CHAPTER 1

INTRODUCTION

1.1 Background

Industrial wastewater treatment is defined as a group of unit processes designed to separate, modify, remove, and destroy undesirable substances carried by wastewater from industrial sources. In other words, industrial wastewater treatment covers the mechanisms and processes used to treat waters that have been contaminated in some way by anthropogenic industrial or commercial activities prior to its release into the environment or its re-use. Those processes are vital to make sure the contaminants in the wastewater do not go beyond the allowable limit set by laws and regulations before it is discharged to the environment. Besides, the treated water can also be used in the recycle streams in order to minimise the usage of fresh water, which contributes to cost optimization.

Various treatment systems have been proposed for phenolic containing wastewaters, including pervaporation, membrane technique, electrochemical treatment and others. Among all the methods, adsorption has been considered as one of the best ways to remove organic compounds. This is because adsorption can be operated more conveniently, is more effective and has relatively low cost too.

Activated carbon (AC) is a well-known commercial material that is effectively used as an adsorbent for the removal of a wide variety of organic and inorganic pollutants dissolved in water or from gaseous emissions (Dr. V Kaur et al., 2010). AC comes in two forms: powdered and granular. Granular Activated Carbon (GAC) is more commonly used in wastewater treatment as it has the ability to adapt better to continuous contacting, thus not needed to be separated from the bulk liquid. On the other hand, Powdered Activated Carbon is less preferred due to its small particle size which causes regeneration and design problems. Even though AC shows good

adsorption capacity with its high specific surface area, it is quite costly and the price is proportional to the quality. Therefore, modification needs to be done on the AC so that the adsorption capacity can be increased, thus minimising the production cost.

This project focuses on modifying the surface of Granular Activated Carbon (GAC), which is in the form of chemical modification by applying acidic method involving nitric acid (HNO_3). In fact, this project aims to find alternatives in improving the efficiency of industrial wastewater treatment plant that is practiced by most companies nowadays. The section in the wastewater treatment system being targeted is Condensate Polishing Plant. It is a plant where high purity of demineralized water is generated based on ion exchange concept. This also means that ion exchange resins will be used in the condensate polisher to remove the contaminants. Somehow, the organic contaminants contained in the wastewater will damage the resins. Hence, carbon filter is installed in order to decrease the organic contaminants entering the ion exchange unit.

1.2 Problem Statement

One of the organic compounds found in industrial wastewater is para-nitrophenol (or p-nitrophenol). P-nitrophenol is a byproduct in the enzymatic hydrolysis of parathion and methyl parathion, two popular organophosphate pesticides. It has been categorized as a major pollutant by the US EPA due to its toxicity on biological systems. Therefore, p-nitrophenol has to be removed from the industrial wastewater treatment to ensure cleaner drinking water for human consumption. In Malaysia, the concentration should not exceed 10μg/L prior to discharging into water bodies from industrial effluent, according to Malaysia Environmental Quality Report 2001.

Apart from that, by allowing p-nitrophenol, which is an organic compound, to enter the ion exchange unit in condensate polishing plant, it actually brings defect to the resin as a result of the great possibility of anion resin to adsorb a large proportion of the natural organics from the wastewater. Furthermore, these organic molecules are hard to be removed from the resin, hence may result in progressive fouling of the resin, drop in resin capacity and prolonged regeneration times because of poor rinsing. Therefore, the resin needs to be cleaned regularly so that the foulants can be removed.

As mentioned above, it is essential to minimize the number of organic contaminants entering the ion exchange unit. Since AC is effective in adsorbing and removing organic contaminants, it is a good move to install carbon filter. However, the current AC sold in the market is expensive. Thus, enhancing the adsorption capacity is an effective approach to reduce the cost since adsorption capacity is one of the factors affecting the operation cost of activated carbon adsorption. This means modification for AC has to be done to increase the surface adsorption and hence removal capacity, as well as to improve the selectivity to organic compounds (K.J Kim et al., 2005).

1.3 Objectives

The objectives of this project include:

- To modify the surface of GAC through chemical acidic method using HNO_3.
- To characterize the activated carbon before and after modification.
- To study the effect of adsorbate concentration on adsorption performance.
- To study the effect of pH on adsorption performance.
- To study the effect of temperature on adsorption performance.
- To make comparison between the overall adsorption capacity of unmodified and modified activated carbon in adsorbing p-nitrophenol.

1.4 Scope of Study

In order to ensure the feasibility of this research project within the time frame given, the boundaries of the project work are narrowed down to a few operating parameters instead of all the factors that can affect the adsorption capacity. The activated carbon and p-nitrophenol used in the experiment are obtained directly from the lab whereas the equipment needed are located in Chemical Engineering Blocks as well as Mechanical Engineering Block.

This project utilizes the fundamental knowledge in Separation Process, especially Adsorption System. The scope of study includes the following:

- Literature review and selection on the type of AC for removal of the chosen pollutant.
- Literature review on the adsorption isotherm in the adsorption system.
- Literature review on the characteristic of activated carbon and the available surface modifications.
- Literature review and preparation of a procedure for the experiment.
- Validation of experimental result with the literature review.

CHAPTER 2

LITERATURE REVIEW AND THEORY

## 2.1 Organic Pollution in Wastewater

The high degree of industrialization and urbanization has resulted in environmental pollution (Sibel Tunali*, Tamer Akar., 2005). Organic contamination exists in effluents of many industries such as petrochemicals, petroleum refineries, coke-oven, steel foundry, insecticides and herbicides industries and etc. (Arinjay Kumar et al., 2007). Tetrachloromethane, chloroform, phenol and p-nitrophenol are among the organic compounds that can be found in industrial wastewater. The presence of organic compounds in the waste water poses great danger to the flora and fauna in the biosphere as those organic compounds are toxic and carcinogenic in nature. Their toxicity on biological systems has led to their classification as priority pollutants by the United States Environmental Protection Agency (W.S. Wan Ngah*, S. Fatinathan, 2006). Hence, it is a must to minimize the discharge of these organic compounds from the effluents into the surface waters.

2.2 Adsorption

Adsorption is a process, similar to absorption, by which a substance in a gas or liquid becomes attached to a solid. The substance can be a pollutant, called an adsorbate, which is attracted to the surface of a special solid. Adsorption occurs naturally, but anthropogenic adsorption methods have been generated to clean up hazardous waste or purify drinking water.

The adsorption process takes place in four more or less definable steps: (1) bulk solution transport, (2) film diffusion transport, (3) pore transport, and (4) adsorption. Bulk solution transport involves the movement of the organic material to be adsorbed through the bulk liquid to the boundary layer of fixed film of liquid surrounding the adsorbent, typically by advection and dispersion in carbon contactors. Film diffusion transport involves the transport by diffusion of the organic material through the stagnant liquid film to the entrance of the pores of the adsorbent. Pore transport involves the transport of the material to be adsorbed through the pores by a combination of molecular diffusion through the pore liquid and/or by diffusion along the surface of the adsorbent. Adsorption involves the attachment of the material to be adsorbed to adsorbent at an available adsorption site (George Tchobanoglous, Franklin L. Burton, and H. David Stensel, 2003). Figure 1 shows the definition sketch for the adsorption of an organic constituent with activated carbon.

Figure 1: Definition sketch for adsorption of an organic constituent
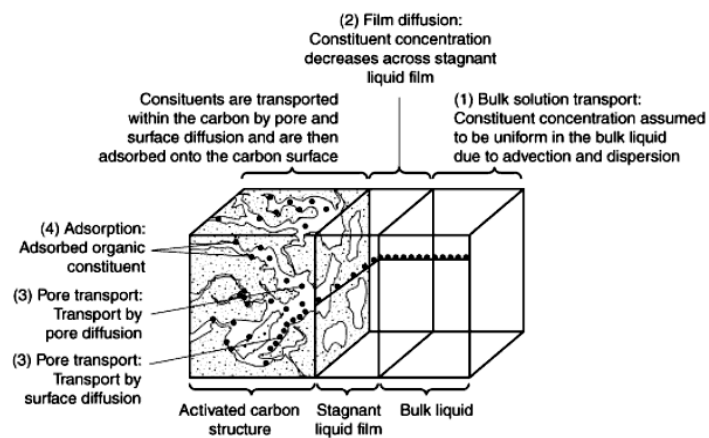
Source: Metcalf and Eddy, Inc., *Wastewater Engineering, Treatment and Reuse*, fourth edition (New York: McGraw-Hill, 2003)

2.2.1 Adsorption Isotherm

Adsorption isotherm is an equation that describes how the amount of a substance adsorbed onto a surface depends on its pressure (if a gas) or its concentration (if in a solution), at a constant temperature. Adsorption isotherm is developed by exposing a given amount of adsorbate in a fixed volume of liquid to varying amounts of activated carbon (George Tchobanoglous, Franklin L. Burton, and H. David Stensel, 2003). There are a few types of isotherm exist, but the most commonly used ones are Langmuir and Freundlich Isotherm.

The Langmuir Adsorption Isotherm describes quantitatively the buildup of a layer of molecules 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:

$$\frac{x}{m} = \frac{abC_e}{1 + bC_e}$$
Equation 1

where x/m = 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 C_e /(x/m) versus C_e and making use of Equation 3 rewritten as:

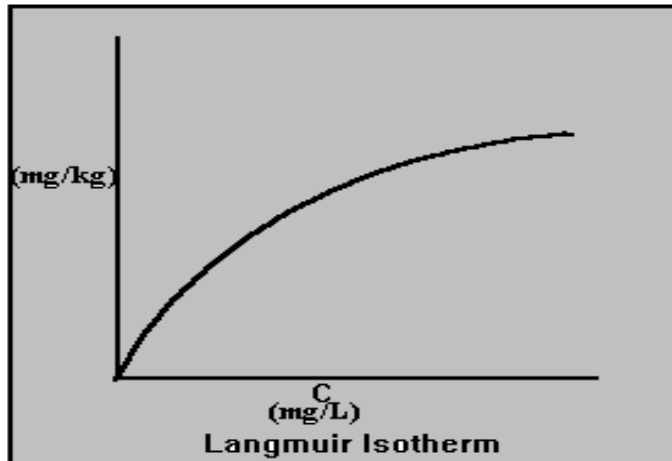$$\left(\frac{C_e}{(x/m)}\right) = \frac{1}{ab} + \frac{1}{a}C_e$$
Equation 2

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:

$$\frac{x}{m} = K_f C_e^{1/n}$$

Equation 3

where x/m = mass of adsorbate adsorbed per unit mass of adsorbent,
mg adsorbate/g activated carbon

K_f = Freundlich capacity factor,
(mg adsorbate/g activated carbon)(L water/mg adsorbate) $^{1/n}$

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

$1/n$ = Freundlich intensity parameter

The constants in the Freundlich isotherm can be determined by plotting log (x/m) versus log C_e and the Equation 1 is rewritten as:

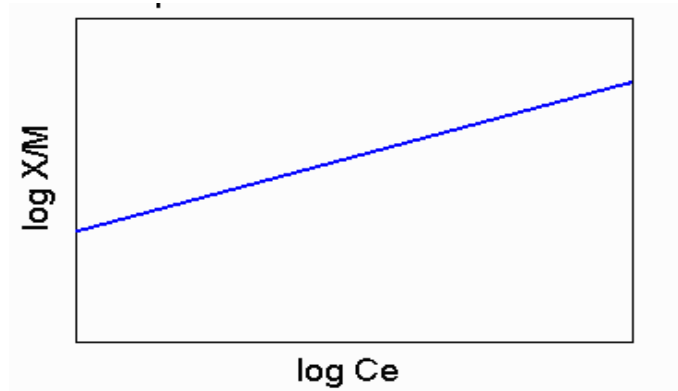$$\log\left(\frac{x}{m}\right) = \log K_f + \frac{1}{n}\log C_e \qquad \text{Equation 4}$$

Figure 3: Freundlich isotherm curve

2.2.2 Activated Carbon

Activated carbon (AC) is a crude form of graphite, except that it has a random imperfect structure which is highly porous over a broad range of pore sizes and visible cracks and crevices to molecular dimension [8]. Trade names for activated carbon include Norit and Ultracarbon.

Activated carbon can remove organic materials from gas streams or solutions. The amount of material removed depends on the capacity of the activated carbon as well as the affinity of the material for the carbon. Typical uses are to remove odors and volatile organic compounds (VOC's).

GAC is used to adsorb the relatively small quantities of soluble organics and inorganic compounds such as nitrogen, sulfides, and heavy metals remaining in the wastewater (Nicholas P.Cheremisinoff, 2002). Although the effectiveness of ACs as an adsorbent for a wide range of pollutants is well known, more research on its modification is gaining prominence due to the need to develop enhanced affinity for specific contaminants and remove them from industrial and drinking water applications (V Gaur and P. A. Shankar, 2008).

The GAC chosen for this experiment is Calgon Activated Carbon F400. It is manufactured by Calgon Carbon Corporation for removal of organic pollutants from municipal or industrial wastewaters. This carbon is manufactured from select grades of bituminous coal to produce a high density, high surface area, durable granular product capable of withstanding the abrasion and dynamics associated with repeated reactivation, hydraulic transport, backwashing and mechanical handling. The applications of this carbon include:

- Applying point source treatment to remove organics
- Polishing effluent from biological waste treatment systems
- Recycling the treated water for replacement of groundwater or for other suitable recycling applications
- Providing total wastewater treatment

Calgon Activated Carbon F400 has several good features. Firstly, it has high surface area. Systems using this carbon can accommodate changes in flow rates and increases in concentration of pollutants whether caused by spills, peak loads, pre-treatment upsets or other variations in the wastewater effluent. Because of its high surface area and abrasion resistance, this carbon can be reactivated repeatedly and returned to service to provide maximum economy. Besides, this carbon is of high density, wet readily, and does not float, thus minimizing loss during backwash operations. As for the pore size, this carbon is produced with an exceptionally high internal surface area of optimum pore size for adsorption of both high and low molecular weight pollutants.

2.3 Surface Modification of Activated Carbon

Based on the type and nature of the targeted impurities, the surface of AC may be modified to enhance the affinity toward the desired impurity (V Gaur and P. A. Shankar, 2008). As an inert porous carrier material having large specific surface area, AC is capable of attracting a variety of chemicals onto its hydrophobic internal surface. Depending on the application, there are different methods to modify AC, which make the surface accessible to a variety of reactants. In general, the surface modification of AC is carried out after the activation step. As shown in Figure 4, the modification can be categorized in three classes: chemical modification, physical modification and biological modification (V Gaur and P. A. Shankar, 2008). The chemical modification may further be divided into two broad groups, those resulting in acidic and basic surface. The third type of chemical modification is the surface impregnation of AC with active metals and their oxides. The physical modification includes mainly heat treatment. The biological modification is a relatively newer approach, wherein biological methods of environmental control can be used for water treatment and other applications.
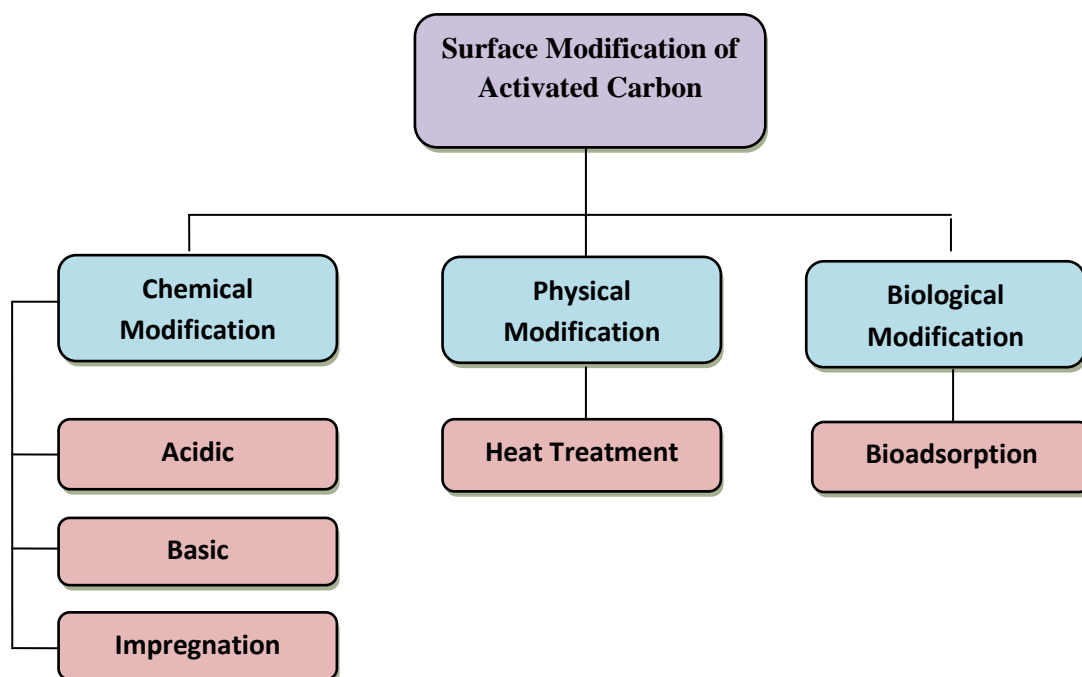
Figure 4: Modification techniques for AC

2.3.1   Chemical Modification

The AC surface can show acidic, basic or neutral behaviour, depending on the presence of the surface functional groups. For the removal of heavy metals from water, acidic functional groups on carbon surfaces have been examined and found to be highly favourable because metal ions have a tendency to form metal-complexes with the negatively charged acid groups. All of the chemical treatments using oxidizing agents employed for creating acidic functional groups are associated with the reduction of specific surface area and total pore volume, mainly due to the destruction of porous structures within AC during oxidation. The chemical modifications of basic groups on the surface are carried out by treating AC with chemicals such as aqueous ammonia and sodium hydroxide. Under alkaline (basic) solutions, it is expected that OH– ions react with the surface functional groups of AC. The alkaline treatment of AC is beneficial in enhancing the adsorption of especially organic species (like phenol) from water (V Gaur and P. A. Shankar, 2008).

Surface impregnation is one of the most important chemical modifications. The term impregnation is defined as the fine distribution of chemicals and metal particles in the pores of AC. The following three reasons are suggested for the impregnation of activated carbon (V Gaur and P. A. Shankar, 2008).

1. To optimize the catalytic properties of AC by promoting its built-in catalytic oxidation capability.
2. To promote synergism between AC and the impregnating agent.
3. To boost the capacity of AC as an inert porous carrier.

2.3.2 Physical Modification

Heat treatment is the major method so far reported for physical modification. AC treated thermally in an inert atmosphere generally becomes basic in nature. Physical modification usually results in enhancement of physical characteristics, including BET area and total pore volume. However, a significant drawback of heat treatment is that the surface oxygen functional groups (which are thermally unstable) can be decomposed at high temperatures. This may sometimes result in lesser adsorption capacity (V Gaur and P. A. Shankar, 2008).

2.3.3 Biological Modification

Growing attention has been given toward the adsorption of microorganisms in water on AC due to:

- the adsorptive properties of AC, which produce an increase in the concentration of nutrients and oxygen as well as the removal of disinfectant compounds;
- the porous structure of AC particles, which provides bacteria with a protective environment;
- the presence of a large variety of surface functional groups on AC, which enhances the adhesion of the microorganisms.

In the GAC chamber or in a carbon block used in water filtration, large-size bacteria get trapped within the activated carbon. These trapped bacteria begin to multiply in the activated carbon chamber, an ideal environment of temperature and organic nutrients for growth. This bio-fouling may cause GAC or carbon blocks to emit a decaying odor if the carbon media is not replaced regularly. New bacteriostatic technologies for activated carbon would be helpful to increase the life of carbon media, control heterotrophic plate count (HPC) growth and prevent malodours (V Gaur and P. A. Shankar, 2008).

2.4 Para-nitrophenol

Para-nitrophenol, with the molecular formula of $C_6H_5NO_3$, is a white to light yellow crystalline solid that is extremely hazardous. Generally, contact with it may severely irritate skin and eyes. Besides, it is also poisonous by ingestion and moderately toxic by skin contact. Para-nitrophenol is soluble in hot water and denser than water. It can decompose violently at 279°C and will burn even in absence of air (USCG, 1999). Inhalation or ingestion of para-nitrophenol will cause headache, drowsiness, nausea, and blue colour in lips, ears, and fingernails (cyanosis). In fact, para-nitrophenol has been listed by the United States Environmental Protection Agency (US EPA) as one of the priority pollutants. From EPA list of Priority Pollutants in year 2001, para-nitrophenol was ranked 256th most hazardous pollutant. Furthermore, it was also ranked as the 239th most annual released toxic phenol-like pollutants for the year 2000, where its emission was 0.007 ton/yr. Despite the fact, it is still accumulating in the environment at a worrisome rate.

2.5 Condensate Polishing Plant

Condensate polishing is an ion exchange process used to purify the *steam condensate* produced in high-pressure steam generation facilities (Larry Drbal, Kayla Westra and Pat Boston, 1996) *(*Brad Buecke, 2000) such as those in large thermal power plants. Steam condensate is the water formed by condensing the exhaust steam from the steam-driven turbines in thermal power plants and which is recycled for reuse as the major part of the steam generation feedwater.

Condensate polishing is a unique application of ion exchange resins that removes suspended and dissolved impurities from the condensate. There are two different systems of condensate polishing. One uses pressure vessels containing mixed beds of cation and anion resins and the other uses pressure vessels containing

powdered resins. Mixed bed systems, which they are being focused in this project, are the most commonly used systems.

In addition to removing dissolved impurities from the influent steam condensate, the beds of mixed ion exchange resins also act as filters to remove insoluble suspended impurities. But somehow, the existence of organics contaminant may cause defect to the resin in ion exchange equipment. Therefore, a carbon filter unit is installed. A degasser is used to remove dissolved carbon dioxide from condensate. Figure 5 shows the schematic diagram of Condensate Polishing Plant.
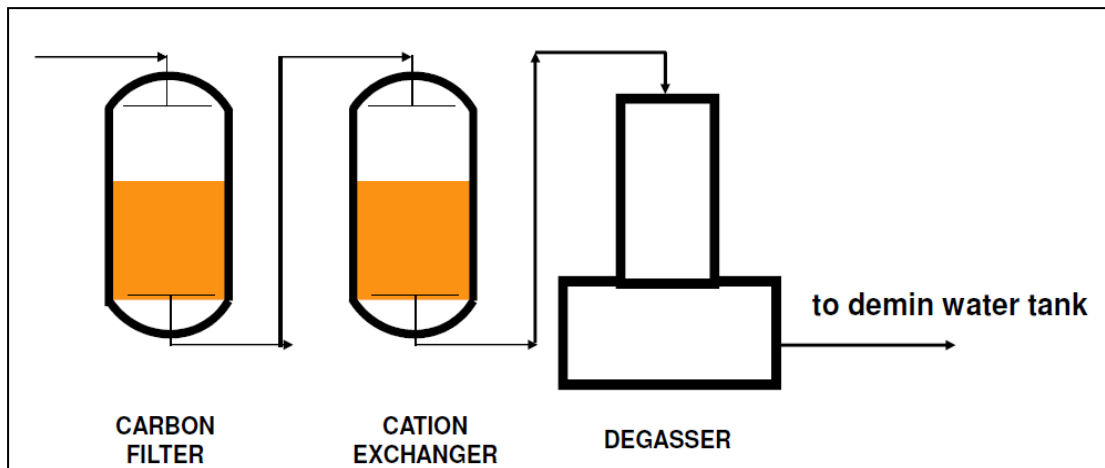

Figure 5: Condensate polishing plant

Since the performance of the carbon in the filter is very important, it is necessary to choose the most suitable adsorbent in order to achieve maximum adsorption of organic pollutants in the wastewater.

CHAPTER 3

METHODOLOGY

3.1 Research Methodology

The research methodology of this project is divided into three major parts. First of all, the commercialized activated carbon is treated chemically by using HNO_3. Then, it is carbonized in turbular furnace. Lastly, it is used in the experiment of determining the adsorption capacity. About 1 kilogram (kg) of activated carbon is used throughout this research.

3.1.1   Preparation of Activated Carbon

The procedure of preparing Pure Activated Carbon (PAC) from Raw Activated Carbon (RAC) is stated as below:

1. 1 kg of RAC was washed with distilled water several times to remove all contaminants such as dust.
2. The RAC was then dried in an oven at 100°C for 24 hours.
3. The dried RAC from the oven was denoted as PAC.

The purpose of washing and drying the AC is to remove all the volatile components as well as moisture content in it.

3.1.2 Chemical Treatment of Activated Carbon

Nitric acid was used as an oxidizing agent for the treatment of AC. The original concentration of nitric acid was used for this research. The AC was oxidized with nitric acid at the ratio of 1:10; meaning 10 grams (g) of AC was soaked in 100 milliliters (ml) of nitric acid. The brief procedure for chemical treatment of AC is shown below:

1. Nitric acid was prepared with its original concentration.
2. 10 g of 1.5-10 mm AC was oxidized with 100 ml of nitric acid in 250 ml beaker (repeated until 500 g of AC was oxidized).
3. The top of the beaker was covered with aluminium foil, letting the sample soak in the acid for 24 hours.
4. The oxidized sample was filtered and washed with distilled water until the filtrate reached neutral condition (pH of the sample = 7).
5. The sample was dried in oven at 100°C for 24 hours.

Refer to Appendices for calculation of HNO_3 concentration.

*Safety Precautions:

Since the nitric acid provided is highly concentrated, the person handling the chemical should wear rubber glove and face mask. The experiment should be done in the fume hood. The used nitric acid should be disposed in a glass waste bottle instead of being poured into the sink as it would cause pipeline corrosion.

3.1.3 Carbonization of Activated Carbon

Carbonization was done onto the AC so that thermal decomposition took place, which would eliminate non-carbon species, fix the carbon mass and also the basic carbon structure. The procedure of carbonizing the AC is as follows:

1. 10 g of treated AC was placed in a crucible.
2. The top of the crucible was sealed with aluminium foil.
3. The crucible was inserted into the turbular furnace when the temperature stabilized at 800°C.
4. The crucible remained in the furnace for 1 hour before the temperature was reduced to 30°C. The sample was then taken out.
5. Sample was weighted and percentage for loss of weight was calculated.

*Safety Precautions:

As the carbonization process is done under extremely high temperature, the person using the furnace should wear thick gloves when placing the sample into the furnace. The temperature of the furnace must be cooled down to 30°C before taking the sample out so that the sample would not turn into ash.

3.1.4 Adsorption Study

To carry out adsorption study for determining the adsorption capacity, the experiment was conducted by placing the sample in a water bath shaker after mixing it with p-nitrophenol solution. The sample had to be filtered (to separate AC from excessive p-nitrophenol) before the p-nitrophenol solution was analyzed using UV-vis Spectrophometer. The adsorption study was performed based on the following steps:

1. 50 ml of 100 ppm p-nitrophenol solution was prepared and mixed with 1 g of carbonized AC.
2. The mixed sample was then inserted into water bath shaker for 2 ½ hours to allow adsorption happen.
3. The sample was filtered and the residual (p-nitrophenol) was observed under UV-vis Spectrophotometer to determine its concentration after undergoing adsorption process.
4. Steps 1 to 3 were repeated by using various manipulated operating parameters to study their effect on the adsorption capacity.
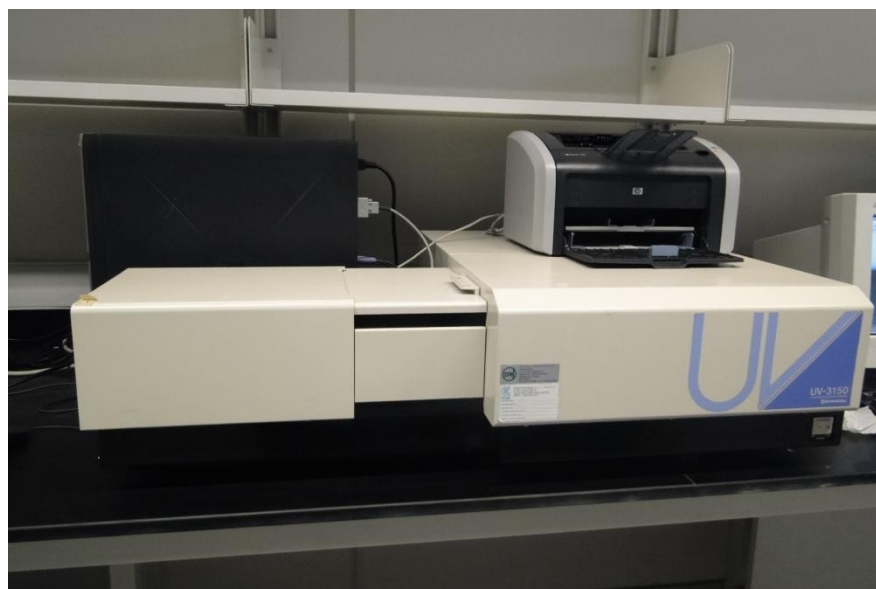

Figure 6: UV-vis Spectrophotometer

3.1.5   Characterization

While doing the adsorption experiment, a set of samples were prepared at the same time to be sent for analysis using Scanning Electron Microscope (SEM) to observe the pore structure of AC and also its development, starting from raw form until the modified form. Besides, the samples were also analyzed using Fourier Transform Infrared Spectroscopy (FTIR), which determines the chemical groups available in the sample through the wavelength measured.

Scanning Electron Microscope (SEM)

SEM is an equipment using electrons rather than light to form images, which are of high resolution. In other words, by using SEM, closely spaced features can be examined at a high magnification. SEM forms a three-dimensional image on a cathode-ray tube by moving a beam of focused electrons across an object and reading both the electrons spotted by the object as well as the secondary electrons generated by it. Under SEM, the pore development can be easily observed due to the combination of higher magnification, larger depth of focus and great resolution.

Figure 7: Scanning Electron Microscope (SEM)

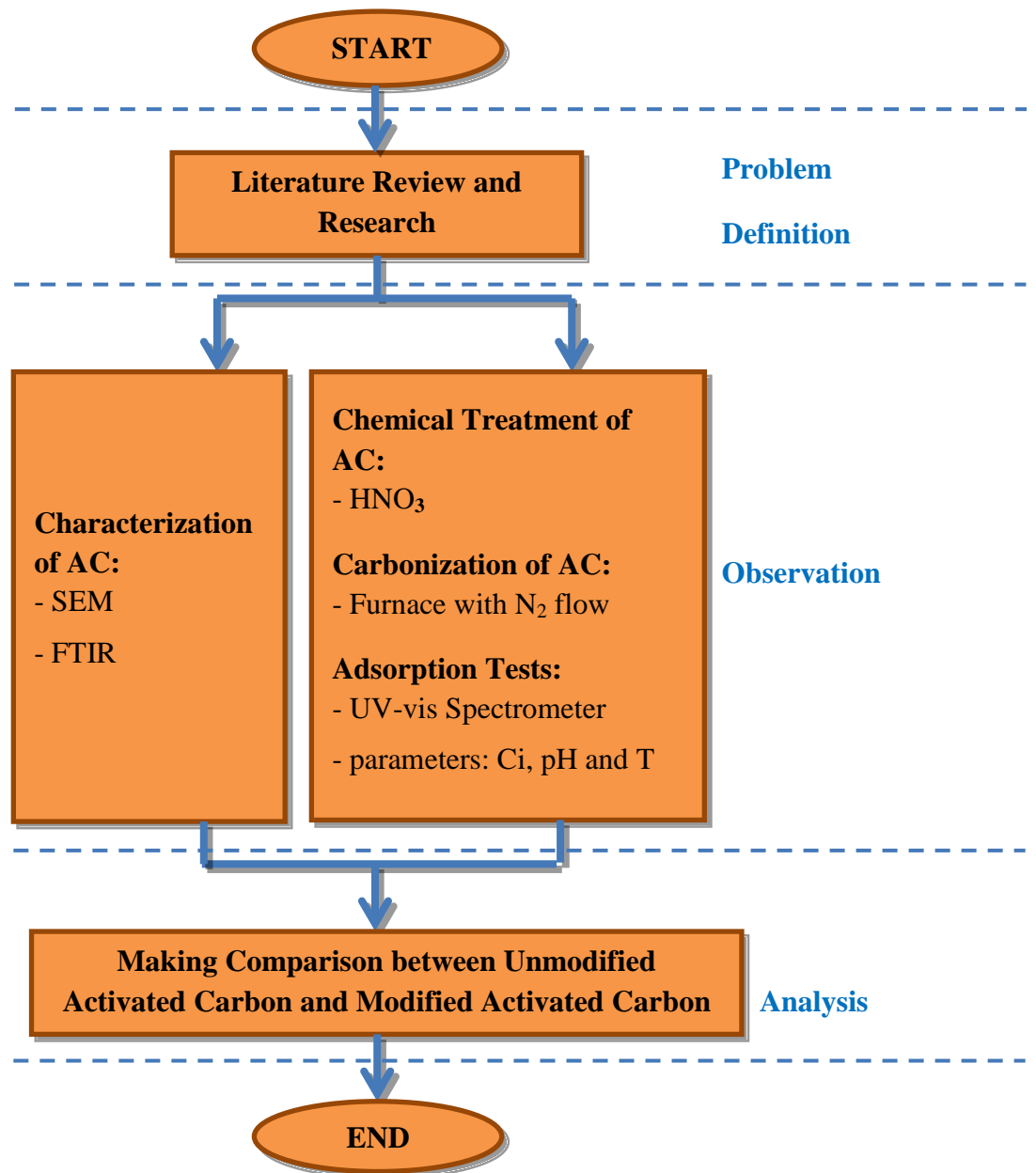(*Source*: JEOL model from Centre for Microscopy & Microanalysis, Nanoworld)

Fourier Transform Infrared Spectroscopy (FTIR)

FTIR is used to obtain an infrared spectrum of adsorption. It simultaneously collects spectral data in a wide spectral range and measures how well a sample absorbs light at each wavelength by shining a beam containing many different frequencies of light at once, and computes how much of that beam is absorbed by the sample. In fact, an infrared spectrum represents a fingerprint of a sample with absorption peaks, which correspond to the frequencies of vibrations between the bonds of the atoms making up the material. Since each different material is a unique combination of atoms, there would definitely be no compound producing the exact same infrared spectrum with any other compound. Therefore, infrared spectroscopy can result in a positive identification (qualitative analysis) of every different kind of material. In addition, the size of the peaks in the spectrum is a direct indication of the amount of material present. This feature enables us to determine what surface functional groups are available in the sample tested.

Figure 8: Fourier Transform Infrared Spectrophotometer (FTIR)

3.2 Project Activities

```
                         ╭─────────────╮
                         │    START    │
                         ╰─────────────╯
                                │
─ ─ ─ ─ ─ ─ ─ ─ ─ ─ ─ ─ ─ ─ ─ ─│─ ─ ─ ─ ─ ─ ─ ─ ─ ─ ─ ─ ─ ─ ─ ─
                                ▼
                 ┌───────────────────────────┐        Problem
                 │   Literature Review and   │
                 │         Research          │        Definition
                 └───────────────────────────┘
```


Literature Review and Research — Problem Definition

Characterization of AC:
- SEM

- FTIR

Chemical Treatment of AC:
- HNO$_3$

Carbonization of AC:
- Furnace with N$_2$ flow

Adsorption Tests:
- UV-vis Spectrometer

- parameters: Ci, pH and T

Observation

Making Comparison between Unmodified Activated Carbon and Modified Activated Carbon   Analysis

END

3.3 Gantt Chart

3.4 Tools Required

The chemicals required for conducting the experiment are shown in Table 1.

Table 1: List of chemicals

No.	Chemicals	Purpose	Remarks
1.	Para-nitrophenol	Adsorbate (Pollutant)	
2.	Calgon Activated Carbon F400	Adsorbent	
3.	Nitric Acid	Oxidizing agent	65 wt% of HNO_3
4.	Distilled Water	Cleaning AC and diluting solutions	
5.	Hydrochloric Acid	Adjusting pH	
6.	Sodium Hydroxide	Adjusting pH	

The main equipment used to complete this project are listed in Table 2.

Table 2: List of equipment

No.	Equipment	Function	Remarks
1.	Oven	To dry AC	
2.	Turbular Furnace	To carbonize AC	Nitrogen flow
3.	Water Bath Shaker	For adsorption process and to maintain the temperature of the sample	
4.	UV-visible Spectrophotometer	To test the adsorption capacity	
5.	Scanning Electron Microscope (SEM)	To determine the pore structure of AC	
6.	Fourier Transform Infrared Spectroscopy (FTIR)	To determine the surface functional groups of AC	
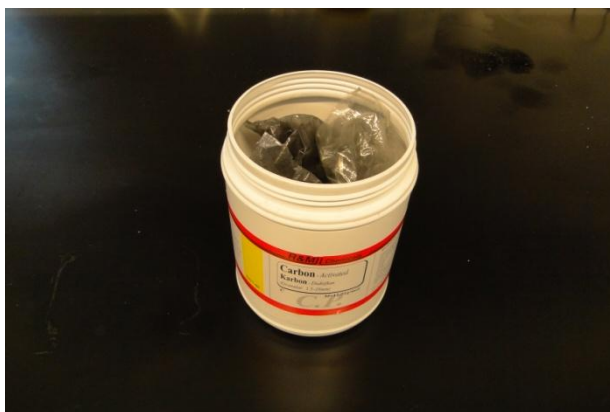
Figure 9: Raw activated carbon

Figure 10: Clean activated carbon
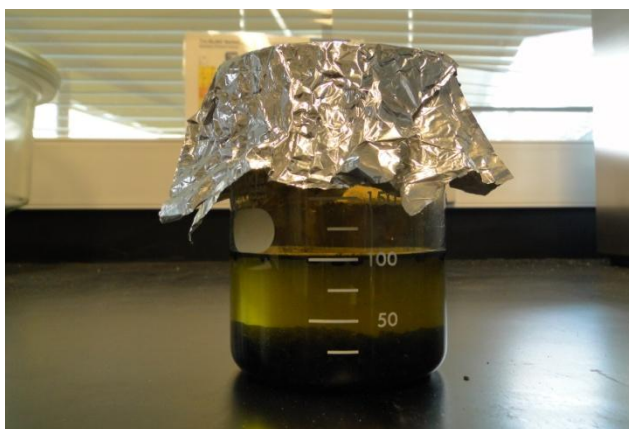
Figure 11: Oxidized activated carbon

Figure 12: Oven

Figure 13: Turbular furnace

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Preparation of Activated Carbon

While the AC was being washed with distilled water, it could be observed that the distilled water coming out from the filter was dark in colour. This showed that the raw activated carbon had a lot of its own ash. Therefore, the AC had to be cleaned for a few times before being dried in the oven to ensure it was free from dust or ash.

4.2 Chemical Treatment of Activated Carbon

500 g from 1000 g of AC is prepared for modified form. Using ratio 1:10, 10 g of AC was oxidized with 100 ml HNO_3. AC was put in the beaker before HNO_3 was poured into it. The beaker was then sealed and left in the fume hood for 24 hours. The AC did not seem to have any physical changes since it remained the same shape and colour as it was before. The pH of the AC was ensured to be around 7. After that, the treated AC was dried in an oven at 100°C for another 24 hours. The purpose of this drying is to remove all the moisture content in the AC.

4.3 Carbonization of Activated Carbon

The AC was carbonized in the turbular furnace under nitrogen flow at 800°C for 1 hour. It was found that the weight of the AC had slightly decreased due to the lost of non-carbon elements such as hydrogen and oxygen in the AC during the carbonization process.

4.4 Characterization

4.4.1 Scanning Electron Microscope (SEM)

Three samples of AC were sent for analysis using SEM: Granular Activated Carbon (the raw AC), AC oxidized with HNO_3 and carbonized AC. The images obtained are shown in Figure 14a, 14b, 15a, 15b, 16a and 16b.
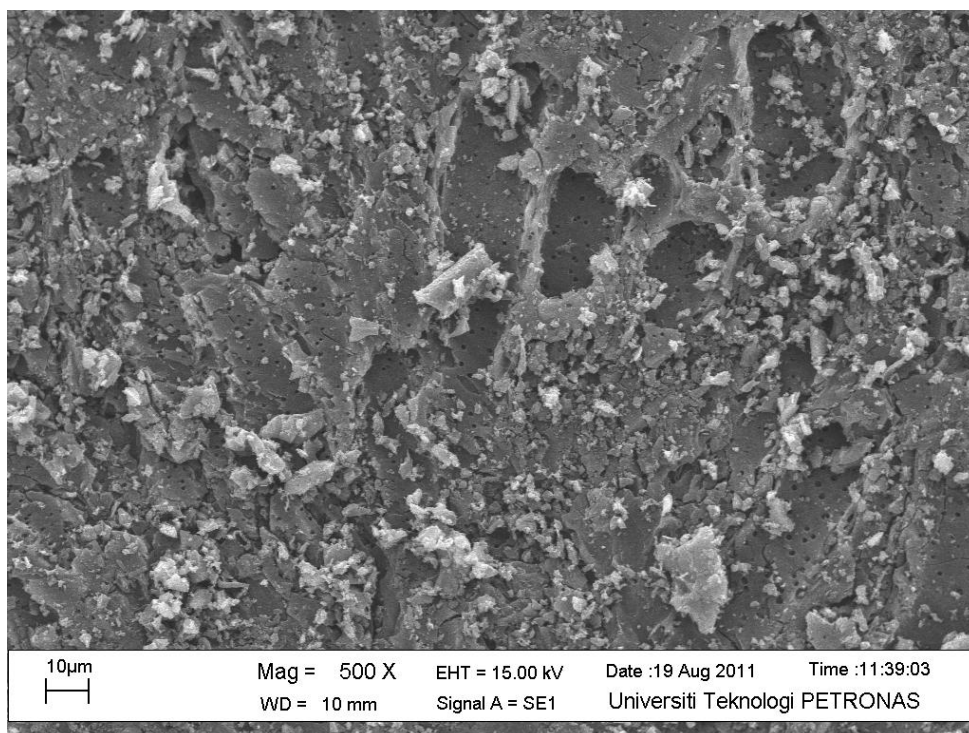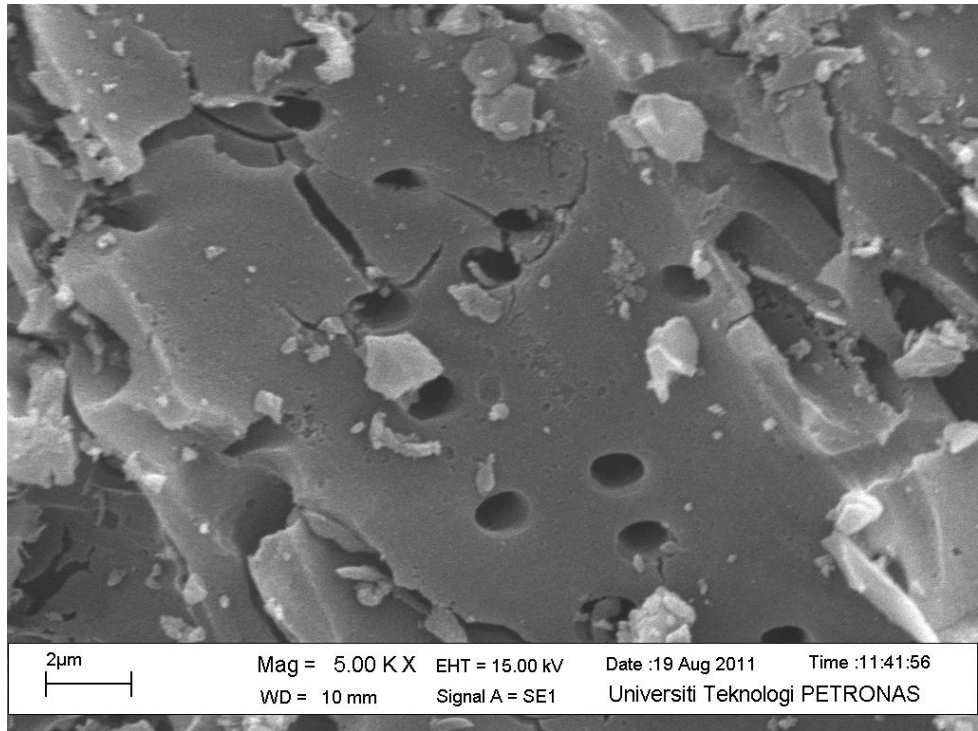

Figure 14a: Raw AC at 500X magnification
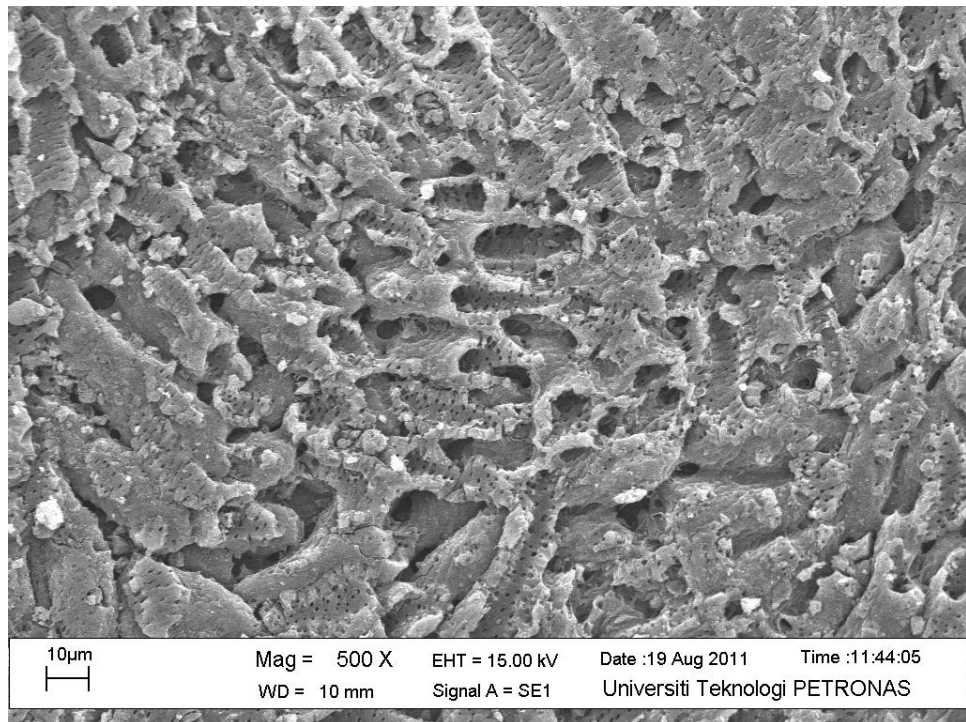
Figure 14b: Raw AC at 5000X magnification
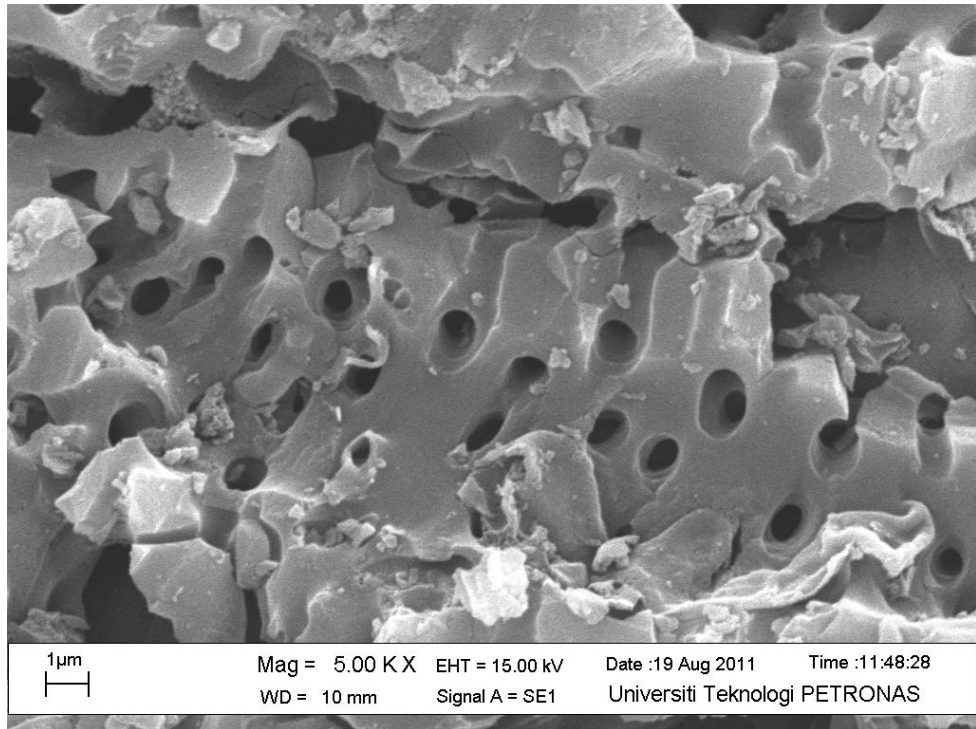

Figure 15a: Oxidized AC at 500X magnification

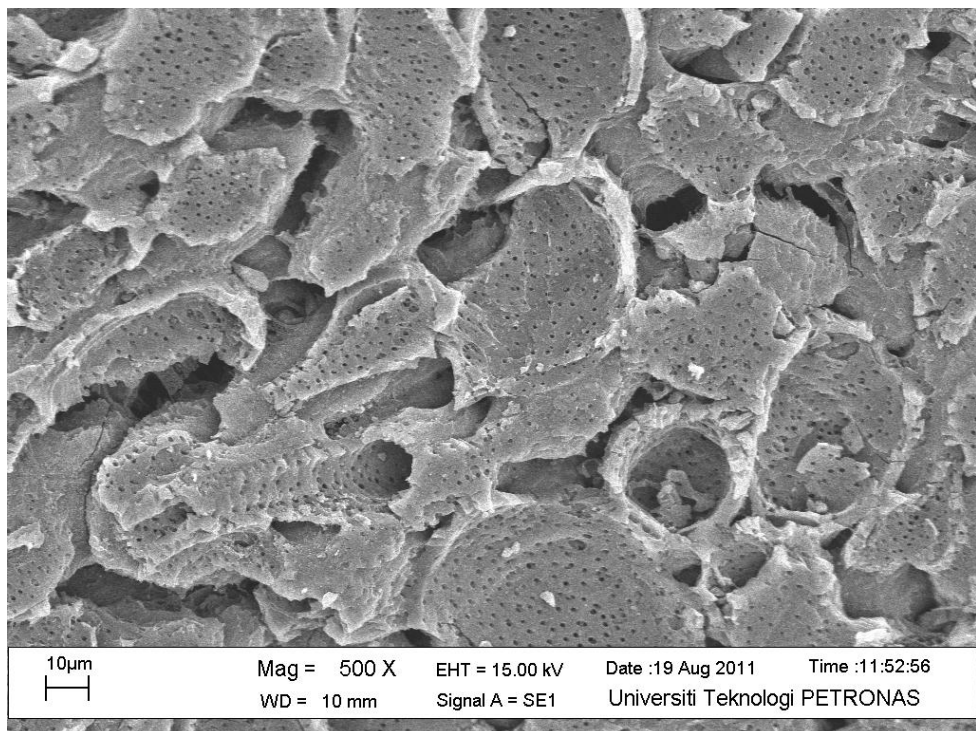Figure 15b: Oxidized AC at 5000X magnification

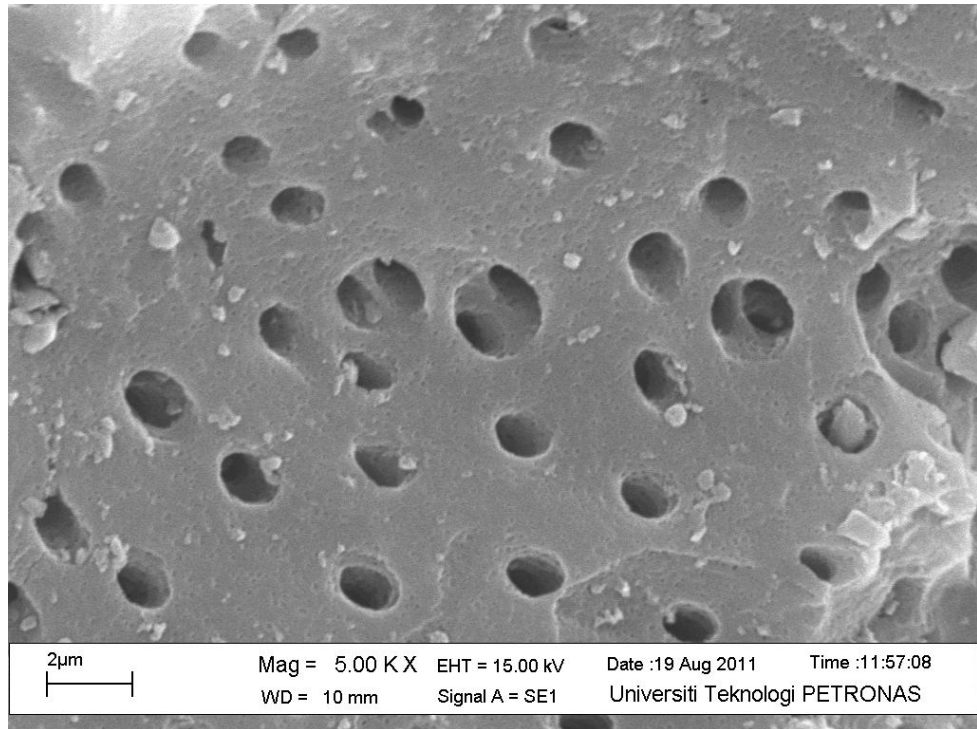Figure 16a: Carbonized AC at 500X Magnification

Figure 16b: Carbonized AC at 5000X Magnification

Figure 14a shows that the raw AC has fair amount of pores (since the commercial AC is meant to act as absorbent). Figure 14b is the nearer distance of observing the individual pore structures. All the pore sizes seem similar. Figure 15a indicates the image of AC after being oxidized with HNO_3. The pore development was observed and it had shown that chemical treatment of AC using HNO_3 could develop the pores in the AC by adding more pores to it. Comparing Figure 15b to 14b, the pores were found to be deeper (meaning more internal surface was created). For Figure 16a, it indicates the pores occupying almost every single place it could. In other words, the amount of pores had increased significantly after carbonization process due to the elimination of non-carbon elements as well as volatile matters, which were trapped in the AC. Lastly, Figure 15b is quite similar compared to Figure 15b. But then, a few pores became deeper, which demonstrates that the internal surface could be further increased. As a conclusion for SEM analysis, it is proven that the pores of AC were developed and many studies have shown that the pore development would result in a better adsorption capacity on organic compounds.

4.4.2 Fourier Transform Infrared Spectroscopy (FTIR)

The samples were also tested using FTIR to determine the chemical groups in the AC since different chemicals possess different infrared spectrum. The result obtained is illustrated in the figure below:
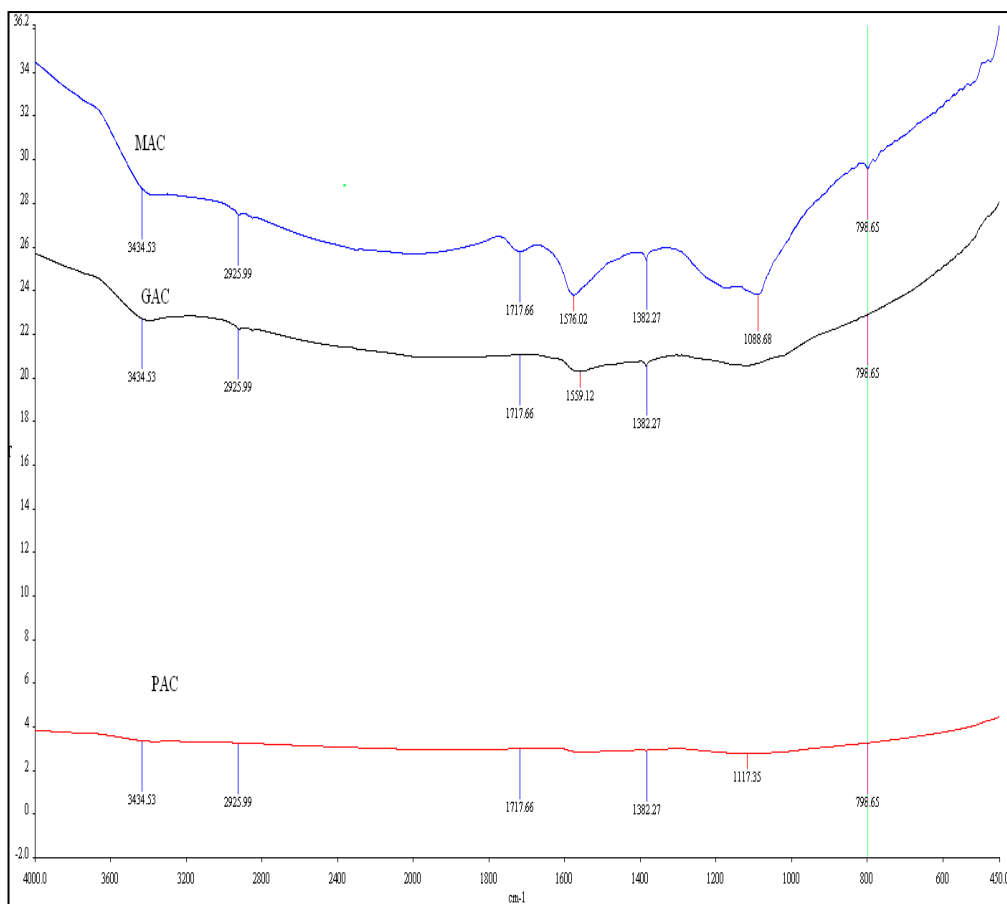

Figure 16: FTIR spectra for GAC, CAC and MAC

All three results have been combined into one graph for easier comparison. It can be seen that MAC has the highest spectra compared to GAC and CAC. There are some peaks identified but they do not show clearly the surface functional groups based on the analysis by the equipment itself. Theoretically, it should have C-O functional groups, which would increase.

4.5 Adsorption Study

4.5.1 Calibration Curve

UV-vis Spectrophotometer was used to test the adsorption capacity of the AC. In order to determine the adsorption performance, calibration curve was required. Therefore, adsorbate was prepared at different concentrations. Then, peak(s) were detected at certain wavelength when the adsorbate was put into the equipment. After that, the value of adsorbance could be obtained from the peak and calibration curve was able to be produced using the values of adsorbate concentration and adsorbance.

The peak found in this study was 210 nm. At this peak, the concentration of adsorbate and adsorption capacity were tabulated as below:

Table 3: Experimental data for calibration curve

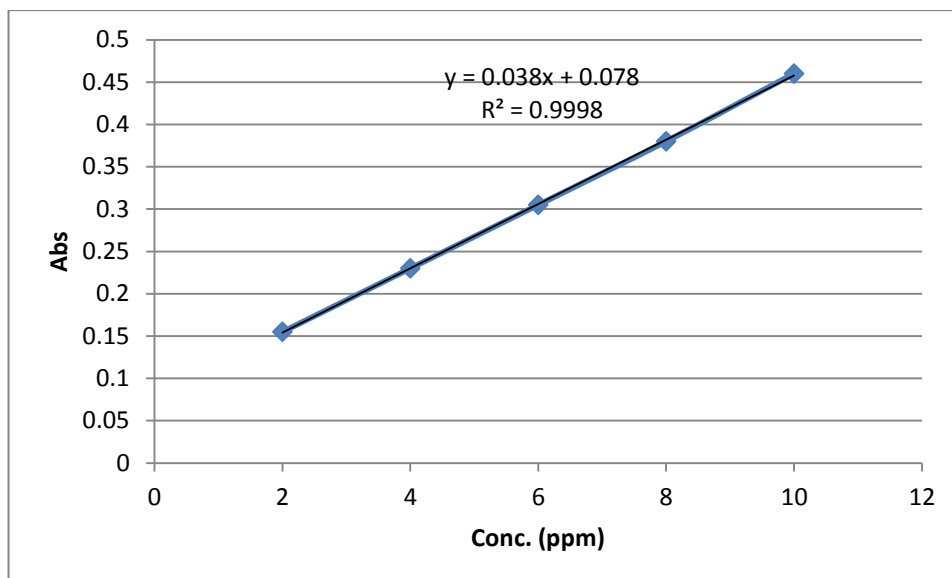| Concentration of Adsorbate (ppm)	Adsorbance
2	0.155
4	0.23
6	0.305
8	0.38
10	0.46

Figure 19: Calibration curve

From the graph in Figure 19, 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 means the adsorbate solution prepared is suitable to be used throughout the whole experiment since the the value of R^2 is near to 1.

4.5.2 Equilibrium Studies

The purpose of equilibrium studies is to determine the time needed for the adsorption to reach equilibrium state. P-nitrophenol was adsorbed by AC in the water bath shaker for around three hours. For every half an hour, a portion of p-nitrophenol was extracted from the sample to be tested its concentration using UV-vis Spectrophotometer. And, the result was shown in the table below:

Table 4: Experimental data for equilibrium studies

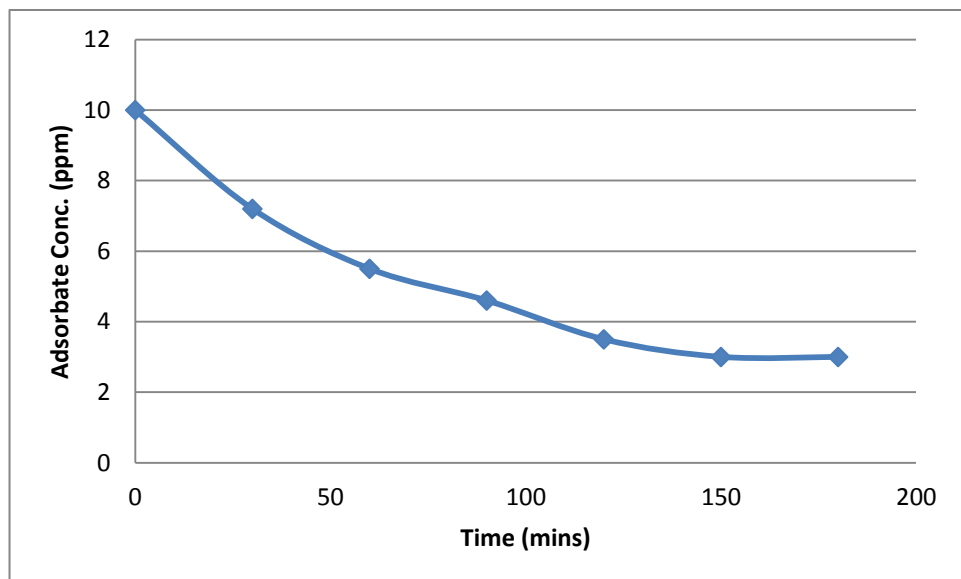| Time (mins)	Concentration (ppm)
0	10
30	7.2
60	5.5
90	4.6
120	3.5
150	3
180	3

Figure 20: Equilibrium studies

The graph shows that the equilibrium time was achieved after 150 minutes. This means that the entire adsorption process should be carried out in the duration of 2 ½ hours. Otherwise, the result might not be accurate as the AC was unable to perform its adsorption to the optimum condition.

4.5.3 Effect of Adsorbate Concentration on Adsorption Capacity

Table 5: Data for different adsorbate concentration for GAC

Adsorbate Concentration (ppm)	Adsorption Capacity (mg P-nitrophenol adsorbed / g AC)
100	1.2
150	6.5
200	10.8
250	16.4
300	19.9

Table 6: Data for different adsorbate concentration for MAC

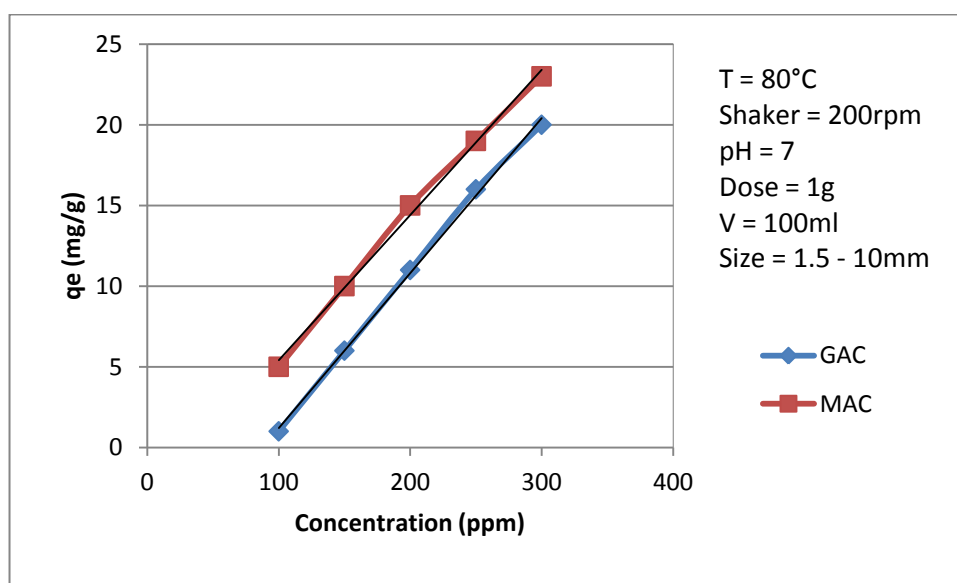| Adsorbate Concentration (ppm)	Adsorption Capacity (mg P-nitrophenol adsorbed / g AC)
100	5.4
150	9.7
200	15.6
250	19.0
300	23.1

Figure 21: Q_e for different concentration

From the graph, it is very obvious that Qe increases as concentration of p-nitrophenol increases. This is because the more concentrated the solution is, the higher the affinity to be adsorbed by the AC. MAC performs better than GAC since the equation line is higher.

4.5.4 Effect of pH on Adsorption Capacity

Table 7: Data for different pH for GAC

pH	Adsorption Capacity (mg P-nitrophenol adsorbed / g AC)
5	8.5
6	9.3
7	9.8
8	10.2
9	9.5

Table 8: Data for different pH for MAC

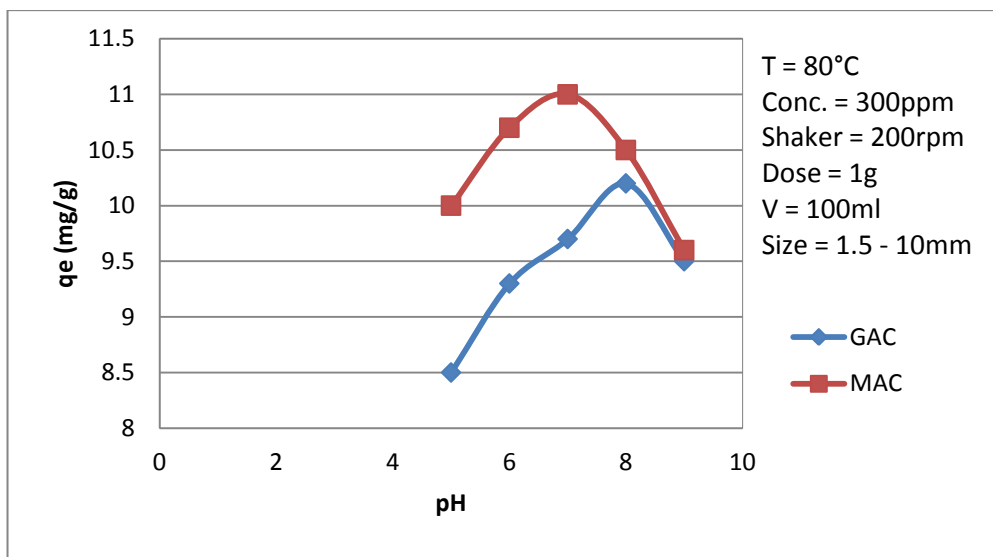| pH	Adsorption Capacity (mg P-nitrophenol adsorbed / g AC)
5	10.0
6	10.7
7	11.0
8	10.5
9	9.6

Figure 22: Q_e for different pH

The pH level plays an important role in the adsorption of organic compounds from aqueous solution. In this study, the pH values tested range from acidic (pH 5) to basic (pH 9) condition. As seen from the graph in Figure 20, the most suitable pH for conducting this experiment is between 7 to 8 (as it involves two types of AC). Therefore, the choice of using pH 7 in the beginning of the experiment is correct. P-nitrophenol itself is in acidic condition, which is around 5 initially. Therefore, the solution is titrated with base (NaOH) to make it neutral. MAC is still performing better than GAC even though pH is varied.

4.5.5 Effect of Temperature on Adsorption Capacity

Table 9: Data for different temperature for GAC

Temperature (°C)	Adsorption Capacity (mg P-nitrophenol adsorbed / g AC)
30	8.1
40	14.5
50	18.2
60	19.8

Table 10: Data for different temperature for MAC

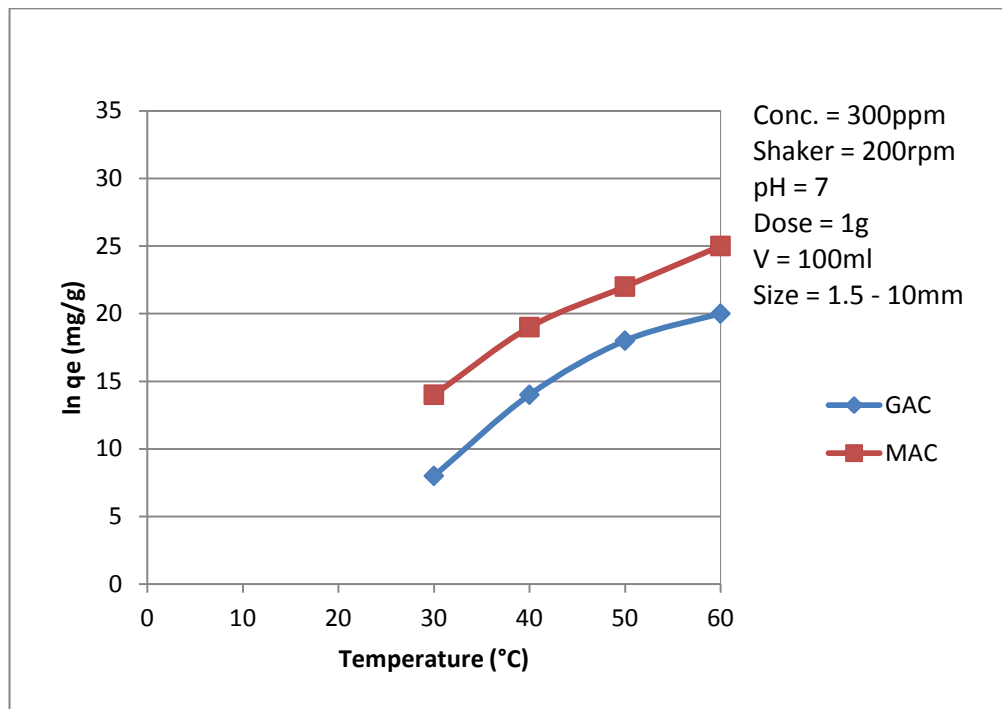| Temperature (°C)	Adsorption Capacity (mg P-nitrophenol adsorbed / g AC)
30	13.8
40	18.7
50	22.0
60	25.3

Figure 23: Q_e for Different Temperature

The temperature has significant effects on the adsorption process. Based on Figure 23, the increasing temperature increases Q_e as well. This is because increasing the temperature will increase the rate of diffusion of the Adsorbate molecules across the external boundary layer and in the internal pores of the adsorbent particle. The temperature is believed to be able to increase further, however, there is a need to bear the risk as too high temperature (which may be 100°C in this case) might cause rupture to the structure of AC, thus resulting in unstable support of its structure.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 CONCLUSION

From the results of this study, several conclusions can be made:

1. The pores of AC are developed after undergoing purification, chemical treatement and also carbinzation process.
2. Adsorption capacity of AC increases with increasing adsorption time until it reaches equilibrium (saturated) condition. It is fast in the beginning and becomes subsequently slow when it is approaching the end.
3. Adsorption capacity of AC increases as concentration of adsorbate increases.
4. Adsorption capacity is performing to its best when the pH is from 7 to 8.
5. As adsorption temperature increases, adsorption capacity also increases.
6. The overall adsorption performance is higher for Modified Activated Carbon compared to Unmodified Activated Carbon.

5.2 RECOMMENDATION

After completing this project, several recommendations can be given to further improve the current research such as:

1. To observe the surface of AC using Braneur-Emmet-Teller (BET) to study the relationship between surface area of AC and adsorption capacity of p-nitrophenol.
2. To observe AC using X-ray Diffraction (XRD) besides FTIR to determine the surface functional groups of AC.
3. To observe the effect of adsorbent dosage on the adsorption activity.
4. To observe the effect of particle size on the adsorption activity.
5. To observe the effect of carbonization temperature on the adsorption activity.
6. To use KOH (basic solution) as oxidizing agent to compare the adsorption performance between AC treated with acid (HNO_3) and AC treated with base.

REFERENCES

Amit Bhatnagar & A K Minocha, Conventional and non-conventional adsorbents for removal of pollutants from water − A review, Indian Journal of Chemical Technology, Vol. 13, May 2006.

Arinjay Kumar, Shashi Kumar, Surendra Kumar, Dharam V. Gutpa, Adsorption of phenol and 4-nitrophenol on granular activated carbon in basal salt medium: Equilibrium and kinetics, Journal of ScienceDirect, January 2007.

Brad Buecker, Fundamentals of Steam Generation Chemistry, 1st Edition, Pennwell, 2000.

Dr. V Gaur, D Roberts & Dr. P.A. Shankar, Activated Carbon: The Next Generation, Journal of Water Quality Products, Volume 15, Number 3, March 2010.

Eduardo J. Bottani, Juan M.D. Tascon, Adsorption by Carbons, 1st Edition, Elsevier, 2008.

George Tchobanoglous, Franklin L. Burton, and H. David Stensel, Wastewater Engineering Treatment and Reuse, 4th Edition, McGraw-Hill, 2003.

J.D. Seader, Ernest J. Henley, Separation Process Principle, John Wiley, 1998.

Jimmy L. Humphrey, George E. Keller II, Separation Process Technology, McGraw-Hill, 1997.

K.J Kim, C.S Kang, Y.J. You, M.C. Chung, M.W Woo, W.J. Jeong, N.C Park, & H.J Ahn, Adsorption–desorption characteristics of VOCs over impregnated activated carbons, Journal of Catalysis Today, December 2005.

Larry Drbal, Kayla Westra and Pat Boston, Power Plant Engineering, 1st Edition, Springer, 1996.

McGraw-Hill Dictionary of Scientific & Technical Terms, 6E, Copyright © 2003 by The McGraw-Hill Companies, Inc.

Michael D. LaGrega, Phillip L. Buckingham, Jeffrey C. Evans, Hazardous Waste Management, 2nd Edition, 2001.

Natural Solutions Environmental Inc. (2004).What is Activated Carbon. Retrieved March 2010 from http://nseproducts.com/whatcarb.htm

Nicholas P.Cheremisinoff , Handbook of Water and Wastewater Treatment Technologies, 1st Edition, Butterworth Heinemann, 2002.

Norzilah Abdul Halif, Wan Mohd Ashri Wan Daud, Iskandar Mohd Noor, Che Rosmani Che Hassan, The effect of temperature on the adsorption of 4-nitrophenol onto palm shell based activated carbon, journal of University of Malaya.

S. Haydar, M.A. Ferro-Garcia, J. Rivera-Ultrilla, J.P. Joly, Adsorption of p-nitrophenol on an activated carbon with different oxidations, Journal of PERGAMON, August 2002.

V Gaur and P. A. Shankar, Surface Modification of Activated Carbon for the Removal of Water Impurities, June 2008.

W.S. Wan Ngah, S. Fatinathan, Chitosan flakes and chitosan-GLA beads for adsorption of p-nitrophenol in aqueous solution, journal of ScienceDirect, January 2006.

http://www.wisegeek.com/what-is-adsorption.htm

http://www.highbeam.com/doc/1O81-adsorptionisotherm.html

http://www.chromatography-online.org/topics/freundlidh/adsorption/isotherm.html

http://en.citizendium.org/wiki/Condensate_polishing#cite_ref-4

APPENDICES

APPENDIX I

<u>Calculation of molarity of the acid stock solution</u>

Based on the specifications of the nitric acid stock solution given by laboratory technicians:

- Nitric acid - 65 wt%
- Density = 1.40 g/mL
- Molecular Weight = 63.01 g/mole

Since the nitric acid provided is 65% by mass, so 100 g of solution contains 65 g of pure nitric acid. The mass of nitric acid in one liter of concentrated solution is:

Density = 1.40 g/mL $\times$ 1000 mL/L

$\qquad$ = 1.40 x 10^3 g solution/L concentration solution

Molarity, M (number of moles in one liter solution)

$$\frac{1.4 \times 10^3 g \_ solution}{L \_ concentration \_ solution} \times \frac{65 g \_ HNO_3}{100 g \_ concentrated \_ solution} \times \frac{1.0 mole \_ HNO_3}{63.0 g \_ HNO_3}$$

= 14.44 M acid

APPENDIX II

Calculation of adsorption capacity, Q_e

Volume solution to be diluted: $C_1V_1 = C_2V_2$

$$V_1 = C_2V_2/C_1$$

Dilution factor = initial concentration / final concentration

Diluted concentration:

From equilibrium curve at 210nm, the linear equation is:

$$y = 0.038x + 0.078$$
where, y: adsorption, Å
x: concentration, mg/l

concentration, $x = (y + 0.078) / 0.038$

Adsorption capacity, $q = \dfrac{V(c_o - c_f)}{m}$

Calculation for new K* and 1/n*:

Plot ln(q) vs. ln(C) given linear equation of $y = mx + c$

$q = kC^{1/n}$

$\ln q = (1/n) \ln(C) + \ln(k)$

$1/n = m$

$\ln(k) = c; \ k = e^c$

Calculated adsorption capacity, $q = kC^{\frac{1}{n}} = e^c C^{\frac{1}{n}}$

Extra Photos

Machine for compressing the sample of FTIR

FTIR sample (after compression)