solid film. Diffusivity can be determined when intraparticle resistance is negligible. However since PKS AC particle size is small, liquid film resistance is not negligible, thus, liquid film mass coefficient has to be accounted. [35]



## CHAPTER 3: METHODOLOGY

### 3.1 Research Methodology



**Figure 3.1** *Research Methodology Flow Chart*

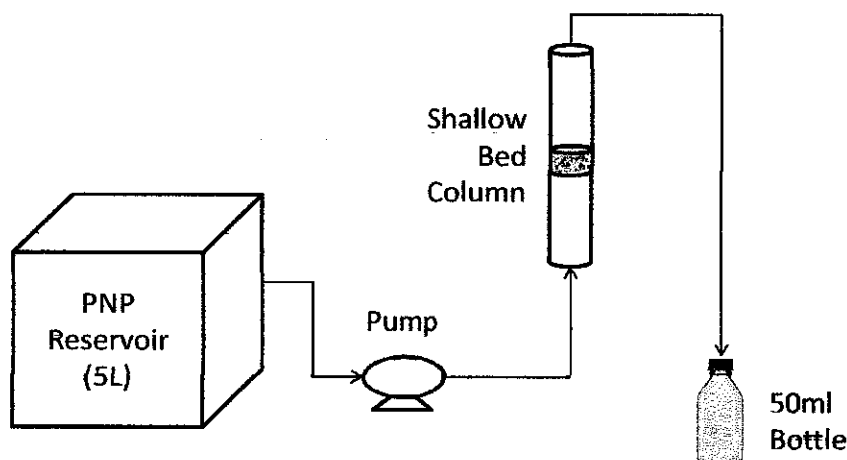
There are TWO phases involved in this study. Basically, PHASE 1 contained several steps taken to calculate adsorption capacity using Shallow Bed technique. In order to obtain diffusivity,  $D_s$  and liquid mass transfer coefficient,  $k_f$ , integrated process with several data (experiment and simulation) was concluded in PHASE 2. Simulation data was produced by Prof Eiji Furuya from Meiji University, Japan using experimental results from this study.

### 3.1.1 Experiment and Sampling

#### PHASE 1

##### *Shallow Bed Adsorption*

Firstly, the adsorbent needs to be prepared. The principle is quite simple. Wastewater reservoir containing PNP was pumped through a shallow bed column containing the activated carbon adsorbent. Sampling was done at the outlet of column for every 30 second until all the wastewater in the reservoir has finished. The wastewater used in this study was synthetic PNP prepared in the laboratory. The initial concentration of PNP used was 1600mg/L. Sample was collected in 50ml bottle and diluted before analyzing using spectrophotometer.



**Figure 3.1.1.1** *Shallow Bed Adsorption Experiment Setup*

#### PHASE 2

##### *Batch Adsorption Experiment*

The PNP solutions (200mg/l, 400mg/l, 800mg/l, 1200mg/l, 1600mg/l, 2000mg/l) were added into 6 sample bottles with volume of 60ml per bottle. The PKS AC with various amount were added into each bottle; 0.7524g, 0.6214g, 0.4752g, 0.3702g, 0.2621g, 0.1883g. All bottles were properly capped and mildly shaken twice per day for 7-days. Solutions from each sample were diluted and analyzed using spectrophotometer. The results of  $k$  and  $1/n$  in this experiment will be used to simulate Biot Number vs  $T_{0.8}/T_{0.2}$  graph.

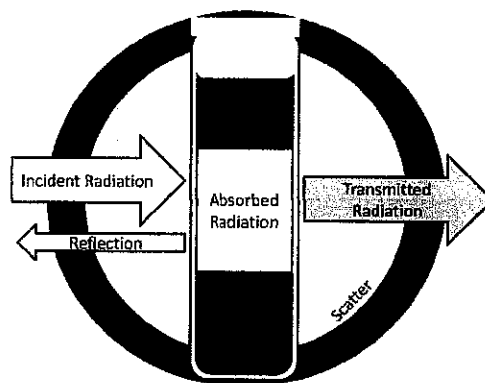


**Figure 3.1.1.2** *Batch Adsorption Experiment Setup*

Data from Shallow Bed Experiment was utilized to determine  $T_{0.8}/T_{0.2}$  from Experimental Adsorption Uptake Curve (EAUC). Experimental Biot Number ( $Bi$ ) was obtained from the plot. Theoretical Uptake Curve (TUC) was calculated with the experimental  $Bi$ . The EAUC and TUC were matched to determine  $T/t$  ratio which was used in  $D_s$  and  $k_F$  calculation.

### 3.1.2 Testing and Dilution

UV-Spectrophotometer will be used to test the PNP sample for its simplicity, speed, accuracy and cost-effectiveness. When a beam of radiation strikes any object, it can be absorbed, transmitted, scattered or reflected. These processes are illustrated in Figure 3.1.2. The process concerned in spectrometer is absorption and transmission. Usually the conditions under which the sample is examined are chosen to keep reflection and scatter to a minimum.

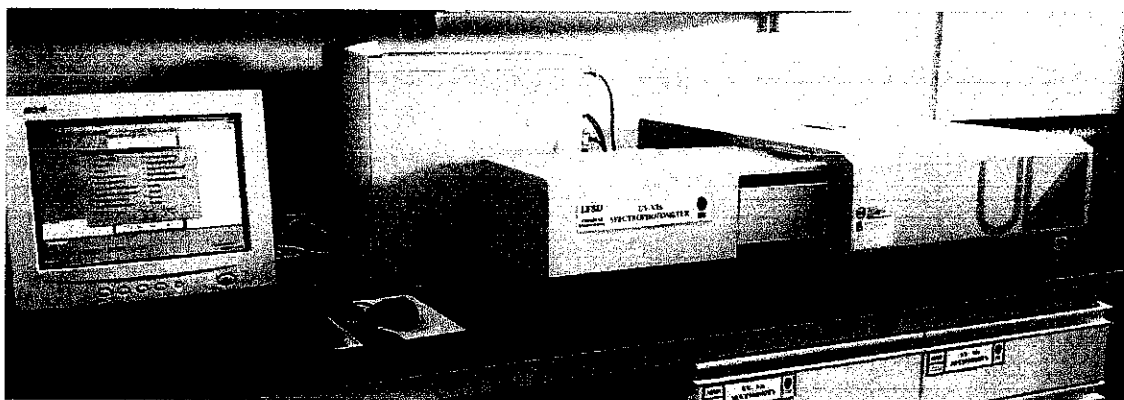


**Figure 3.1.2.1** *Interaction of light and matter*

The Beer-Lambert Law states that the concentration of a substance in solution is directly proportional to the absorbance 'A' of the solution. Thus, construction of calibration curve is very important for the accuracy of analysis which will be explained further in Section 3.4.

Apparently, the spectrophotometer could not give absorption reading for very high concentration of PNP solution. Therefore, dilution of all the sample is needed. Dilution factor is calculated to get the original concentration in the adsorption capacity calculation. For example,

$$\begin{aligned} C_1 V_1 &= C_2 V_2 \\ 1600\text{mg/L} \times 1\text{mL} &= C_2 \times 100\text{mL} \\ \text{Thus, } C_2 &= 8\text{mg/L} \\ \text{Dilution Factor} &= C_1 / C_2 = 1600/8 = 200 \end{aligned}$$



**Figure 3.1.2.2** UV Spectrophotometer together with installed software in the computer for data analysis



**Figure 3.1.2.3** Cuvette used in UV Spectrophotometer

### 3.2 Tools/Apparatus

**Table 3.2** *Tools and apparatus required for research study*

Tool/Apparatus	Description	Amount (unit)
<b>Beaker (Reservoir)</b> Capacity: 5L	The beaker will act as reservoir; it contains 5L PNP solution with 1600mg/L to be supplied to the activated carbon bed in a column.	1
<b>Pump</b>	To transfer the PNP solution from reservoir to the column. Before usage, need to be calibrated.	1
<b>Column</b> Diameter: 20mm	To provide an activated carbon shallow packed bed for the column adsorption study.	1
<b>Connection tube</b>	To provide connection between the equipments, for PNP flow (acts a pipeline)	
<b>Glass bed + Wool</b>	To prevent displacement of activated carbon bed while PNP flowing in and out from the column through the activated carbon bed.	
<b>Laboratory Bottles</b> Capacity: 50mL	For PNP sampling to obtain result for adsorption capacity.	300
<b>Spectrophotometer</b>	To test the PNP samples and obtain PNP concentration data for analysis.	1
<b>Weight Scale</b>	To measure the weight of activated carbon and PNP solid to synthesis 1600mg/L of PNP solution.	1
<b>Timer</b>	To determine sampling duration will took place.	1
<b>Pipette</b>	To transport 1mL of PNP solution for dilution purposes	10
<b>Pipette Pump</b>	To control handling of liquid in the pipette	1
<b>Volumetric Flask</b> Capacity: 5L	To synthesis 1600mg/L PNP solution before pouring in the reservoir beaker.	1
<b>Volumetric Flask</b> Capacity: 100mL	To dilute original sample of PNP after adsorption to lower concentration.	10

### 3.3 Software

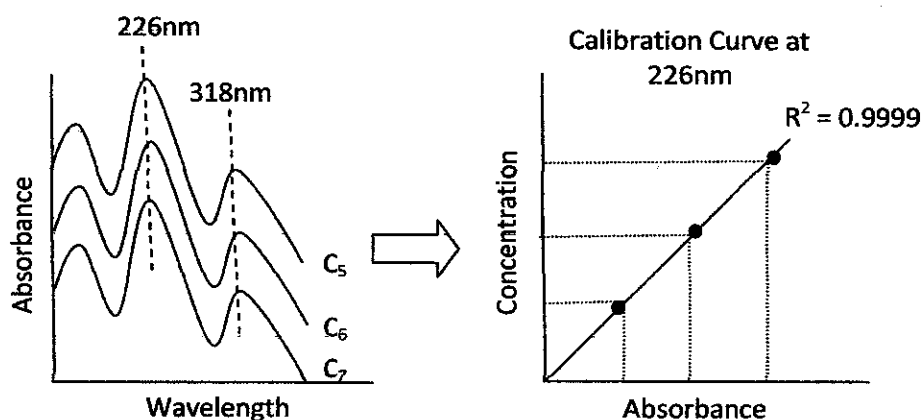
**Table 3.3** Software required for research study

Software	Description
Shimadzu UV-VIS Spectrophotometer	This software is used to acquire data from the spectrophotometer. The software includes extensive analytical capabilities for spectral analysis.

### 3.4 Project Activities

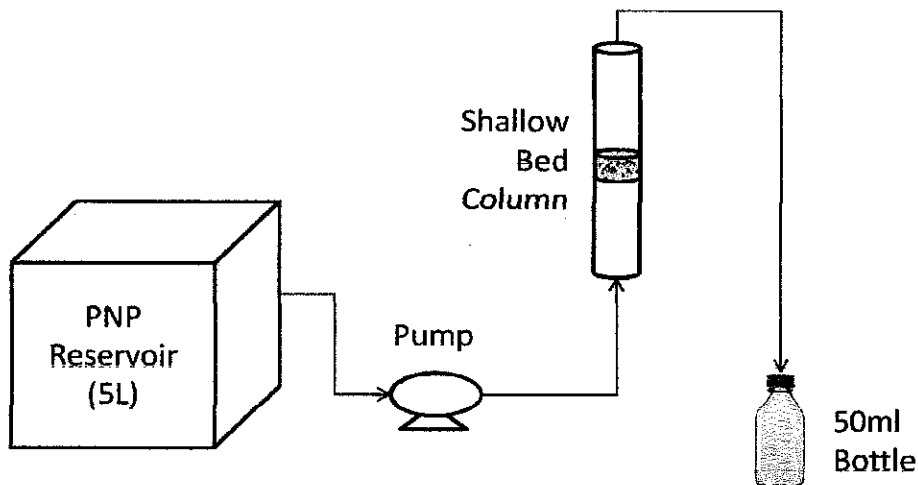
Experiment	Description
PNP Removal using PKS AC: Shallow Bed Technique [35]	The main objective of this study is to evaluate and obtain the adsorption capacity of Palm Kernel Shell activated carbon for removal of p-nitrophenol (PNP). The advantage of shallow bed system is that the adsorption rate can be obtained directly, without having to depend on a material balance because the mass transfer resistance at the fluid-to-solid film surrounding adsorbent particles in this shallow bed column can be negligible. The apparatus used must be clean, rinse and dry well to avoid contamination to the PNP concentration. Furthermore, less contact with PNP solution is favourable since PNP is very hazardous.
	<p><b>1. Preparation of Calibration Curve</b></p> <p>8g PNP + 5L Water = 1600mg/L (<math>C_1</math>)</p> <p>1<sup>st</sup> Dilution using, <math>C_1V_1 = C_2V_2</math></p> <p>2<sup>nd</sup> Dilution using, <math>C_2V_2 = C_5V_5</math></p> <p>Spectrophotometer</p> <p><math>C_1 = 1600\text{mg/L}</math> <math>C_2 = 1200\text{mg/L}</math> <math>C_3 = 800\text{mg/L}</math> <math>C_4 = 400\text{mg/L}</math></p> <p><math>C_5 = 160\text{mg/L}</math> <math>C_6 = 120\text{mg/L}</math> <math>C_7 = 80\text{mg/L}</math> <math>C_8 = 40\text{mg/L}</math></p>

From spectrophotometer, at certain wavelength we can see TWO things. First, PNP creates same pattern even at different concentration. Second, there are several peaks of absorbance; take the peak for calibration curve. Plot concentration versus absorbance at the wavelength chosen. The curve with nearest value of  $R^2$  to 1, will be selected as the calibration curve for result analysis later on.



## 2. Setup Experiment

The setup of experiment will be as below:



## 3. Column Preparation

- Palm Kernel Shell Activated Carbon: 3g
- Glass Bed + Wool
- Velocity PNP: 1.11 ml/s

#### 4. Mother Solution (Shallow Bed Technique)

Sampling  
50ml Bottle  
(150 Units)



Dilution



Spectrophotometer



$$C_1 V_1 = C_2 V_2$$

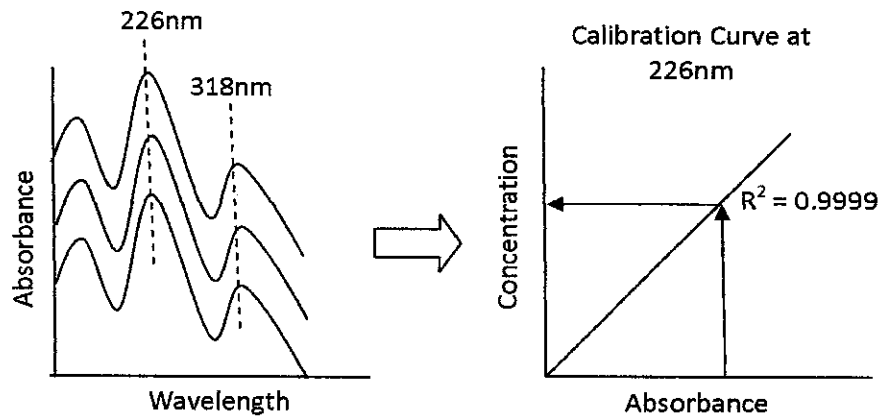
$$1600 \text{mg/L} \times 1 \text{mL} = C_2 \times 100 \text{mL}$$

Thus,  $C_2 = 8 \text{mg/L}$

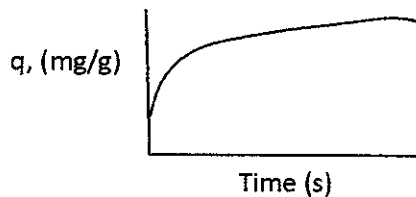
$$\text{Dilution Factor} = C_1 / C_2 = 1600 / 8 = 200$$

#### 5. Expected Result

From spectrophotometer, at the chosen wavelength (obtained from calibration curve) take the absorbance data for every sample. From calibration curve, get the value for PNP concentration after adsorption.



Then, adsorption capacity  $q$  can be calculated. Finally, we can produce  $q$  over time to illustrate the capacity of PKS activated carbon to adsorb PNP.



Adsorption Capacity,

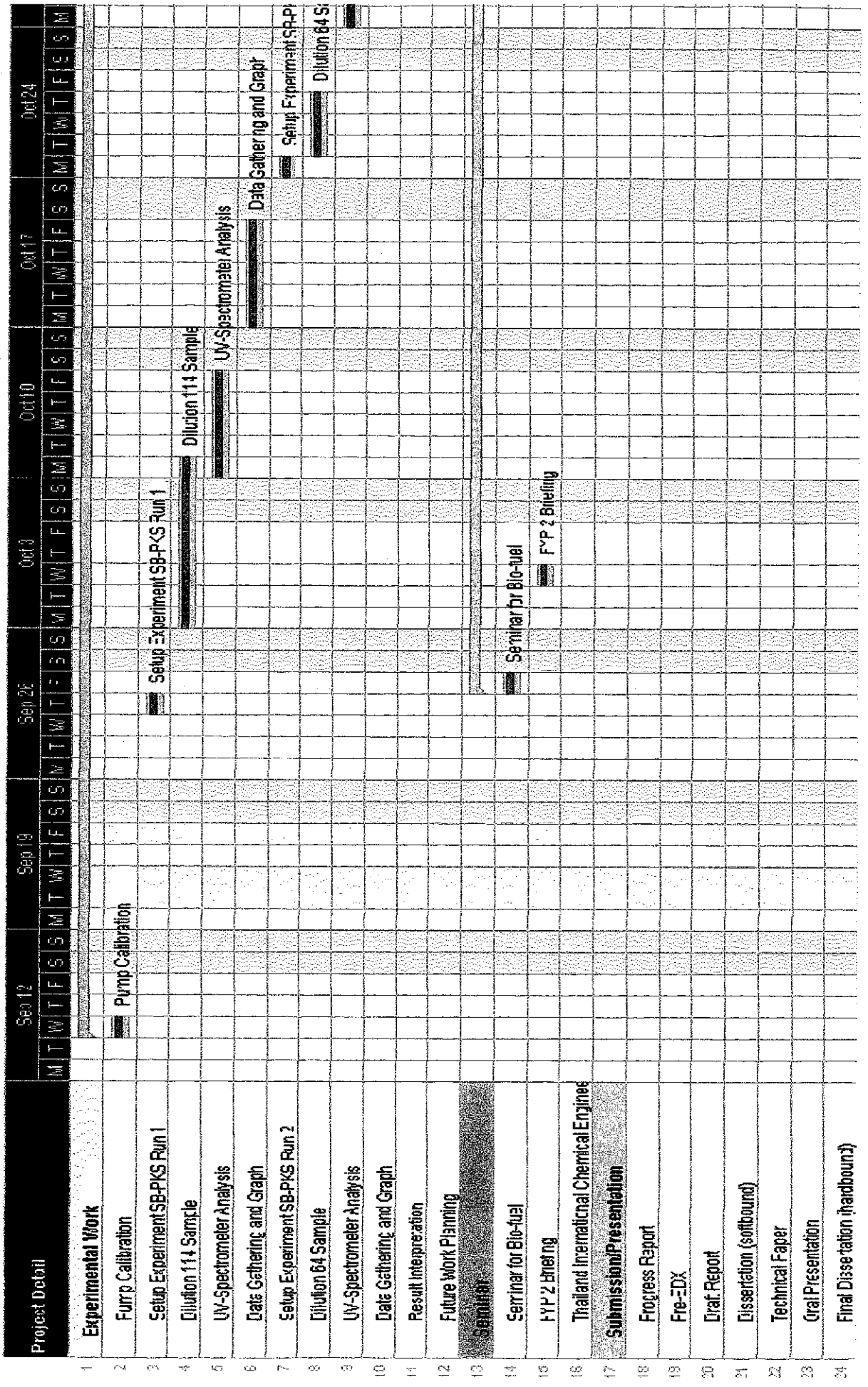
$$\Delta q = \frac{\Delta \text{Concentration} \times \text{Volume (L)}}{\text{Weight}_{\text{GAC}}}$$





### 3.5 Project Timeline

Table 3.5 FYP II Project Timeline



## CHAPTER 4: RESULT AND DISCUSSIONS

### 4.1 Result Run 1

**Table 4.1 Shallow Bed Adsorption Run 1**

Date of Experiment	29 <sup>th</sup> September 2011
Initial Volume of Sample (V)	5000 mL
Flowrate (v)	1.11 mL/s
Amount of GAC ( $W_{GAC}$ )	2.9957 g
Particle Size PKS GAC	1.7-2.4 mm
Bed Diameter	2.6 cm
Bed Height	1.2027 cm
Bulk Density	0.4691 g/cm <sup>3</sup>
Calibration curve	$C = 21.957 (\text{Absorbance}) - 0.0314$

mple	Time (s)	V (ml)	Absorbance of diluted sample	Concentration of diluted sample	Dilution factor	C (mg/L)	$\Delta q$ (mg/g)	$\Sigma \Delta q$ (mg/g)	$\Sigma \Delta q/q_0$
								$q_0$ roughly	
IR	0	5000	0.586	12.9029	142.857	1843.2676	0.0000		
0	30	33	0.683	15.0418	100	1504.1833	3.7591	3.7591	0.0105
1	60	33	0.199	4.3691	200	873.8298	10.7471	14.5061	0.0407
2	90	33	0.186	4.0825	200	816.4972	11.3827	25.8888	0.0727
3	120	33	0.429	9.4409	100	944.0879	9.9682	35.8570	0.1006
4	150	33	0.473	10.4111	100	1041.1123	8.8926	44.7496	0.1256
5	180	33	0.45	9.9040	100	990.3950	9.4549	54.2045	0.1521
6	210	33	0.468	10.3009	100	1030.0868	9.0148	63.2193	0.1774
7	240	33	0.486	10.6978	100	1069.7786	8.5748	71.7941	0.2015
8	270	33	0.508	11.1829	100	1118.2908	8.0370	79.8311	0.2240
9	300	33	0.506	11.1388	100	1113.8806	8.0859	87.9170	0.2467
10	330	33	0.514	11.3152	100	1131.5214	7.8903	95.8074	0.2689
11	360	33	0.522	11.4916	100	1149.1622	7.6948	103.5021	0.2905
12	390	33	0.522	11.4916	100	1149.1622	7.6948	111.1969	0.3121
13	420	33	0.525	11.5578	100	1155.7775	7.6214	118.8184	0.3335
14	450	33	0.533	11.7342	100	1173.4183	7.4259	126.2442	0.3543
15	480	33	0.572	12.5942	100	1259.4172	6.4725	132.7167	0.3725
16	510	33	0.539	11.8665	100	1186.6489	7.2792	139.9959	0.3929
17	540	33	0.557	12.2634	100	1226.3407	6.8392	146.8351	0.4121
18	570	33	0.522	11.4916	100	1149.1622	7.6948	154.5299	0.4337
19	600	33	0.588	12.9470	100	1294.6988	6.0814	160.6113	0.4508
20	630	33	0.564	12.4178	100	1241.7764	6.6681	167.2793	0.4695
21	660	33	0.597	13.1454	100	1314.5447	5.8614	173.1407	0.4859
22	690	33	0.544	11.9767	100	1197.6744	7.1570	180.2977	0.5060
23	720	33	0.587	12.9249	100	1292.4937	6.1058	186.4035	0.5231
24	750	33	0.593	13.0572	100	1305.7243	5.9591	192.3626	0.5399
25	780	33	0.564	12.4178	100	1241.7764	6.6681	199.0307	0.5586
26	810	33	0.6	13.2116	100	1321.1600	5.7880	204.8187	0.5748
27	840	33	0.566	12.4619	100	1246.1866	6.6192	211.4379	0.5934
28	870	33	0.696	15.3285	100	1532.8496	3.4413	214.8792	0.6031
29	900	33	0.748	16.4751	100	1647.5148	2.1701	217.0493	0.6092
30	930	33	0.699	15.3946	100	1539.4649	3.3679	220.4172	0.6186
31	960	33	0.735	16.1885	100	1618.8485	2.4879	222.9051	0.6256

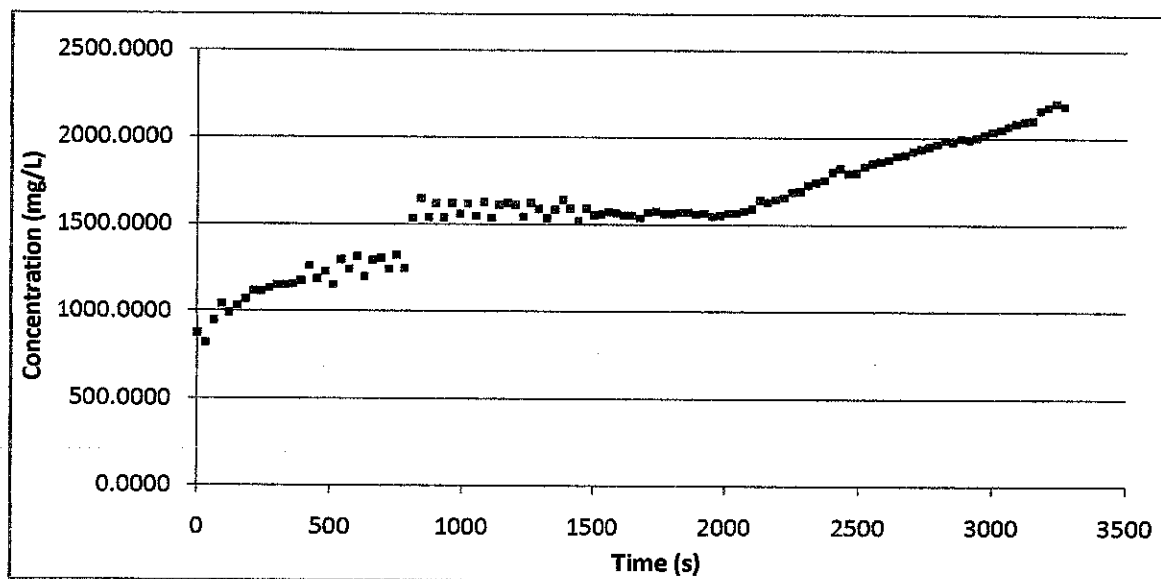
32	990	33	0.697	15.3505	100	1535.0547	3.4168	226.3219	0.6352
33	1020	33	0.737	16.2326	100	1623.2587	2.4390	228.7609	0.6420
34	1050	33	0.708	15.5931	100	1559.3108	3.1479	231.9088	0.6509
35	1080	33	0.735	16.1885	100	1618.8485	2.4879	234.3967	0.6578
36	1110	33	0.703	15.4829	100	1548.2853	3.2701	237.6668	0.6670
37	1140	33	0.739	16.2767	100	1627.6689	2.3901	240.0569	0.6737
38	1170	33	0.699	15.3946	100	1539.4649	3.3679	243.4248	0.6832
39	1200	33	0.733	16.1444	100	1614.4383	2.5368	245.9616	0.6903
40	1230	33	0.736	16.2105	100	1621.0536	2.4634	248.4251	0.6972
41	1260	33	0.733	16.1444	100	1614.4383	2.5368	250.9618	0.7043
42	1290	33	0.702	15.4608	100	1546.0802	3.2946	254.2564	0.7136
43	1320	33	0.736	16.2105	100	1621.0536	2.4634	256.7199	0.7205
44	1350	33	0.721	15.8798	100	1587.9771	2.8301	259.5500	0.7284
45	1380	33	0.697	15.3505	100	1535.0547	3.4168	262.9668	0.7380
46	1410	33	0.72	15.8577	100	1585.7720	2.8546	265.8214	0.7460
47	1440	33	0.745	16.4090	100	1640.8995	2.2434	268.0648	0.7523
48	1470	33	0.723	15.9239	100	1592.3873	2.7812	270.8460	0.7601
49	1500	33	0.689	15.1741	100	1517.4139	3.6124	274.4584	0.7703
50	1530	33	0.723	15.9239	100	1592.3873	2.7812	277.2396	0.7781
51	1560	33	0.706	15.5490	100	1554.9006	3.1968	280.4364	0.7871
52	1590	33	0.708	15.5931	100	1559.3108	3.1479	283.5844	0.7959
53	1620	33	0.714	15.7254	100	1572.5414	3.0012	286.5856	0.8043
54	1650	33	0.711	15.6593	100	1565.9261	3.0746	289.6602	0.8129
55	1680	33	0.706	15.5490	100	1554.9006	3.1968	292.8570	0.8219
56	1710	33	0.705	15.5270	100	1552.6955	3.2213	296.0782	0.8310
57	1740	33	0.699	15.3946	100	1539.4649	3.3679	299.4461	0.8404
58	1770	33	0.712	15.6813	100	1568.1312	3.0501	302.4963	0.8490
59	1800	33	0.716	15.7695	100	1576.9516	2.9523	305.4486	0.8573
60	1830	33	0.71	15.6372	100	1563.7210	3.0990	308.5477	0.8659
61	1860	33	0.71	15.6372	100	1563.7210	3.0990	311.6467	0.8746
62	1890	33	0.714	15.7254	100	1572.5414	3.0012	314.6479	0.8831
63	1920	33	0.714	15.7254	100	1572.5414	3.0012	317.6492	0.8915
64	1950	33	0.708	15.5931	100	1559.3108	3.1479	320.7971	0.9003
65	1980	33	0.711	15.6593	100	1565.9261	3.0746	323.8716	0.9090
66	2010	33	0.703	15.4829	100	1548.2853	3.2701	327.1418	0.9181
67	2040	33	0.706	15.5490	100	1554.9006	3.1968	330.3386	0.9271
68	2070	33	0.711	15.6593	100	1565.9261	3.0746	333.4132	0.9357
69	2100	33	0.704	15.5049	100	1565.9953	3.0738	336.4870	0.9444
70	2130	33	0.702	15.4608	100	1577.0018	2.9518	339.4388	0.9526
71	2160	33	0.702	15.4608	100	1592.4626	2.7804	342.2192	0.9604
72	2190	33	0.716	15.7695	100	1640.0297	2.2531	344.4722	0.9668
73	2220	33	0.704	15.5049	100	1628.0149	2.3863	346.8585	0.9735
74	2250	33	0.705	15.5270	100	1645.8572	2.1885	349.0470	0.9796
75	2280	33	0.703	15.4829	100	1656.6653	2.0687	351.1156	0.9854
76	2310	33	0.711	15.6593	100	1691.2002	1.6858	352.8014	0.9901
77	2340	33	0.705	15.5270	100	1692.4381	1.6721	354.4735	0.9948
78	2370	33	0.713	15.7034	100	1727.3699	1.2848	355.7583	0.9984
79	2400	33	0.713	15.7034	100	1743.0733	1.1107	356.8691	1.0016
80	2430	33	0.713	15.7034	100	1758.7767	0.9367	357.8057	1.0042
81	2460	33	0.726	15.9900	100	1806.8729	0.4035	358.2092	1.0053
82	2490	33	0.726	15.9900	100	1822.8630	0.2262	358.4354	1.0060

83	2520	33	0.71	15.6372	100	1798.2792	0.4987	358.9342	1.0074
84	2550	33	0.704	15.5049	100	1798.5689	0.4955	359.4297	1.0088
85	2580	33	0.712	15.6813	100	1834.7135	0.0948	359.5245	1.0090
91	2760	33	0.71	15.6372	100	1923.3768	-0.8881	356.6812	1.0010
92	2790	33	0.709	15.6152	100	1936.2797	-1.0311	355.6500	0.9981
93	2820	33	0.708	15.5931	100	1949.1385	-1.1737	354.4764	0.9948
94	2850	33	0.709	15.6152	100	1967.5100	-1.3773	353.0990	0.9910
95	2880	33	0.71	15.6372	100	1985.9257	-1.5815	351.5175	0.9865
96	2910	33	0.702	15.4608	100	1978.9827	-1.5045	350.0130	0.9823
97	2940	33	0.702	15.4608	100	1994.4435	-1.6759	348.3371	0.9776
98	2970	33	0.695	15.3064	100	1989.8379	-1.6249	346.7122	0.9731
99	3000	33	0.694	15.2844	100	2002.2556	-1.7625	344.9497	0.9681
100	3030	33	0.695	15.3064	100	2020.4507	-1.9642	342.9855	0.9626
101	3060	33	0.696	15.3285	100	2038.6900	-2.1664	340.8190	0.9565
102	3090	33	0.694	15.2844	100	2048.1088	-2.2708	338.5482	0.9501
103	3120	33	0.696	15.3285	100	2069.3470	-2.5063	336.0419	0.9431
104	3150	33	0.696	15.3285	100	2084.6755	-2.6762	333.3657	0.9356
105	3180	33	0.695	15.3064	100	2096.9830	-2.8127	330.5530	0.9277
106	3210	33	0.692	15.2403	100	2103.1603	-2.8811	327.6719	0.9196
107	3240	33	0.706	15.5490	100	2161.3118	-3.5258	324.1461	0.9097
108	3270	33	0.707	15.5711	100	2179.9480	-3.7324	320.4137	0.8993
109	3300	33	0.71	15.6372	100	2204.8466	-4.0084	316.4053	0.8880
110	3330	33	0.699	15.3946	100	2186.0402	-3.7999	312.6053	0.8773

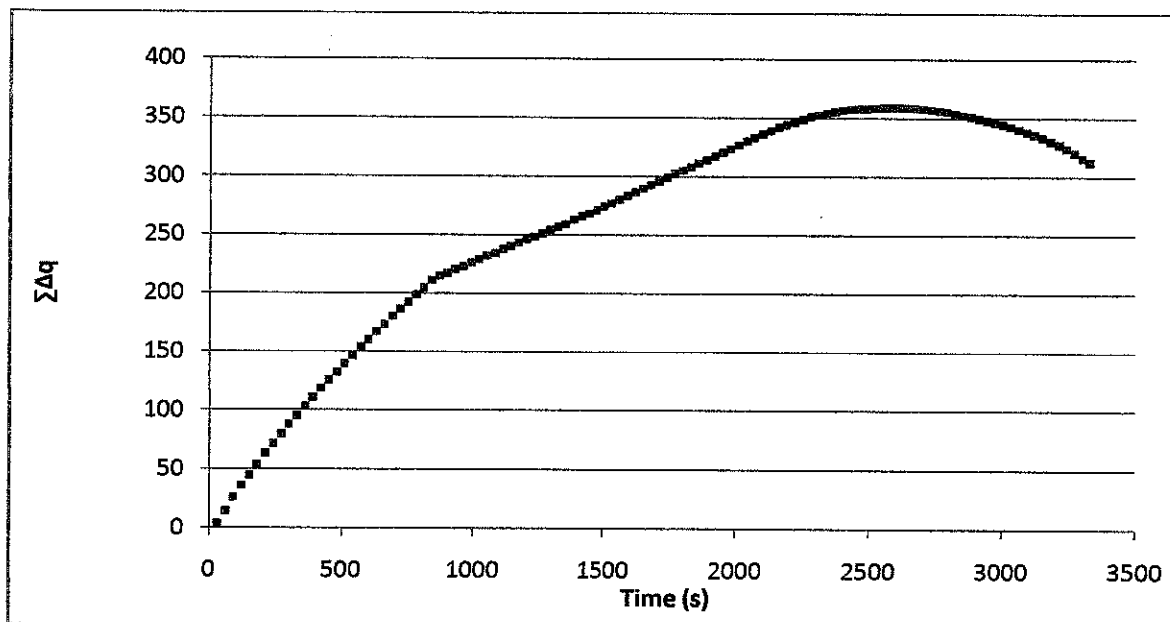
### Pump Calibration

Volume (mL)	Time (s)			Flow rate (mL/s)		
	30	31	24	29	0.967741935	1.25
60	57	48	57	1.052631579	1.25	1.05263158
90	83	72	88	1.084337349	1.25	1.02272727
<b>1.107172497</b>						

The adsorption data were acquired by using shallow bed adsorber. The p-nitrophenol concentration after adsorption was plotted against the process time in Figure 4.1.1. The concentration increases with an increase in time. While Figure 4.1.2 shows the adsorption capacity of Palm Kernel Shell activated carbon increasing with time till around 2760 second, then decreases.



**Figure 4.1.1** PNP concentration after adsorption Run 1 versus time



**Figure 4.1.2** Adsorption capacity of PKS GAC versus time (Breakthrough Curve Run 1)

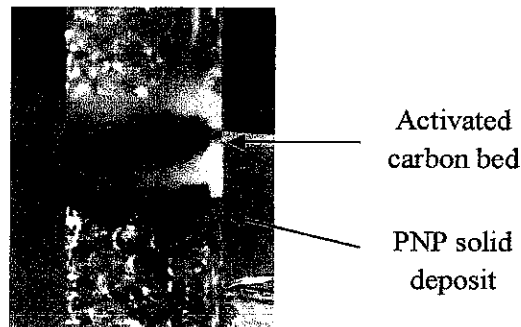
## 4.2 Error and Recommendation

There are several factors affecting the decrease in adsorption capacity of Palm Kernel Shell activated carbon which suppose to be constant after the activated carbon bed exhausted.

Based on calculation,

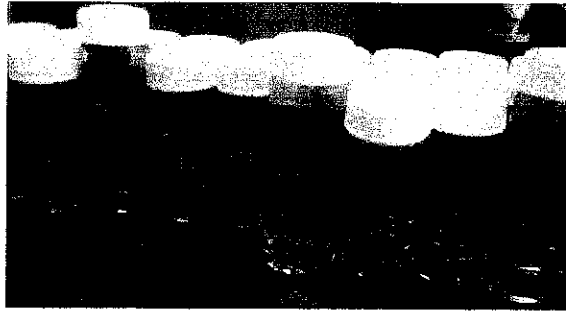
$$\text{Adsorption Capacity,}$$
$$\frac{\text{Amount PNP adsorbed (mg)}}{\text{Amount of adsorbent (g)}}$$
$$\Delta q = \frac{(C_{\text{initial}} - C_{\text{final}}) \times \text{Volume (L)}}{\text{Weight}_{\text{GAC}}}$$

First, final concentration of PNP after adsorbed will be less than or equal to the initial concentration ( $C_0=1843.2676$  mg/L). Sample 91 to 110 reading (refer to Table 4.1) from UV-spectrometer gives higher than initial concentration thus producing negative value in the  $q$  which leads to decreasing amount of summation adsorption capacity.



**Figure 4.2.1** Deposit of PNP solid found in the adsorption bed

Secondly, error might also caused by deposition of impurities solid happened causing the increase of PNP concentration at the end phase of adsorption process.



**Figure 4.2.2** *Uneven sampling bottle size*

Third factor might be because spillage of sample from sampling bottle. The sample was taken every 30 second without moving the sample bottles. The observation during sampling is that the bottle sizing is uneven; there are 30mL and 50mL clean sample bottle provided. But for 30 second at 1.1mL/s flowrate, the volume of p-nitrophenol collected is around 33mL. Several samples were spilled because of overflow. This may deviate the PNP concentration, producing the fluctuation in Figure 4.1.1.



**Figure 4.2.3** *Inconsistent data from UV-Spectrophotometer*

In Run 1, 114 samples were taken for UV-Spectrophotometer test. The sample batch can only be finished by Day 14 due to limited unit cuvette (1 pair). Data taken from UV-Spectrophotometer also vary from day to day even though same sample was injected in the cuvette.

From the error observation, repetition of Shallow Bed Adsorption using Palm Kernel Shell activated carbon is needed.



### 4.3 Result Run 2

**Table 4.3 Shallow Bed Adsorption Run 2**

Date of Experiment	24 <sup>th</sup> October 2011
Initial Volume of Sample (V)	5000 mL
Flowrate (v)	1.429 mL/s
Amount of GAC ( $W_{GAC}$ )	1.0012 g
Particle Size PKS GAC	1.7-2.4 mm
Bed Diameter	2.6 cm
Bed Height	0.4019 cm
Bulk Density	0.4691 g/cm <sup>3</sup>
Calibration curve	$C = 21.957 (\text{Absorbance}) - 0.0314$

Sample	Time (s)	V (ml)	Absorbance of diluted sample	Concentration of diluted sample	Dilution factor	C (mg/L)	$\Delta q$ (mg/g)	$\Sigma \Delta q$ (mg/g)	$\Sigma \Delta q/q_0$
								$q_0$ roughly	356.3118
IR	0	5000	0.380	8.3123	100	831.226	0.0000	0.0000	0.0000
1	40	57.16	0.293	6.4020	100	640.200	10.9060	10.9060	0.0306
2	80	57.16	0.301	6.5777	100	657.766	9.9031	20.8091	0.0584
3	120	57.16	0.306	6.6874	100	668.744	9.2763	30.0854	0.0844
4	160	57.16	0.325	7.1046	100	710.463	6.8946	36.9800	0.1038
5	200	57.16	0.325	7.1046	100	710.463	6.8946	43.8746	0.1231
6	240	57.16	0.330	7.2144	100	721.441	6.2678	50.1424	0.1407
7	280	57.16	0.333	7.2803	100	728.028	5.8917	56.0341	0.1573
8	320	57.16	0.334	7.3022	100	730.224	5.7664	61.8004	0.1734
9	360	57.16	0.337	7.3681	100	736.811	5.3903	67.1907	0.1886
10	400	57.16	0.340	7.4340	100	743.398	5.0142	72.2050	0.2026
11	440	57.16	0.338	7.3901	100	739.007	5.2649	77.4699	0.2174
12	480	57.16	0.344	7.5218	100	752.181	4.5128	81.9827	0.2301
13	520	57.16	0.345	7.5438	100	754.377	4.3875	86.3702	0.2424
14	560	57.16	0.345	7.5438	100	754.377	4.3875	90.7576	0.2547
15	600	57.16	0.346	7.5657	100	756.572	4.2621	95.0197	0.2667
16	640	57.16	0.336	7.3462	100	734.615	5.5157	100.5354	0.2822
17	680	57.16	0.346	7.5657	100	756.572	4.2621	104.7975	0.2941
18	720	57.16	0.348	7.6096	100	760.964	4.0114	108.8089	0.3054
19	760	57.16	0.339	7.4120	100	741.202	5.1396	113.9485	0.3198
20	800	57.16	0.349	7.6316	100	763.159	3.8860	117.8345	0.3307
21	840	57.16	0.350	7.6536	100	765.355	3.7607	121.5952	0.3413
22	880	57.16	0.341	7.4559	100	745.594	4.8889	126.4840	0.3550
23	920	57.16	0.351	7.6755	100	767.551	3.6353	130.1194	0.3652
24	960	57.16	0.353	7.7194	100	771.942	3.3846	133.5040	0.3747
25	1000	57.16	0.353	7.7194	100	771.942	3.3846	136.8886	0.3842
26	1040	57.16	0.353	7.7194	100	771.942	3.3846	140.2732	0.3937
27	1080	57.16	0.354	7.7414	100	774.138	3.2593	143.5324	0.4028
28	1120	57.16	0.354	7.7414	100	774.138	3.2593	146.7917	0.4120
29	1160	57.16	0.354	7.7414	100	774.138	3.2593	150.0509	0.4211
30	1200	57.16	0.354	7.7414	100	774.138	3.2593	153.3102	0.4303
31	1240	57.16	0.354	7.7414	100	774.138	3.2593	156.5694	0.4394
32	1280	57.16	0.354	7.7414	100	774.138	3.2593	159.8287	0.4486
33	1320	57.16	0.355	7.7633	100	776.334	3.1339	162.9626	0.4574
34	1360	57.16	0.357	7.8072	100	780.725	2.8832	165.8458	0.4655
35	1400	57.16	0.357	7.8072	100	780.725	2.8832	168.7289	0.4735

36	1440	57.16	0.347	7.5877	100	758.768	4.1367	172.8657	0.4852
37	1480	57.16	0.357	7.8072	100	780.725	2.8832	175.7489	0.4932
38	1520	57.16	0.346	7.5657	100	756.572	4.2621	180.0110	0.5052
39	1560	57.16	0.356	7.7853	100	778.529	3.0085	183.0195	0.5136
40	1600	57.16	0.356	7.7853	100	778.529	3.0085	186.0280	0.5221
41	1640	57.16	0.356	7.7853	100	778.529	3.0085	189.0366	0.5305
42	1680	57.16	0.357	7.8072	100	780.725	2.8832	191.9198	0.5386
43	1720	57.16	0.350	7.6536	100	765.355	3.7607	195.6804	0.5492
44	1760	57.16	0.357	7.8072	100	780.725	2.8832	198.5636	0.5573
45	1800	57.16	0.359	7.8512	100	785.116	2.6325	201.1961	0.5647
46	1840	57.16	0.359	7.8512	100	785.116	2.6325	203.8286	0.5721
47	1880	57.16	0.358	7.8292	100	782.921	2.7578	206.5864	0.5798
48	1920	57.16	0.358	7.8292	100	782.921	2.7578	209.3442	0.5875
49	1960	57.16	0.358	7.8292	100	782.921	2.7578	212.1020	0.5953
50	2000	57.16	0.360	7.8731	100	787.312	2.5071	214.6092	0.6023
51	2040	57.16	0.361	7.8951	100	789.508	2.3818	216.9909	0.6090
52	2080	57.16	0.358	7.8292	100	782.921	2.7578	219.7487	0.6167
53	2120	57.16	0.359	7.8512	100	785.116	2.6325	222.3812	0.6241
54	2160	57.16	0.358	7.8292	100	782.921	2.7578	225.1390	0.6319
55	2200	57.16	0.358	7.8292	100	782.921	2.7578	227.8969	0.6396
56	2240	57.16	0.357	7.8072	100	780.725	2.8832	230.7800	0.6477
57	2280	57.16	0.358	7.8292	100	782.921	2.7578	233.5379	0.6554
58	2320	57.16	0.358	7.8292	100	782.921	2.7578	236.2957	0.6632
59	2360	57.16	0.359	7.8512	100	785.116	2.6325	238.9282	0.6706
60	2400	57.16	0.358	7.8292	100	782.921	2.7578	241.6860	0.6783
61	2440	57.16	0.358	7.8292	100	782.921	2.7578	244.4438	0.6860
62	2480	57.16	0.358	7.8292	100	782.921	2.7578	247.2017	0.6938
63	2520	57.16	0.358	7.8292	100	782.921	2.7578	249.9595	0.7015
64	2560	57.16	0.358	7.8292	100	782.921	2.7578	252.7173	0.7093

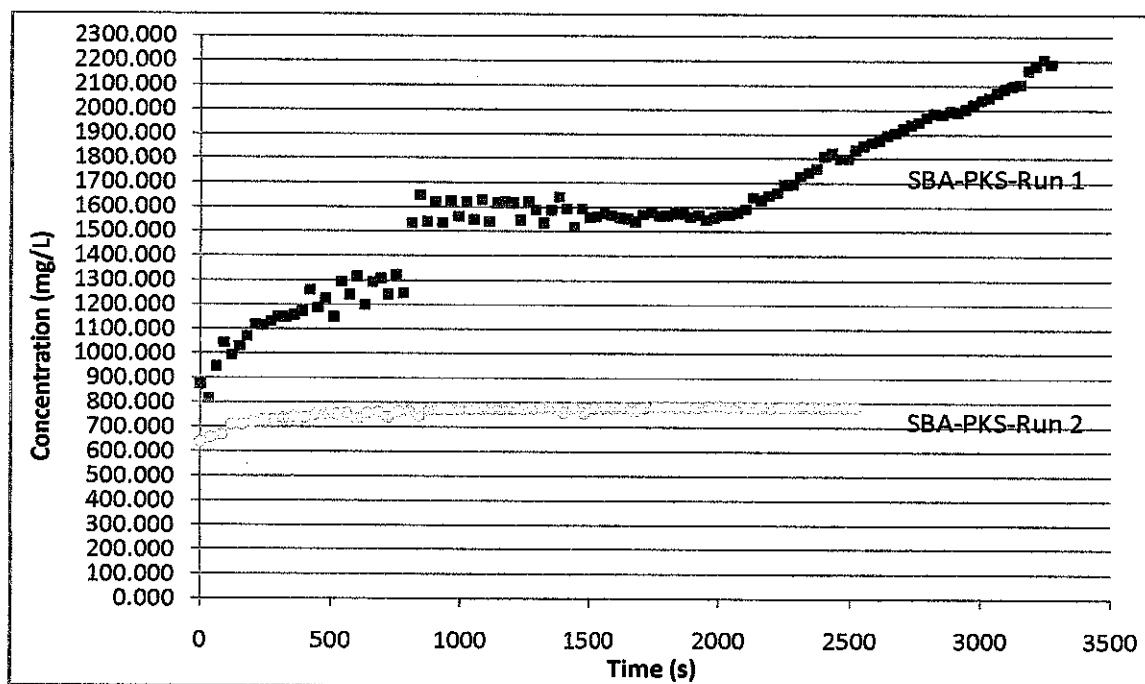
### Pump Calibration

Volume (mL)	Time (s)		Flow rate (mL/s)	
20	14	14	1.429	1.429
40	28	28	1.429	1.429
60	42	42	1.429	1.429
80	56	56	1.429	1.429
1.429				

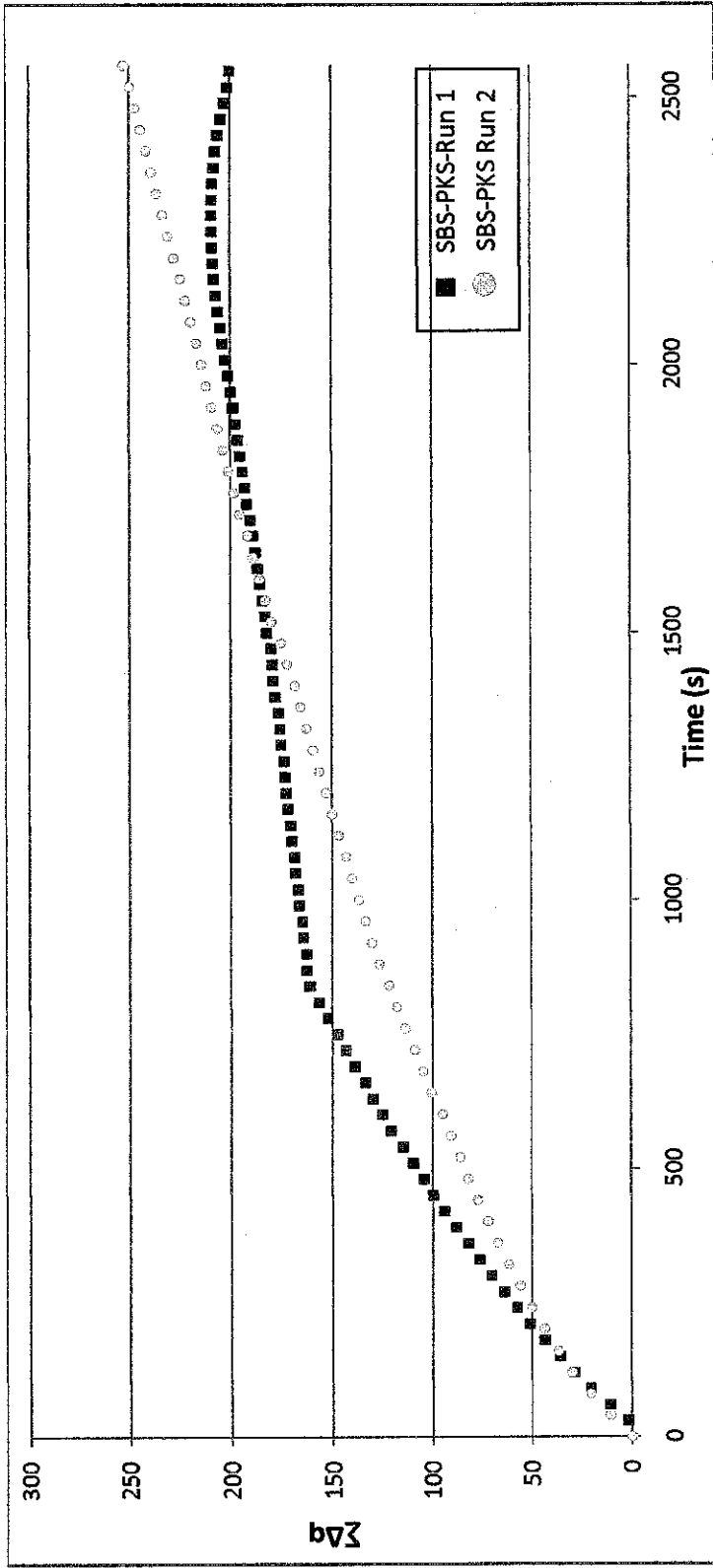


Figure 4.3.1 Run 2 samples in 80mL bottle

The adsorption data for Run 2 was acquired by using shallow bed adsorber but reducing the concentration of p-nitrophenol solution from 1600mg/L to 800mg/L and weight of Palm Kernel Shell activated carbon from 3g to 1g. The purpose is to accelerate the adsorption process while observing the breakthrough curve behavior. Hundred units of 80mL bottles were prepared to avoid spillage and deviation in concentration. The samples were successfully tested using spectrophotometer in ONE DAY, thus eliminating inconsistent data error. The comparison of p-nitrophenol concentration after adsorption in Run 1 and Run 2 was plotted against the process time in Figure 4.3.2. The concentration increases smoothly with an increase in time. While Figure 4.3.3 shows the adsorption capacity of Palm Kernel Shell activated carbon increasing until the reservoir was empty. This indicates that the 1g PKS activated carbon bed can have more capacity towards adsorption before the bed is fully loaded.



**Figure 4.3.2** Comparison of PNP concentration after adsorption versus time



**Figure 4.3.3 Comparison of adsorption capacity of PKS GAC versus time (Breakthrough Curve)**

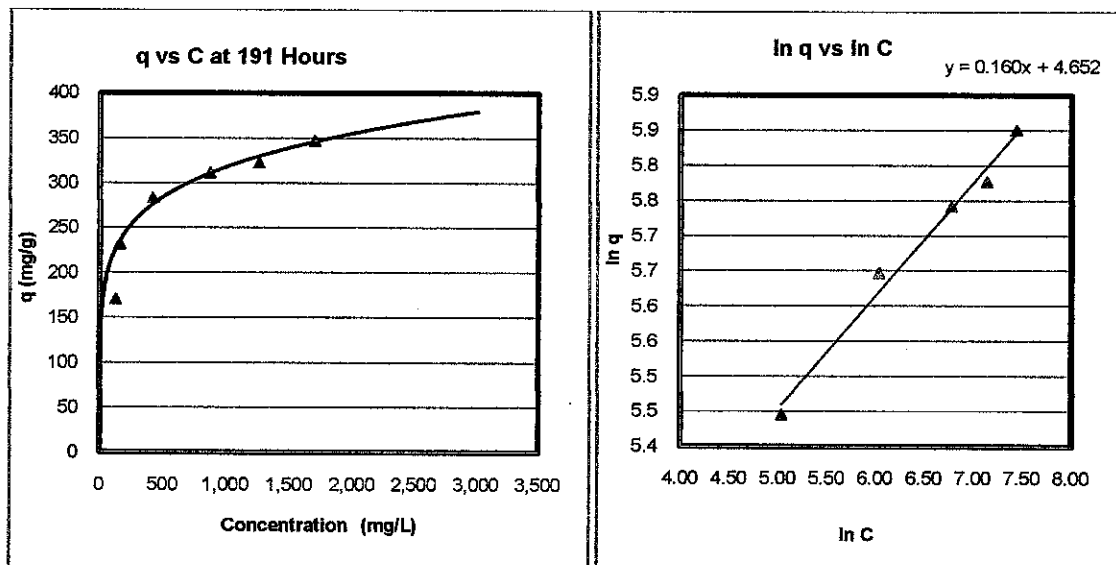
From Run 2 of Shallow Bed Adsorption, the adsorption capacity reached 252.7173 mg/g. This value shows 252.7173mg of PNP can be absorbed by using 1g of Palm Kernel Shell activated carbon.

#### 4.4 Batch Adsorption Experiment

**Table 4.4** Batch Adsorption Experiment Result

Date of Experiment	20 <sup>th</sup> July 2011 – 28 <sup>th</sup> July 2011
Duration	191 hours
Initial Volume of Sample, V	50mL
Initial Concentration of Sample, C <sub>0</sub>	2959.474mg/L
Calibration curve	C = 21.957 (Absorbance) – 0.0314

Sample	Amount of GAC	V (ml)	Abs of diluted sample	Conc of diluted sample	Dilution factor	C (mg/L)	q (mg/g)	ln C	ln q
0			0.271	5.9189	500	2959.4735			
1	0.8300	50	0.114	2.4717	50	123.5849	170.8367	4.8169	5.1407
2	0.6057	50	0.071	1.5275	100	152.7547	231.6922	5.0288	5.4454
3	0.4483	50	0.381	8.3342	50	416.7109	283.6006	6.0324	5.6476
4	0.3351	50	0.398	8.7075	100	870.7486	311.6570	6.7694	5.7419
5	0.2637	50	0.574	12.5719	100	1257.1918	322.7686	7.1366	5.7769
6	0.1822	50	0.310	6.7753	250	1693.8175	347.3260	7.4347	5.8503



**Figure 4.4** Adsorption isotherm measured for PNP-PKS AC adsorption

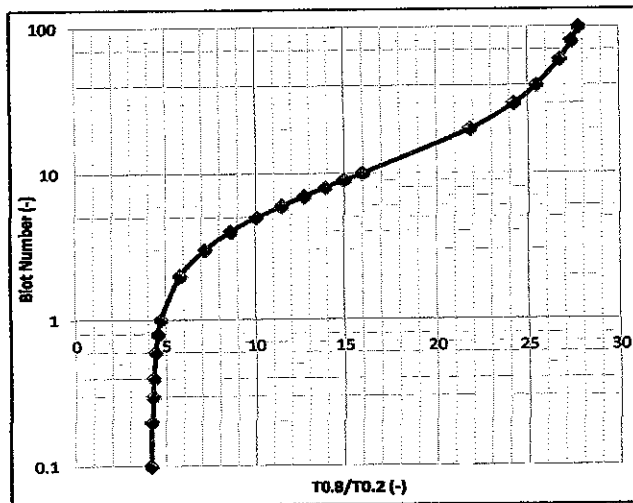
Figure 4.4 shows the result of PNP adsorption with PKS AC. From this result, Freundlich isotherm ( $q=kc^{(1/n)}$ ) was determined as  $q=105c^{(1/6.23)}$ . Thus, the value of k and 1/n obtained was 105 and 0.1605, respectively. These values were needed to simulate Biot Number.

#### 4.5 Biot Number

Biot Number (Bi) was simulated by Prof Furuya from Meiji University using Batch Adsorption experimental values. Bi is essential in calculating  $D_s$  and  $k_f$ .

**Table 4.5** *Compiled Simulation Results of various Bi with  $T_{0.8}/T_{0.2}$*

Bi	$T_{0.8}$	$T_{0.2}$	$T_{0.8} / T_{0.2}$
0.1	6.948E-02	2.918E-01	4.19977
0.2	6.807E-02	2.880E-01	4.230939
0.3	6.760E-02	2.887E-01	4.27071
0.4	6.737E-02	2.908E-01	4.316461
0.6	6.714E-02	2.974E-01	4.42955
0.8	6.704E-02	3.062E-01	4.567422
1	6.675E-02	3.157E-01	4.729588
2	6.692E-02	3.913E-01	5.84728
3	6.729E-02	4.856E-01	7.216525
4	6.790E-02	5.879E-01	8.658321
5	6.880E-02	6.939E-01	10.08576
6	7.001E-02	8.022E-01	11.45836
7	7.153E-02	9.117E-01	12.7457
8	7.335E-02	1.022E+00	13.9332
9	7.545E-02	1.133E+00	15.01657
10	7.780E-02	1.245E+00	16.00257
20	1.085E-01	2.371E+00	21.85253
30	1.444E-01	3.503E+00	24.259
40	1.818E-01	4.637E+00	25.50605
60	2.579E-01	6.906E+00	26.77782
80	3.347E-01	9.176E+00	27.4156
100	4.118E-01	1.145E+01	27.80476



**Figure 4.5**  $T_{0.8} / T_{0.2}$  versus Bi

#### 4.6 Diffusivity and Liquid Mass Transfer Coefficient

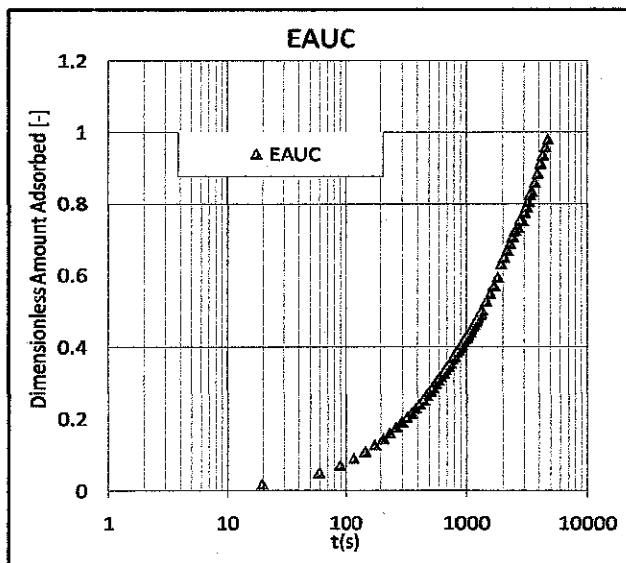
Diffusivity,  $D_s$  and Liquid Mass Transfer Coefficient,  $k_F$  can be calculated using the following equations:

$$D_s = T/t \times r_p^2$$

$$k_F = \frac{Bi \times \rho_p \times q_0 \times D_s}{r_p \times C_0}$$

- Where,
- $D_s$ , diffusivity
  - $T/t$ , ratio of EAUC and TUC
  - $r_p$ , activated carbon pore radius
  - $k_F$ , liquid mass transfer coefficient
  - $Bi$ , biot number
  - $\rho_p$ , density of activated carbon
  - $q_0$ , adsorption capacity

Data from SBA Run 2 (Figure 4.3.3) was transformed into log based time versus dimensionless amount adsorbed as shown in Figure 4.6.1 while TUC in Figure 4.6.2 was simulated using experimental  $Bi$  obtained in Figure 4.5.



**Figure 4.6.1** *Experimental Adsorption Uptake Curve (EAUC)*

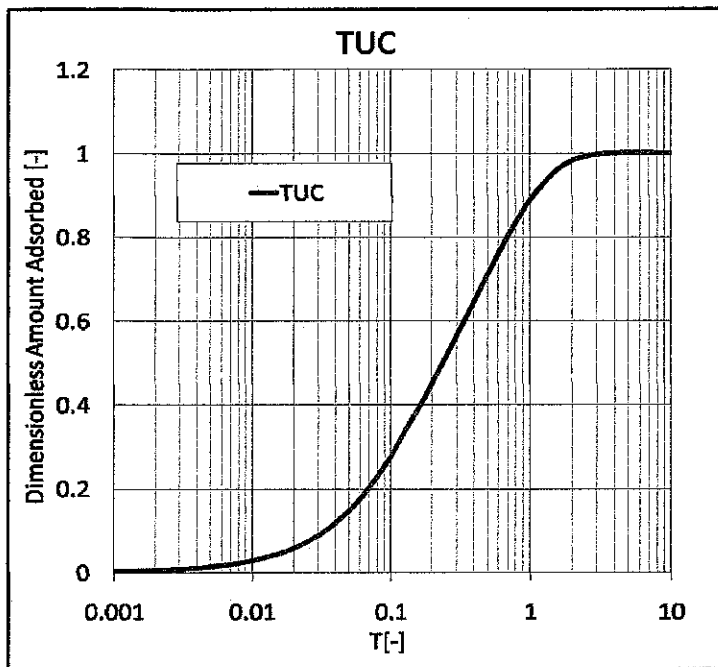


Figure 4.6.2 Theoretical Uptake Curve (TUC)

By matching EAUC with TUC,  $T/t$  value was obtained to calculate  $D_s$ . The method is by moving EAUC towards TUC using ratio number ( $T/t$ ) as shown in Figure 4.6.3.

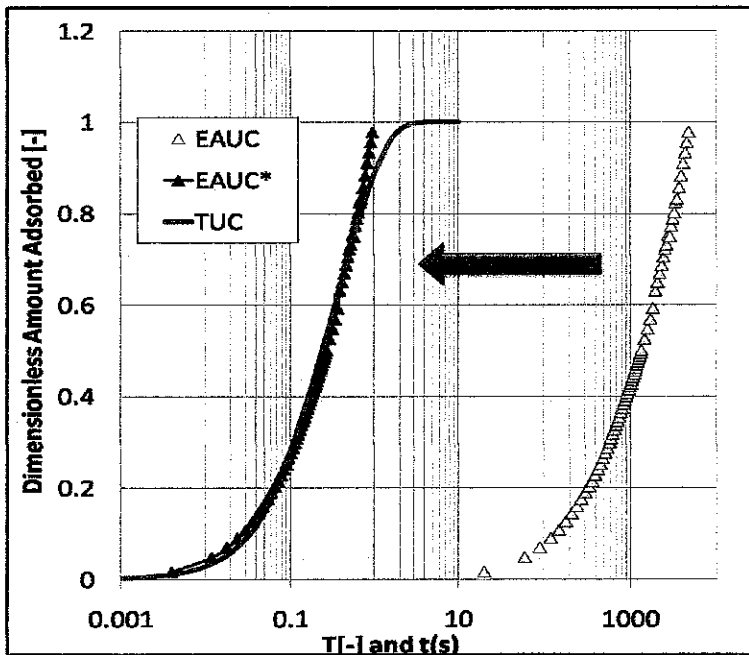


Figure 4.6.3 Determination of  $T/t$



Finally, the  $D_s$  and  $k_F$  was calculated as:

**Diffusivity**

$$\begin{aligned} D_s &= T/t \times r_p^2 \\ &= 2.1013 \times 10^{-6} \text{ cm}^2/\text{s} \end{aligned}$$

**Liquid Mass Transfer Coefficient**

$$\begin{aligned} k_F &= \frac{Bi \times \rho_p \times q_0 \times D_s}{r_p \times c_0} \\ &= 0.0181 \text{ cm/s} \end{aligned}$$

## CHAPTER 5: CONCLUSION

In this study, adsorption behavior of *p*-nitrophenol onto Palm Kernel Shell activated carbon using Shallow Bed Column was investigated experimentally. Shallow Bed technique helps to overcome intraparticle resistance problem. Adsorption rate can be obtained directly.

From the SBA-PKS-Run 1 Experiment, the adsorption capacity is increase smoothly till 2760 second before it decreases. The causes of error were discussed and recommendation steps were taken in the SBA-PKS-Run 2. Adsorption capacity reached **252.7mg/g** throughout the experiment indicates high adsorptive capacity for PKS AC.

Diffusivity and liquid mass transfer coefficient are important parameters in optimization of adsorption system. The obtained  $D_s$  and  $k_F$  are about  **$2.1013 \times 10^{-6} \text{ cm}^2/\text{s}$**  and **0.0181 cm/s**, respectively.

## CHAPTER 6: RECOMMENDATION

There are several recommendations for future work or the expansion of this research:

1. Compare PKS AC parameter with another commercial AC. F400 activated carbon from Japan are available in the laboratory.
2. Propose another method to analyze PNP concentration after removal for better accuracy. High Performance Liquid Chromatography is recommended but further study on the equipment must be done.
3. Dilution method can be improved by using disposable pipette tips to increase accuracy of diluted concentration and save process time. The current tool used is glass tips which need to be rinsed, cleaned and dried before diluting another sample.
4. Control studies need to be done, to determine the efficiency of adsorption bed in Shallow Bed technique since the length of glass wool is very thick. (Run experiment without Activated Carbon placed in the bed)
5. Complexity of adsorption caused by multi-component in real wastewater should be studied. This study only discusses the behavior of single component in wastewater: P-nitrophenol.

## REFERENCES

- [1] J. Zawala, K. Swiech, K. Malysa, (2007). "A simple physicochemical method for detection of organic contaminants in water" Institute of Catalysis and Surface Chemistry Polish Academy of Sciences and Jagiellonian University, Faculty of Chemistry, Poland.
- [2] N. S. Kumar, M. Suguna, M. V. Subbaiah, A. S. Reddy, N. P. Kumar and A. Krishnaiah, (2010). "Adsorption of Phenolic Compound from Aqueous Solutions onto Chitosan-Coated Perlite Beads as Biosorbent" Technical papers, Biopolymers and Thermophysical Laboratories, Department of Chemistry, Sri Venkateswara University, India and Department of Safety Environmental System Engineering, Dongguk University, Gyeongju, Korea.
- [3] U.S. Environmental Protection Agency, (1994). "Integrated Risk Information System (IRIS) on p-Nitrophenol" National Center for Environmental Assessment, Office of Research and Development, Washington, DC.
- [4] Environmental Quality Act 1974, "Environmental Quality (Industrial Effluent) Regulation 2009, P.U. (A) 434"
- [5] Jia-Ming Chern, Yi-Wen Chien, (2001). "Adsorption of Nitrophenol onto Activated Carbon: Isotherms and Breakthrough Curves" Department of Chemical Engineering, Tatung University, Taiwan.
- [6] S. Phillip, J. R. Bailey, (1999). "Organic Chemistry" California Polytechnic State University Press, California.
- [7] Lewis Rj, Sac NI, (1987). "Hawley's Condensed Chemical Dictionary" 11<sup>th</sup> Edition, Van Nostrand Reinhold Co, New York, NY.
- [8] ICSC, (1998). "P-nitrophenol".
- [9] JH Potgieter, SO Bada, SS Potgier-Vermaak, (2009). "Adsorptive Removal of Various Phenols From Water by South African Coal Fly Ash" Water SA (Online) Volume 35 Pretoria.
- [10] Munaf E, Zein R, Kurniadi R and Kurniadi I, (1997). "The use of rice husk for removal of phenol from waste water as studied using 4-aminoantipyrine spectrophotometric method." Environmental Technology 18, 355-358.

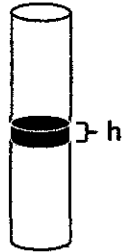
- [11] Bertoncini C, Raffaelli J, Fassino L, Odetti Hs and Botani Ej, (2003). "*Phenol adsorption on porous and non-porous carbons*" Carbon 41, 1101-1111.
- [12] Khalid M, Joly G, Renaud A and Magnoux P, (2004). "*Removal of phenol from water by adsorption using zeolites*" Ind. Eng. Chem. Res. 43 5275-5280.
- [13] Aksu Z, (2005). "*Application of biosorption for the removal of organic pollutants: A review*" Process Biochem. 40 997-1026.
- [14] Denizli A, Cihanger N, Taner A, Taner M and Alsancak G, (2004). "*Removal of chlorophenols from synthetic solutions using Phanerochaete chrysosporium*" Process Biochem. 39 2025-2030.
- [15] J. M. Montgomery, (1985). "*Water Treatment Principles and Design*" Consulting Engineers Inc, USA.
- [16] R. P. Schwarzenbach, M. P Gschwend, D. M. Imboden, (2003). "*Environmental Organic Chemistry*" John Wiley and Sons Inc. Publication, Canada.
- [17] Kenneth Russell Carrington, (2009), "*Fabrication and Optimization of Nano-structured Composites for Energy Storage*"
- [18] N. C. Sawyer, P. I. Mc Carty, G. F Parkin, (1994). "*Chemistry for Environmental Engineering*" Mc Graw Hill International Edition, Singapore.
- [19] Urano, K. and Tachikawa, H., (1991). "*Process development for removal and recovery of phosphorus from wastewater by a new adsorbent*" Ind. Eng. Chem. Res., 30, 1893-1896
- [20] Kenneth E. Noll, Vassilios Gounaris, Wain-Sun Hou, (1992). "*Adsorption Technology for Air and Water Pollution Control.*" Lewis Publishers Inc.
- [21] F. A. Banat, B. A. Bashir, S. A. Asheh, O. Hayajneh, (2000). "*Adsorption of phenol by betonite*" Environmental Pollution, 107, pg. 391-398.
- [22] N. Roostai, E. H. Tezel, (2004). "*Removal of Phenol from Aqueous Solution by Adsorption*" Journal of Environmental Management 70, pg 157.
- [23] S. Rengaraj, S. H. Moon, R. Sivabalan, V. Murugesan, B. Arabindoo, (2002). "*Agricultural solid waste for the removal of organics; adsorption of phenol from water and wastewater by palm seed coat activated carbon*" Waste Management 22, pg 543.
- [24] B. C. Punmia, K. J. Ashok, K. J. Arun, (1995). "*Water Supply Engineering*" Second Edition, Firewall Media, Laxmi Publications Ltd, New Delhi.

- [25] Francisco Rodriguez-Reinoso, Harry Marsh, (2006). "*Activated Carbon*" 1<sup>st</sup> Edition, Elsevier Inc.
- [26] Steven D. Aust, Al Bourquin, John C.Loper, Joseph P. Salanitro, William A. Suk, James Tiedje, (1994). "*Biodegradation of Hazardous Waste*" Environmental Health Perspectives Supplements, Vol. 102 Suppl 1:245-252
- [27] Adel Al-Kdasi, Azni Idris, Katayon Saed, Chuah Teong Guan, (2005). "*Treatment of Textile Wastewater by Advanced Oxidation Process – A Review*" Department of Chemical & Environmental Engineering, Department of Civil Engineering, Faculty Engineering, Universiti Putra Malaysia.
- [28] Metcalf and Eddy, (2003). "*Wastewater Engineering: Treatment and Reuse*" Mc. Graw Hill International Edition, New York.
- [29] G. M. Loudon, (1995). "*Organic Chemistry*" The Benjamin/ Cummings Publishing Company Inc., California.
- [30] J.A Kent, (1992). "*Riegel's Handbook of Industrial Chemistry*" 9<sup>th</sup> Edition, Van Nostrand Reinhold Publications, New York.
- [31] P. V. Atkins, (1994). "*Physical Chemistry*" 5<sup>th</sup> Edition, Oxford University Press, Oxford.
- [32] M. Ahmaruzzaman, D. K. Sharma, (2005). "Adsorption of Phenols from Wastewater" Centre for Energy Studies, Indian Institute of Technology Delhi, India.
- [33] National Institute for occupational Safety and Health, (1998), "*International Chemical Safety Card: p-nitrophenol*"
- [34] "*Phenolics, Spectrophotometric, Manual 4-AAP with Distillation*", Editorial Revision for NPDES, (1978).
- [35] Hafizah Afif<sup>a</sup>, Usama Mohamed<sup>a</sup>, Wissam N. Omar<sup>a</sup>, Eiji Furuya<sup>b</sup>, (2011). "*Removal of P-Nitrophenol from water using activated carbon.*" <sup>a</sup>Chemical Engineering Department, Universiti Teknologi PETRONAS, Malaysia, <sup>b</sup>Department of Applied Chemistry, Meiji University, Japan.

## Appendix 1

### LIST OF FORMULA

1) Bed Height =  $\frac{W_{GAC} / \rho_{GAC}}{\pi D^2 / 4}$



$$V = W_{GAC} / \rho_{GAC}$$

$$V = \pi r^2 h$$

$$h = V / \pi r^2$$

- 2) Concentration of diluted sample = 22.051 (Absorbance) - 0.019
- 3) Concentration of sample = Dilution Factor x Concentration of diluted sample
- 4) Adsorption Capacity,  $\Delta q = \frac{\text{Amount PNP adsorbed (mg)}}{\text{Amount of adsorbent (g)}}$   
 $= \frac{(C_{\text{initial}} - C_{\text{final}}) \times \text{Volume (L)}}{\text{Weight GAC}}$
- 5) Summation of adsorption capacity,  $\sum \Delta q = \Delta q_1 + \Delta q_2 + \dots$
- 6)  $q_0 = kc^{1/n}$ ,  $k = 66.653$ ,  $1/n = 0.2259$  (Based on Batch Adsorption using PKS Activated Carbon)
- 7) Percentage of adsorption capacity =  $\sum \Delta q / q_0$
- 8) Sample volume (mL) = flowrate (mL/s) x time (s)
- 9) Carbon usage rate (g carbon/L wastewater) =  $\frac{\text{Total impurity removed (mg/L)}}{\text{Adsorption capacity (mg/g)}}$