# Monoethanolamine (MEA) Wastewater Treatment via Adsorption using Activated Carbon Derived from Sawdust

by

Tong Yeong Yit
(13411)

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the requirements for the
Bachelor of Engineering (Hons)
(Chemical Engineering)

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University Teknologi PETRONAS
Bandar Seri Iskandar
31750 Tronoh
Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

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Approved by,

Azry Borhan
Lecturer
Chemical Engineering Programme
Universiti Teknologi PETRONAS
31750 Tronoh
Perak Darul Ridzuan, MALAYSIA.

2/01/14

(Azry Borhan)

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
September 2013

# CERTIFICATION OF ORIGINALITY

This is to certify I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

(TONG YEONG YIT)

# ABSTRACT

Utilization of sawdust as a raw material for manufacturing activated carbon is one of the most environmental friendly approach of turning residual biomass waste into value-added products. Sawdust, which is low cost and produced abundantly from wood industry, was tested as a precursor for the production of porous carbons in a chemical scheme using phosphoric acid. Various synthesis parameters such as impregnation ratio, activation temperature and activation time affecting the adsorption properties of activated carbons were studied in order to optimize these preparation parameters. The experimental results indicated that activated carbon can reach a relatively higher value in surface area and pore volume when sawdust is impregnated with ratio of 1:1 and treated with activation temperature of 500°C for a period of 60 minutes. Through nitrogen adsorption-desorption isotherm analysis, existence of mesopores was proven when a combination of Type-I and Type-II isotherms were exhibited by the activated carbon produced. The results from the final adsorption test found that the material synthesized from the above mentioned parameter is capable of removing up to 93% of MEA from aqueous solution, suggesting that it could be a promising adsorbent in MEA wastewater treatment.

# ACKNOWLEDGEMENT

The success and final outcome of this research project required active involvements and contributions from many parties and individuals and I am extremely fortunate to have got this all along the completion of my project work. They have played a very significant role in this research study and I would like to take this opportunity to extend my appreciation to them.

First and foremost, thank God for the wisdom and perseverance that He has been bestowed upon me during this research project. Deepest gratitude goes to **Mr. Azry Borhan**, this dissertation could not have been written without him, who not only served as my project supervisor but also encouraged and challenged me throughout my academic program. Advice given by him has been a great help and I am particularly grateful for his valuable and constructive suggestions during the planning and development of this research work. His willingness to give his time so generously has been very much appreciated.

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Last but not least, I wish to thank my parents for their love and undivided support, both financially and emotionally throughout my years of study. Not to forget, my fellow colleagues and friends for their generous support.

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# CHAPTER 1

# INTRODUCTION

## 1.1 Background of Study

Monoethanolamine (MEA) with molecular formula of $NH_2CH_2CH_2OH$, is an organic compound which has both primary amine and primary alcohol in its functional group. MEA is a weak base with properties of being toxic, flammable and corrosive. At physical state, it presents as colouress liquid with ammonia odour. In contact with skin, it may result in systemic poisoning while ingestion irritates mouth, throat respiratory tract and causes abdominal pain. Industrial application of MEA can be found in gaseous treatment especially in gas systems containing carbon dioxide, MEA can be used as a selective absorber. However, the high solubility of MEA in water causes it to be readily dissolved in wastewater stream and need to undergo treatment before discharged

Bansal et.al. (1988) in their appropriately titled book "Activated Carbon", has brought up the most concise definition of activated carbon (AC). The term "AC" in its broadest sense includes a wide range of amorphous carbon-based materials prepared to exhibit a high degree of porosity and an extended interparticulate surface area. The first-class features of high porosity and large surface area impart AC with excellent adsorption characteristics, which make carbon very useful in many processes such as filtration, separation, decolourization and purification. In order to obtain high quality of AC, these carbon-based materials first need to be activated and carbonized through a series of optimum processes to draw out and make full use of its enormous potential. The resultant product often has an incredibly large surface area per unit volume, and a great distribution of microscopic pores where adsorption takes place. An amazing fact is that the surface area of one pound of carbon (a quart container) can reach up to six football fields' size (Deithorn & Mazzoni, 2013).

The history of AC can be traced back as early as 1500 B.C. In the olden days, charcoal was used for drinking water filtration by ancient Hindus in India, and carbonized wood was used by the Egyptians as an adsorbent for medical purposes and also as a purifying agent. Gradually, all these precursor of AC developed into industrial scale production of active carbons. AC was first generated industrially in early 20th century when carbon activated from mixture of materials comprising vegetable origin was produced for use in sugar refining. Activated carbons with enhanced decolourizing power were prepared using wood as raw material and other materials with high carbon content. In the late 1930s, a novel breakthrough was achieved in the field of manufacturing AC when AC were produced from sawdust by chemical activation with zinc chloride for volatile solvent recovery and removal of benzene from tower gas.

Utilization of sawdust as a raw material for manufacturing AC is indeed a wise approach of turning residual biomass waste into value-added products. World Wildlife Fund (WWF) in its latest installment of Living Forests Report estimated that the amount of wood society takes from forests and plantations per year could triple by 2050 due to rising population and demand, as well as an increase in use of wood for bioenergy. Moreover, in the midst of converting the raw logs into the sawn timber, the yield estimated is only around 58.5% (Indonesia Furniture, 2013). In other words, this means out of 100% volume of raw timber logs, only 58.5% of sawn timber is gained. The remaining 41.5% becomes wood chips and sawdust, resulting in the generation of substantial amount of residual biomass, which is why many research works has been carried out to utilize sawdust generated in the process of wood sawing to develop high surface area of AC.

In line with the zero waste concept of viewing waste as a potential resource with value to be realized, sawdust can be made into useful AC products rather than as a waste management problem to be dealt with. Today, sawdust is used in removal of heavy metals from aqueous solution by means of adsorption with proven potential to adsorb metal ions such as lead, cadmium and nickel. Nonetheless, not much study is done so far on determining the effectiveness of sawdust to adsorb monoehtanolamine (MEA) in wastewater.

## 1.2 Problem Statement

In petrochemical industry, especially in natural gas processing plant, raw natural gas contains significant amount of carbon dioxide ($CO_2$). Prior to further processing activities, the gas stream needs to undergo treatment to remove $CO_2$ to meet specifications for successful liquefaction LNG process. The most important commercially applied technology for $CO_2$ removal is the absorption process by using amine-based solvent. One of the important amines is monoethanolamine (MEA) which is used in most acid gas recovery system as it provides sufficient alkalinity to absorb $CO_2$ (Rinprasertmeechai et. al., 2012). However, the amine may degrade over time and the corrosive by-products need to be removed as wastewater.

In view of the fact that MEA wastewater is produced abundantly from petrochemical plants as well as other processing plants such as coal fired power station and ammonia synthesis plant, the research needs is essential to find out the alternative route methods for treating MEA wastewater which is inexpensive, simple, economically viable and environmental friendly. In this study, sawdust is used as the adsorbent and its feasibility in adsorbing MEA is explored and examined. Sawdust is chosen because it is one of the carbonaceous materials, which has the potential of exhibiting high porosity and high specific surface area after being activated and carbonized. Nevertheless, the porous structure and final properties of activated carbon do not depend solely on nature of the precursor, but also take into account the activation process conditions. Various operative parameters such as types of chemical agent used, size of sawdust, impregnation ratio, temperature and time of activation might bring significant effects to the performance of activated carbon produced. Aside from excellent adsorptive characteristics, utilization of sawdust as a raw material for producing activated carbon promotes sustainable development in a way that residual biomass is transformed into useful products instead of disposing it as waste. As increasing amount of waste has been a worldwide concern, reclamation of this useful material should not be overlooked.

In some unexpected cases, incidents involving spillage or leakage of MEA can occur anytime at anywhere. Not only in the operation phase that spillage is more prone to occur, spillage problem also arises during the transportation of material due to unforeseen circumstances like road accidents or leakage from drum. Getting the chemical spills cleared up is not a trivial problem, if done manually it increases the risk of workers being exposed to excessive hazardous material. Therefore, an immediate remedy is required to put the critical situation under control and this would be the time when neutralizing agent and treatment material take place. Sawdust, if proven to show positive outcome in treating MEA, would be a great "cleaning tool" for such emergency.

In brief, the problem statements can be summarized as below:

1. Increasing amount of residual biomass from wood industry causes waste management issue.
2. Lack of direct and cost-effective alternative methods in treating MEA wastewater.
3. Various operating parameters (impregnation ratio, activation time and activation temperature) manipulating the chemical activation of sawdust without preset specification.
4. Uncontrollable spillage or leakage is possible to occur when dealing with amine-based solution.

## 1.3 Objectives

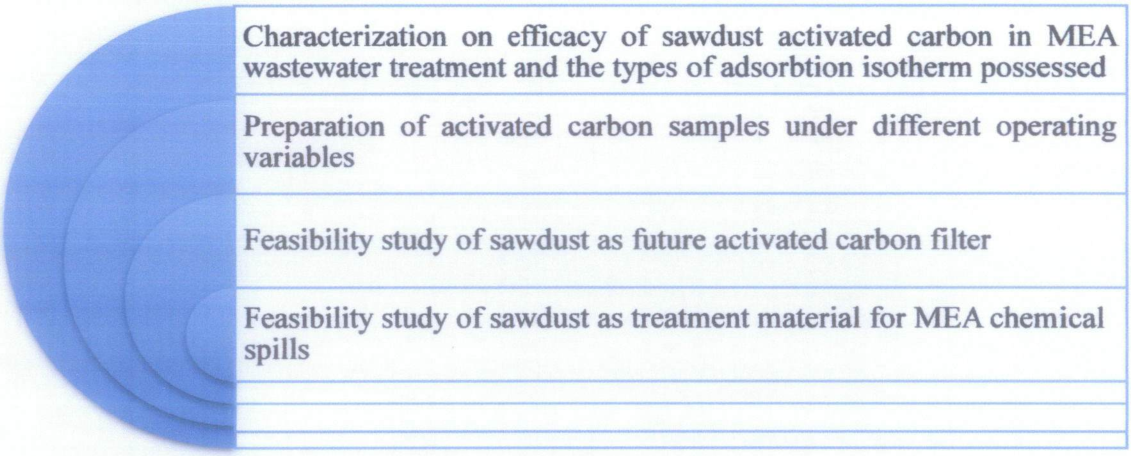
To the knowledge of the author no work has been attempted on chemical activation of sawdust to treat MEA wastewater. Hence, the objectives of present study are:

1. To study the potential of recycling wood residue as activated carbon in MEA wastewater treatment

2. To determine the effectiveness of sawdust in adsorbing MEA from aqueous solution
3. To assess the effect of different operating variables with respect to the specific surface area and pore volume of sawdust activated carbon and suggest the best process condition
4. To study the potential of sawdust in treating MEA chemical spills during emergency

## 1.4 Scope of Study

In achieving the objectives stated above, several scopes of study have been identified:



Characterization on efficacy of sawdust activated carbon in MEA wastewater treatment and the types of adsorbtion isotherm possessed

Preparation of activated carbon samples under different operating variables

Feasibility study of sawdust as future activated carbon filter

Feasibility study of sawdust as treatment material for MEA chemical spills

Figure 1: Scope of study

## 1.5 Relevancy of Project

Basically, the overall idea of this project is to examine the performance of sawdust in adsorbing MEA from the wastewater stream. As mentioned earlier in Section 1.2, in view of the fact that MEA wastewater is produced abundantly from petrochemical plants and other major processing plants, identification of alternative route method which is inexpensive, simple, economically viable and environmental friendly for treating MEA wastewater is indeed crucial. Although the existing technology and facilities are capable of treating all kinds of wastewater contaminated by anthropogenic industrial activities, but the entire system seems to be complex and costly. Prior to effluent release or reuse, the conventional treatment system often involves an array of processes ranging from chemical treatment methods to mechanical treatment methods. Therefore, the present study intends to introduce a simple yet cost-effective treatment method of using sawdust as adsorbent for removal of the amine.

The potential of using sawdust as alternative adsorbent for the treatment of MEA wastewater would become a research interest in the near future. Though the ultimate result of this research work might not be favourable, but several studies have shown that sawdust which is cheap and easily available appears to be a promising adsorbent for removal of heavy metal from wastewater. Thus, it can be said that this project is relevant to be carried out since it has the potential of giving significant contribution towards the development of activated carbon which is suitable for MEA wastewater treatment in industry. In addition, the methodology of this project is closely monitored by supervisor and the procedures carried out are meticulously planned to ensure the validity of the data. As long as the variables and operating parameters are similar, data obtained from the experimental results will be compared with previous research works. To sum up, the entire project's progression is under attention and guidance of the author's supervisor.

## 1.6 Feasibility of Project

In terms of resources, Universiti Teknologi PETRONAS (UTP) has allocated an amount of RM500 research grant to every final year student doing final year project. This amount is sufficient for purchasing raw material and chemicals required in this project. Aside from that, UTP itself is an established research university equipped with complete facilities to carry out research works. All the analytical equipment and apparatus are available within the premises to ease the student's work so that the research is driven with high productivity.

Period of 28 weeks, with 14 weeks allocated for each semester is fairly a long time frame. Therefore, the project activities must progress in line with the Gantt chart to ensure that the project does not fall behind schedule.

# CHAPTER 2

# LITERATURE REVIEW

## 2.1 Manufacture of Active Carbon from Sawdust

Activated carbons as porous adsorbent with high specific surface area are widely used in industrial application for aqueous phase adsorption, gas purification and wastewater treatment. Theoretically, most organic matter with high carbon content could be activated to improve its sorptive characteristics. Other factors to be considered when selecting a suitable raw material are presence of minimum inorganic materials, volume and cost of the raw material as well as its storage life and workability. Wood (at 130,000 tons/year) is by far the most common source of activated carbon, followed closely by coal (100,000 tons); coconut shell (35,000 tons) and peat (35,000 tons) (Bansal et.al., 1988). Each material has its unique properties, thus activated carbon produced from different raw materials might exhibit different adsorbent qualities.

Table 1: Properties of some raw materials used in the manufacture of activated carbon

| Raw Material | Carbon (%) | Volatiles (%) | Density (kg/L) | Ash (%) | Texture of activated carbon | Application of activated carbon |
|---|---|---|---|---|---|---|
| Soft wood | 40 – 45 | 55 – 60 | 0.4 – 0.5 | 0.3 – 1.1 | Soft, large pore volume | Aqueous phase adsorption |
| Hard wood | 40 – 42 | 55 – 60 | 0.55 – 0.80 | 0.3 – 1.2 | Soft, large pore volume | Aqueous phase adsorption |
| Lignin | 35 – 40 | 58 – 60 | 0.3 – 0.4 | – | Soft, large pore volume | Aqueous phase adsorption |
| Nutshells | 40 – 45 | 55 – 60 | 1.4 | 0.5 – 0.6 | Hard, large micropore volume | Vapour phase adsorption |

| | | | | | | |
|---|---|---|---|---|---|---|
| Lignite | 55 – 70 | 25 – 40 | 1.00 – 1.35 | 5 – 6 | Hard, small pore volume | Wastewater treatment |
| Soft coal | 65 – 80 | 20 – 30 | 1.25 – 1.50 | 2 – 12 | Medium hard, medium micropore volume | Liquid and vapour phase adsorption |
| Petroleum coke | 70 – 85 | 15 – 20 | 1.35 | 0.5 – 0.7 | Medium hard, medium pore volume | Wastewater treatment |
| Semihard coal | 70 – 75 | 10 – 15 | 1.45 | 5 – 15 | Hard, large pore volume | Gas vapour adsorption |
| Hard coal | 85 – 95 | 5 – 10 | 1.5 – 1.8 | 2 – 15 | Hard, large pore volume | Gas vapour adsorption |

Sawdust after activation is a wood-based activated carbon, as the so called lignocellulosic biomass is derived from raw logs. The growth of wood industry in Malaysia has been phenomenal over the past decades. Malaysia with its well-known tropical rainforest climate is considered as the most ideal climatic condition for cultivating timber, and this potential has been fully utilized and exploited. According to Malaysian Investment Development Authority (2012), Malaysia is one of the major timber supplier with total of 1019 sawmills in operation. Out of the total, 671 operate in Peninsular, 177 in Sabah and 171 in Sarawak. Exports of saw logs and sawn timber in 2011 amounted to RM5.2 billion with exports mainly to Thailand, Netherlands, China, Japan and Singapore. However, the depressing fact is that the log wood conversion to sawn timber is estimated to have a yield of only 58.5%, with the remaining 41.5% becomes wood chips and sawdust (Indonesia Furniture, 2013). As a consequence, substantial amount of residual biomass is generated, which is why many research works has been carried out to utilize sawdust generated in the process of wood sawing to develop high surface area of AC. Previous research has shown the potential of Meranti wood (*Shorea Parvifolia*) and Rubber wood (*Hevea brasiliensis*) being high-quality adsorbents with positive development of mesopores and surface area.

The present study is to use the sawdust from Nyatoh wood species to prepare the activated carbons with high adsorption characteristics. Similar to both Meranti and Rubber wood species, Nyatoh wood or scientifically known as *Sapotaceae spp.* is classified as light hardwood. When compared with Meranti wood, their properties are almost identical, which is the reason why sawdust from Nyatoh wood species is chosen with anticipation of new findings or even better results.

Table 2: Timber species in Malaysia

*(**Source**:http://www.mtib.gov.my/index.php?option=com_content&view=article&id=1636&limitstart=3)*

| | |
|---|---|
| **Heavy hardwood** | Chengal (*Neobalanocarpus heimii*)<br>Balau / Selangan Batu (*Shorea spp.*)<br>Merbau (*Intsia spp.*)<br>Belian ( *Eusideroxylon zwageri*)<br>Resak (*Vatica spp. & Cotylelobium spp.*) |
| **Medium hardwood** | Kempas (*Koompassia malaccensis*)<br>Keruing (*Dipterocarpus spp.*)<br>Kapur (*Dryobalanops spp.*) |
| **Light hardwood** | Meranti (*Shorea spp.*)<br>Rubberwood (*Hevea brasiliensis* )<br>Nyatoh ( *Sapotaceae spp.*)<br>Ramin ( *Gonystylus spp.*)<br>Kembang Semangkuk (*Scaphium spp.*)<br>Sepetir ( *Sindora spp. & Copaifera palustris*)<br>Tualang (*Koompassia excelsa*)<br>Jelutong (*Dyera spp.*)<br>Sesendok ( *Endospermum spp.*)<br>Durian ( *Coelostegia spp. / Durio spp. / Neesia spp.*) |
| **Softwood** | Damar minyak (*Agathis borneensis*)<br>Podo (*Podocarpus spp.*)<br>Sempilor (*Dacrydium spp; Phyllocladius spp.*) |

## 2.2 Activation of Carbonaceous Materials

The porous structure and final properties of activated carbon do not depend solely on nature and types of the raw materials, the activation processes also play a vital role. There are two types of activation processes namely physical activation and chemical activation. Physical activation involves the pyrolysis step followed by a stage of controlled oxidation to activate the carbon in the presence of steam or carbon dioxide.

Chemical activation usually is carried out when the raw material is of wood origin, whereby the material is impregnated using chemical agent in the form of concentrated solution to degrade the cellulosic material. Activated carbon produced from chemical activation usually has a relatively higher specific surface area and more mesopores than that in physical activation (Zhang et. al., 2010).

Chemical activation is usually carried out in the temperature range of 400 and 800°C. The recommended time of activation is between 60 to 90 minutes with impregnation ratio ranging from 1:1 to 1:5. All these operative parameters would be manipulated in this study to determine the optimum operating condition for producing activated carbon using sawdust. The main chemical activating agents include zinc chloride, phosphoric acid and potassium hydroxide solution. Phosphoric acid and zinc chloride are used for activating plant dry matter, whereas potassium hydroxide is normally used for activation of coal precursor or chars. When compared with zinc chloride, phosphoric acid is preferred due to the environmental disadvantage associated with zinc chloride (Srinivasakannan & Bakar, 2004). Not only corrosive, zinc chloride is highly toxic to marine life.

## 2.3 Characterization of Activated Carbon

### 2.3.1 Adsorption Isotherm

In adsorption studies, the process behavior is usually illustrated through graphs known as adsorption isotherm. It is a plot of equilibrium amounts adsorbed on the surface of the adsorbent as a function of relative pressure ($p/p^0$) of the adsorbate at constant temperature (Marsh, H. & Rodriguez-Reinoso, F., 2006). In the process of adsorption, adsorbate gets adsorbed on adsorbent.

$$Adsorbate + Adsorbent \underset{\text{Desorption}}{\overset{\text{Adsorption}}{\rightleftharpoons}} Adsorption$$

$$A + B \rightleftharpoons AB$$

There are several remarkable definitions in the basics of adsorption phenomena. In experimental adsorption systems, the gas or vapor of a gas phase, or the solute in a solution, is called the adsorptive (when not in adsorbed state). When existing as an adsorbed phase within a solid adsorbent, it is referred to as the adsorbate. As aforementioned, the variations of extents of adsorption ($n^a$ in mmol $g^{-1}$) with relative pressure ($p/p^o$) of the adsorptive at constant temperature, when plotted, make up the adsorption isotherm. However, when the extents of adsorption ($n^a$ in mmol $g^{-1}$) is varied with temperature of adsorption (T in K) at constant relative pressure, and with adsorption temperature (T in K) at constant amount of adsorbate adsorbed on the adsorbent ($n^a$ in mmol $g^{-1}$), they are known as the adsorption isobar and adsorption isostere respectively (Marsh, H. & Rodriguez-Reinoso, F., 2006). Figure 2 (a) shows the basic adsorption isotherm. From the shape of the graph, it can be interpreted in a way that adsorption does not occur anymore after saturation pressure ($P_s$), that is there are limited numbers of vacancies on the surface of the adsorbent. Under high pressure condition, it would reach a stage where all the sites are occupied and further increase in pressure would not result in significant difference. In other words, it can be said that adsorption is independent of pressure at high pressure condition.

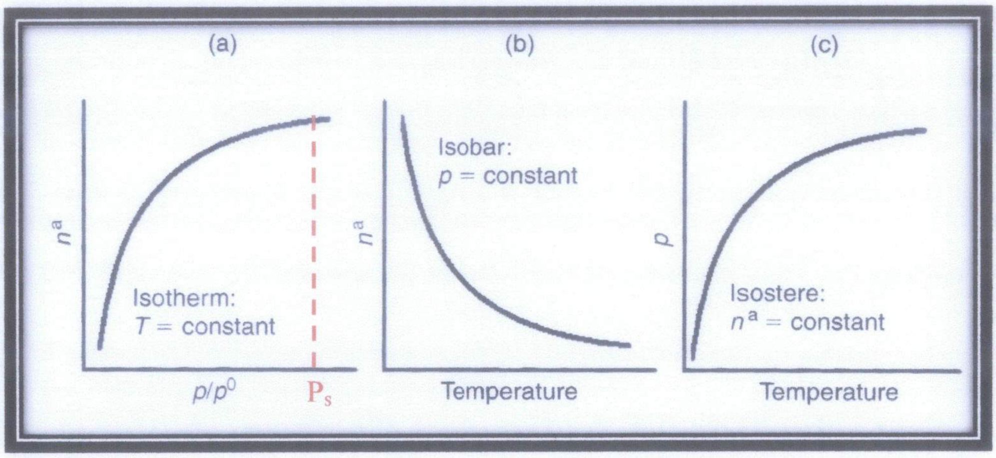


Figure 2: Definitions of terms used to describe adsorption phenomena

Marsh, H. & Rodriguez-Reinoso, F. (2006) in their book entitled "Activated Carbon" highlighted that present advance technology enabling the development of automatic adsorption equipment and the computerized analysis of adsorption data, has created a tendency to underestimate the value and significance of the adsorption isotherm. The concept of "surface area" which is pretty much in current use, dominates the assessment studies of activated carbon instead. Most of the computerized equipment is programmed to re-assemble adsorption data into the coordinates of the Freundlich, Langmuir, or Brunauer-Emmett-Teller (BET) equations and to generate the best fit line through data, and so to obtain a value for a surface area. Although the computer-based values of surface area can be obtained within short period of time by omitting all the tedious manual calculation methods, but the adsorption isotherm is often neglected and not printed out. There is a need to do this as the isotherm provides considerable information about extents of adsorption and the porous networks into which the adsorption process has taken place, simply from a visual inspection. For example, two activated carbon samples having the same surface area, say 1000 $m^2g^{-1}$, may differ in adsorption properties. An initial, comparative visual inspection of the isotherm shapes would immediately pinpoint differences between the two.

Nonetheless, there is also a problem associated with the interpretation of an adsorption isotherm. Normally, the isotherm is a smooth continuous curve with no clear-cut to indicate a point which could be related directly and precisely to a surface area measurement. Hence, the need to use adsorption equations which contain a parameter for surface coverage leading to exact quantification of surface area is equally important. In brief, both qualitative and quantitative interpretation of isotherms must co-exist to ensure complete characterization.

### 2.3.2 Qualitative Interpretation of Isotherms

For pure gases in gas phase adsorption, experimental physisorption isotherms are classified into six shapes as shown in Figure 3.

**Type-I isotherms** – An inherent property of Type-I isotherms is that adsorption is limited to the completion of single monolayer, or at most a few molecular layers only. In the context of physical adsorption, Type-I isotherms are observed on microporous solid whose pore sizes are not exceedingly large when compare to the molecular diameter of the adsorbate. Physical adsorption that shows Type-I isotherm indicates that the pores are microporous and that the exposed surface resides mostly within the micropores, which once filled with adsorbate, leave little or no space for additional adsorption to take place (Lowell, S. & Joan, E., n.d.). The gradients of the initial part of the isotherm, from p/p$^0$ value between zero to 0.05, are indicative of the dimensions of the microporosity. The steeper the slope is, the smaller the size of the micropores.

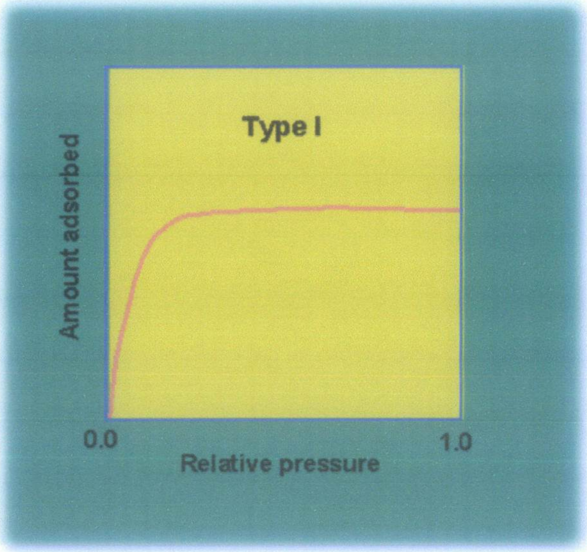


Figure 3: Type-I adsorption isotherm

**Type-II isotherms** – Unlike Type-I isotherms which exhibit saturation limit, Type-II isotherms indicate indefinite multi-layer formation after completion of the monolayer and is found in adsorbents with pore diameters larger than micropores. The inflection point usually occurs near the end of the first adsorbed monolayer, which falls in the region of $p/p^0 > 0.1$. Due to subsequent increase in relative pressure, successive layers are completed until at saturation, the number of adsorbed layers becomes infinite.

**Type-III isotherms** – The isotherm explains the formation of multilayer as there is no flattish portion in the graph that indicates monolayer formation is missing. It is encountered when the amount of gas adsorbed becomes infinite as its relative pressure, p/p$^0$ value approaches 1. This type of isotherm however is undesirable because the rate of adsorption is low unless at high pressure.

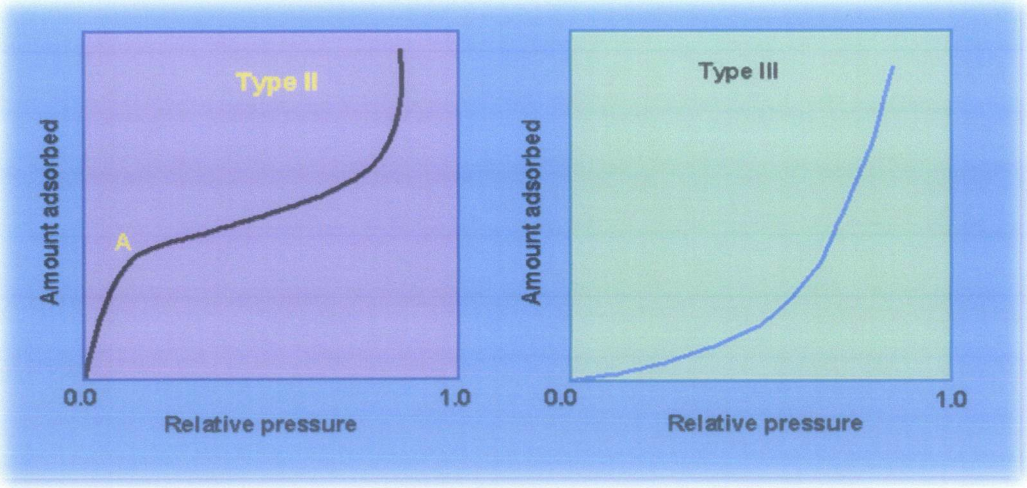


Figure 4: Type-II and Type-III adsorption isotherm

**Type-IV isotherms** – The starting trend of Type-IV isotherm is quite similar to Type-II isotherm, this explains the formation of monolayer followed by multilayer. It is a variation of Type II but with a finite multilayer formation corresponding to complete filling of capillaries. The isotherm may exhibit hysteresis, and hysteresis is indicative of mesoporosity.

**Type-V isotherms** – Type-V isotherm is similar variation of Type III, but presents with a hysteresis loop. Materials of low energy, homogeneous solid surface possessing mesoporosity are likely to be associated with this isotherm.

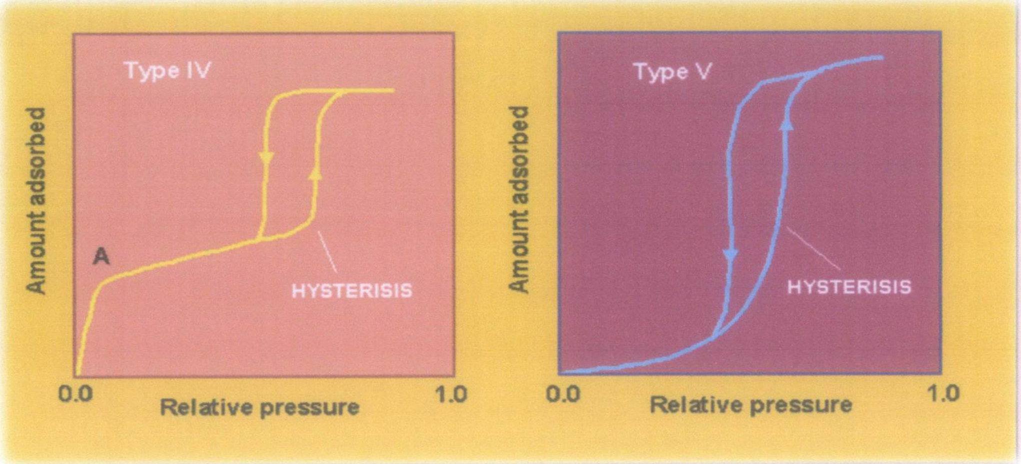


Figure 5: Type-IV and Type-V adsorption isotherm

### 2.3.3 Quantitative Interpretation of Isotherms

Aside from qualitative assessment, the isotherm somehow has to be interpreted quantitatively to enable comprehensive evaluations to be made between carbons. There is a need to know how much porosity there is in a given carbon, and the data is best represented through numbers. The adsorption isotherm has to be interpreted mathematically and one way to do this is to model the adsorption process. There are several models used for predicting the equilibrium distribution, namely linear, Freundlich, Langmuir and Brunauer, Emmet and Teller (BET). The most commonly used isotherms for the application of activated carbon in wastewater treatment are the Freundlich and Langmuir isotherms (Adsorption equilibira, n.d.).

**Freundlich Isotherm**

Freundlich Isotherm is an empirical equation representing the isothermal variation of adsorption of a quantity of gas adsorbed by unit mass of solid adsorbent with pressure.

$$\frac{x}{m} = kP^{\frac{1}{n}}$$

where x is the mass of the gas adsorbed on mass m of the adsorbent at pressure p and k, n are constants whose values depend upon adsorbent and gas at particular temperature.

At low pressure condition, the model correctly established the relationship of direct proportionality between extent of adsorption and pressure, that is the rate of adsorption increases with pressure. The drawback of this adsorption equation is that it failed to predict value of adsorption at higher pressure.

**Langmuir Isotherm**

Langmuir equation depicts a relationship between the number of active sites of the surface undergoing adsorption with respect to pressure.

$$\frac{p/p^0}{n^a} = \frac{1}{bn_m^a} + \frac{p/p^0}{n_m^a}$$

where p = equilibrium vapour pressure (Pa), $p^0$ = saturation vapour pressure (Pa), $n^a$ = amount adsorbed (mmol/g), $n_m^a$ = monolayer capacity (mmol/g). The model is developed by making the following assumptions (Langmuir adsorption isotherm, 2010).

1. Fixed number of vacant or adsorption sites are available on the surface of solid.
2. All the vacant sites are of equal size and shape on the surface of adsorbent.
3. Each site can hold maximum of one gaseous molecule and a constant amount of heat energy is released during this process.
4. Dynamic equilibrium exists between adsorbed gaseous molecules and the free gaseous molecules.
5. Adsorption is monolayer or unilayer.

## Brunauer, Emmet and Teller (BET) Isotherm

The BET equation is written as

$$\frac{p}{V(p^0 - p)} = \frac{1}{V_m c} + \frac{(c-1)p}{V_m c p^0}$$

where V= amount adsorbed in volume STP ($cm^3/g$), $V_m$= monolayer capacity in volume STP ($cm^3/g$). BET is a more general, multi-layer model. It assumes that Langmuir isotherm is applied to each layer and no transmigration takes place between layers. Except for first layer, the model also assumes equal energy of adsorption on each layer.

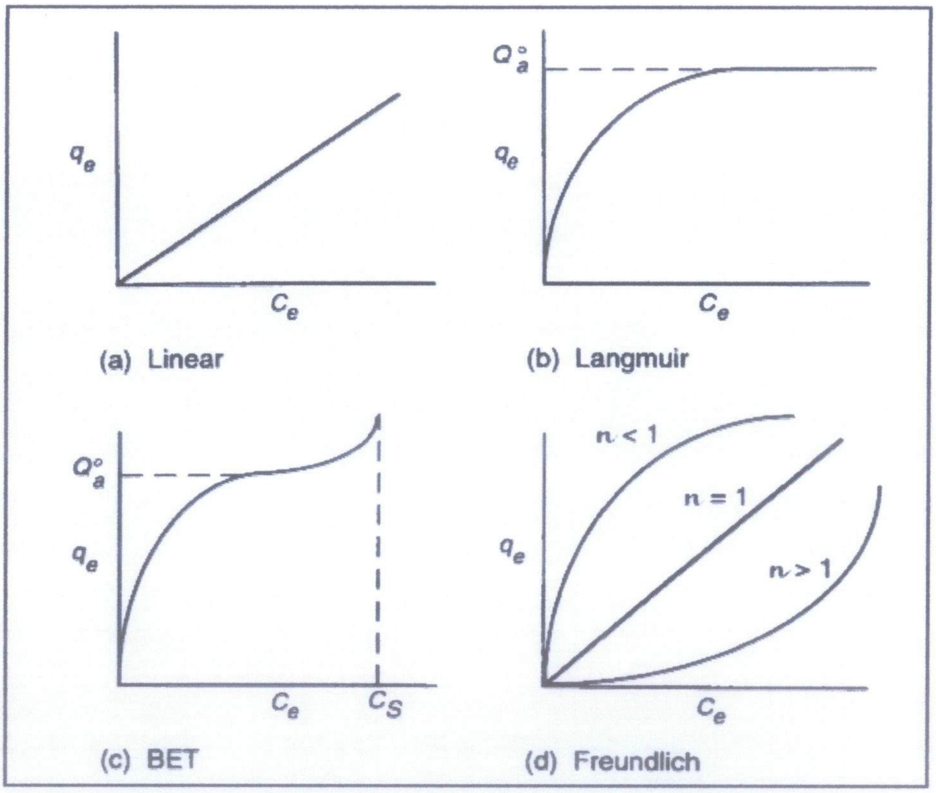


Figure 6: Shapes of linear, Langmuir, BET and Freundlich isotherms

### 2.3.4 Characterization Test

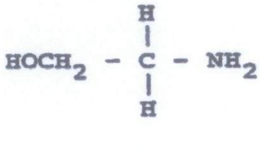
In order to evaluate the performance of activated carbon, certain characterization tests have to be carried out. For parameters like surface area, pore volume and pore size, nitrogen adsorption-desorption isotherm method can be used to provide figure data. Further information on pore structure could be obtained from observing the isotherm shape. The physisorption isotherms can then be classified based on the schemes for Type-I to Type-V curves. Aside from nitrogen adsorption-desorption isotherm method, literature also suggests another technique of sample characterization known as iodine adsorption, which involves the determination of iodine number. Iodine number is defined as the number of milligrams of iodine adsorbed from an aqueous solution by 1g of activated carbon when the iodine concentration in the residual filtrate is 0.02 normal (European Council of Chemical Manufacturers' Federations, 1986). Basically, it is a measure of the iodine adsorbed in the pores, which provides an indirect measurement to the pore volume and surface area available in the activated carbon.

Although the determination of iodine number is a simple, quick test, and able to give accurate indication of the adsorption capacity and internal surface area possessed by activated carbon sample, but current study opt to employ nitrogen adsorption-desorption isotherm method instead due to several reasons. Firstly, it is because iodine adsorption is usually associated with micropores due to small size of iodine molecule. High iodine number means an increase in surface area and pore volume, but the types of pores develop is disregarded in this test. Even micropore is able to cope with the size of iodine molecule, therefore development of mesopore and macropore could not be detected through this test. Furthermore, by using nitrogen adsorption-desorption isotherm method, both qualitative and quantitative measurement are achieved.

## 2.4 Monoethanolamine (MEA)

MEA is a liquid organic compound derived from ethylene oxide and ammonia. With molecular formula of $NH_2CH_2CH_2OH$, the compound exists in liquid state at room temperature. One of the distinct properties of MEA under physical state is that it presents as white viscous liquid with mild ammoniacal odour.

Table 3: Physical and chemical properties of MEA
*(Source: Material Safety Data Sheet)*

| | |
|---|---|
| Molecular formula |  $HOCH_2-\overset{H}{\underset{H}{C}}-NH_2$ |
| Molecular weight | 61.08 g/mol |
| Physical state | Liquid |
| Melting point | 10.3°C (50.5°F) |

|  |  |
|---|---|
| Boiling point | 171°C (340°F) |
| Specific gravity | 1.018 (Water =1) |
| Vapor density | 2.1 (Air = 1) |
| Vapor pressure | 0.1 kPa at 20°C |
| pH | 11.5 – 12.2 (Aqueous solution) |
| Solubility | Soluble in water and alcohol, slightly soluble in benzene |

Primary routes of exposure include inhalation and direct contact through skin and eyes. Prolonged exposure to MEA may cause lung irritant. In case of direct contact, the effect is slightly hazardous due to its corrosivity. In contact with skin, it may be absorbed and causes systemic poisoning, whereas eyes contact in worst case may lead to permanent corneal damage and blindness. Environmental wise, release of MEA to water streams brings adverse effects to aquatic life. Since MEA is an organic matter, there is a risk that MEA will upset the water stream by increasing the Chemical Oxygen Demand (COD). A high COD value signifies oxygen deficiency in water. Decomposition of organic matter will consume the amount of water-dissolved oxygen, which in turn leads to lack of oxygen and ultimately destroys the aquatic ecosystem. According to the Soil and Groundwater Remediation Guidelines for Monoethanolamine and Diethanolamine from Alberta Environment (2012), the maximum allowable limit for MEA and DEA are:

Table 4: Surface water quality guidelines for MEA and DEA

|  | **MEA** | **DEA** |
|---|---|---|
| **Water Use** | **mg/L** | **mg/L** |
| Human drinking water | 0.6 | 0.06 |
| Freshwater aquatic life | 0.075 | 0.45 |

The most recent accident chemical release pertaining MEA occurred in Taminco plant, a worldwide manufacturer of amine products. Three people were admitted to hospital for immediate medical treatment as a result of exposure to dimethylamine (DMA60). The cloud of dimethylamine was accidentally released during a rail transfer at the Taminco Pace Plant. According to the spokesperson, the percentage of the leak is well below what is considered safe. However, the odour of the chemical release was so strong to the extent that one can smell it off-site. That is because DMA60 gives out such a strong irritant smell that even one drip at the plant can be detected off-site (Hough, 2013). Therefore, precautionary measures must be taken to prevent similar incident to recur. Engineering controls at the source for instance local exhaust ventilation is mandatory to put in place a demonstrably sound occupational health and safety workplace.

## 2.5 Monoethanolamine (MEA) Wastewater Treatment via Adsorption Method

Currently, aqueous MEA is widely used in removing carbon dioxide and hydrogen sulphide from flue gas stream. Like any other amines, MEA is relatively toxic, flammable and corrosive. According to the result obtained from an industrial survey, most of the petrochemical plants in Malaysia are disposing MEA wastewater to Kualiti Alam due to treatment complication. The cost of disposal is very high because MEA wastewater is categorized as scheduled waste. Eventually, frequent disposal of MEA wastewater has resulted in reduction of profit margin due to high disposal cost (Razali, 2011).

Several researches have been conducted and suggested a few methods to treat MEA wastewater. Generally, the treatment methods proposed to separate amines from wastewater are based on physical, chemical and biological separation methods. Razali et. al. (2010) in their study, had presented that the most rational way of treating the MEA wastewater is to achieve quality suited for recycling it back to the system. Adsorption method was used for the treatment with four types of adsorbents (chitosan, activated carbon, alum and zeolite) employed. In all adsorbents investigated in this study, none of the adsorbents manage to lessen the concentration of MEA but promising results were shown in reducing the chemical oxygen demand (COD), suspended solid and oil concentration in the MEA wastewater. After preliminary assessment, the treated MEA wastewater is believed to have the potential of being recycled and reused in the $CO_2$ removal unit.

# CHAPTER 3

# METHODOLOGY

## 3.1 Project Activities

### 3.1.1 Sample preparation

1. Sawdust was collected from a local sawmill. The type of sawdust acquired was originated from Nyatoh wood (*Sapotaceae spp.)*.
2. The sawdust was sieved according to size of 250µm and 1mm.
3. The sieved sawdust was then washed with distilled water several times to remove impurities and ashes that were collected together.
4. After washing, the sawdust was kept in an oven overnight at 80°C for drying purpose.
5. The dried and cleaned sawdust was placed in an airtight container for further process.

### 3.1.2 Carbonization and activation

1. Sieved sawdust that has been prepared was impregnated with phosphoric acid at different impregnation ratio (1:1, 1:2 and 1:3).
2. The impregnation process was allowed to sit for overnight to ensure that the chemical reagent is fully adsorbed to the raw material.

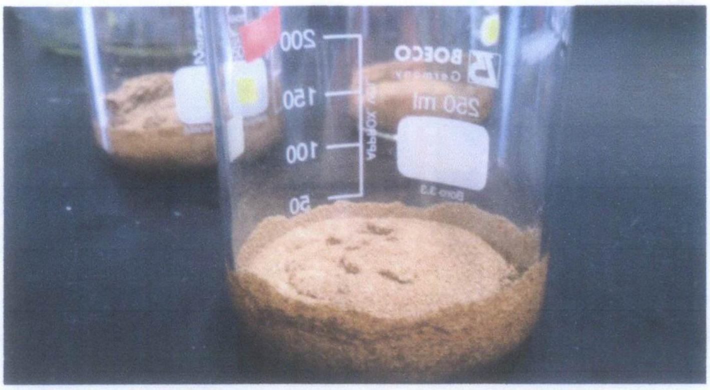


Figure 7: Impregnation by mixing sawdust with desired ratio of phosphoric acid

3. The sawdust that has been impregnated was carbonized in a Fixed Bed Activation Unit at different operating activation temperature (400, 500, 600 and 700°C) and activation time (30, 60, 90, 120, 180 minutes).

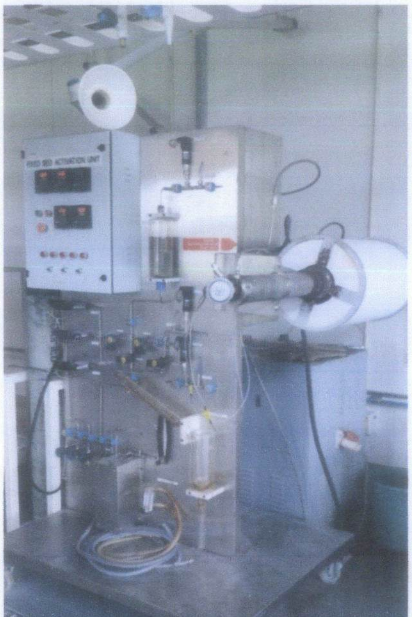


Figure 8: Fixed bed activation unit

4. The activated carbon that has been produced was left to sit in ambient temperature before being washed with distilled water to remove remaining chemical.

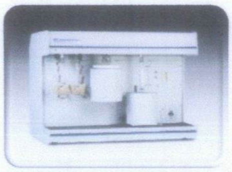
5. It was then dried in an oven overnight at 80°C. Dried activated carbon was placed in a desiccator to protect it from the water vapour in atmosphere.

### 3.1.3 Sample characterization

To determine the best operating parameter for producing activated carbon from sawdust, testing and characterization were carried out using the following equipment:

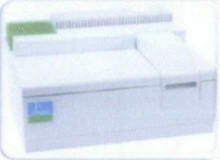
**Field-emission scanning electron microscopy (FESEM)**

- FESEM uses electrons instead of light to form an image
- FESEM also allows the determination of elemental composition of sample through Energy Dispersive X-ray (EDX) Spectroscopy



**Micrometrics ASAP 2020**

- The ASAP 2020 is used to determine the high surface areas of adsorbents, and to determine the microporosity.
- The characterization process is done by using nitrogen adsorption-desorption isotherm whereby nitrogen gas acts as the adsorbate and is set to flow at 350°C for 2hours.



**UV-Vis Spectrophotometer**

- UV-Vis Spectrophotometer is used to measure the concentration of MEA and determine the adsorption rate of activated carbon adsorbing MEA in sysnthetic MEA wastewater.

### 3.1.4 Adsorption Test

1. The experiment was carried out using UV-Vis Spectrophotometer set at wavelength of 195nm to detect the concentration of monoethanolamine (MEA) in synthetic MEA wastewater.

2. Calibration was performed using standard solution of 100ppm, 300ppm and 500ppm prepared by diluting MEA (analyte) with distilled water (solvent) in 1-L volumetric flask.

Table 5: Preparation of standard solutions

| No. | Concentration of MEA (ppm) | Volume of MEA required (mL) | Volume of distilled water added (mL) |
|---|---|---|---|
| 1 | 100 | 0.1 | 999.9 |
| 2 | 300 | 0.3 | 999.7 |
| 3 | 500 | 0.5 | 999.5 |

3. Adsorption test was done by adding 1g of activated carbon into 200mL of 500ppm synthetic MEA wastewater.
4. The mixture was allowed to sit for 100 minutes with stirring speed of 250rpm. Samples were extracted from the mixture and readings were taken at interval of 10 minutes.
5. The graph of MEA concentration versus time was plotted to study the effectiveness of activated carbon in adsorbing MEA.

## 3.2 Apparatus and Materials

Table 6: List of chemicals used for impregnation

| No. | Chemicals | Amount (Litre) |
|---|---|---|
| 1 | Zinc chloride ($ZnCl_2$) | 1 |
| 2 | Monoethanolamine ($C_2H_7NO$) | 1 |

Table 7: List of glassware and apparatus used in experimental procedure

| **No.** | **Apparatus** | **Amount (unit)** |
|---|---|---|
| 1 | 500-mL beaker | 6 |
| 2 | Measuring cylinder | 1 |
| 3 | Spatula | 2 |
| 4 | Electronic balance | 1 |
| 5 | Desiccator | 1 |
| 6 | 1-L volumetric flask | 1 |
| 7 | Siever | 1 |
| 8 | Vacuum oven | 1 |

## 3.3 Process Flow Chart

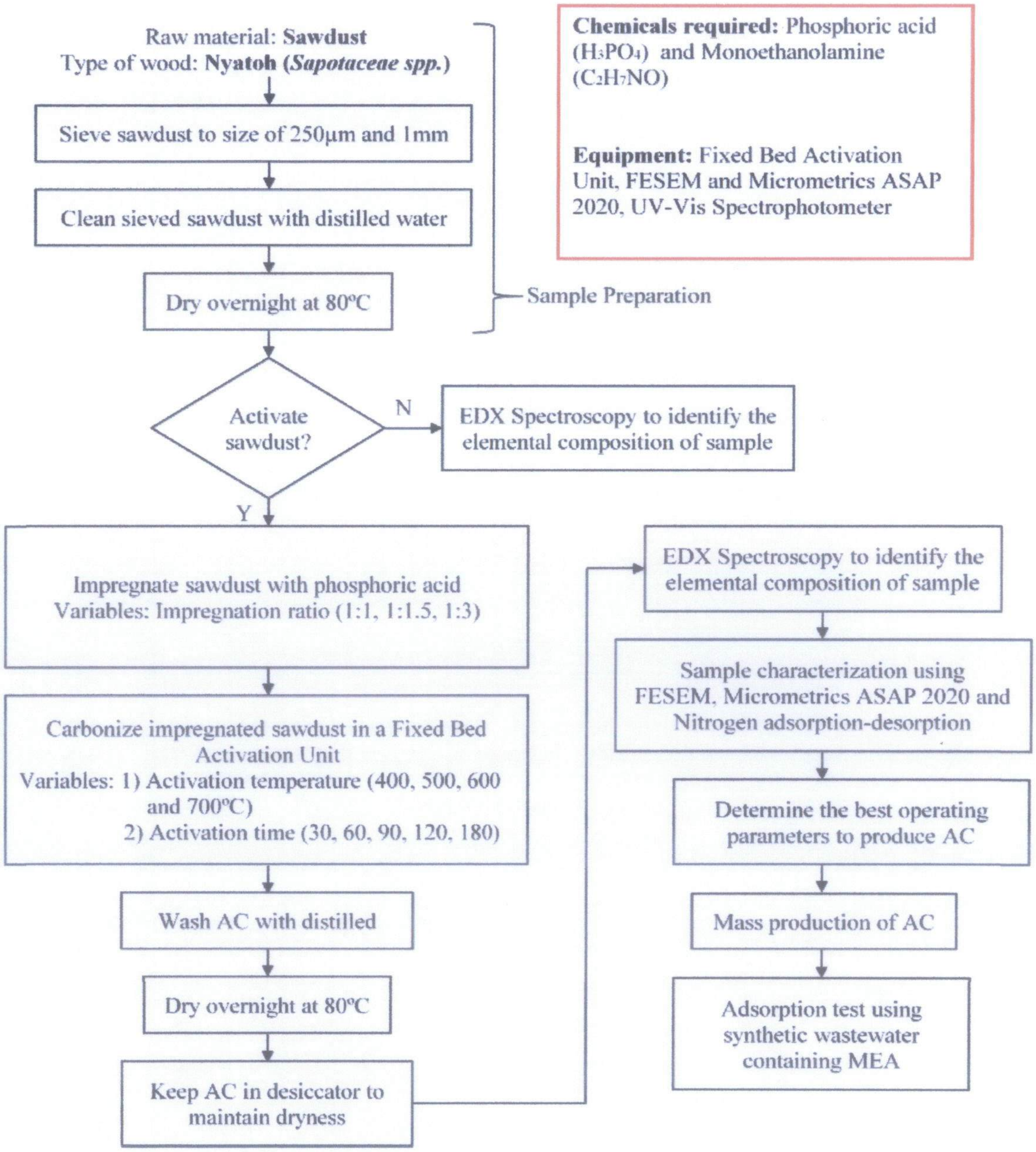
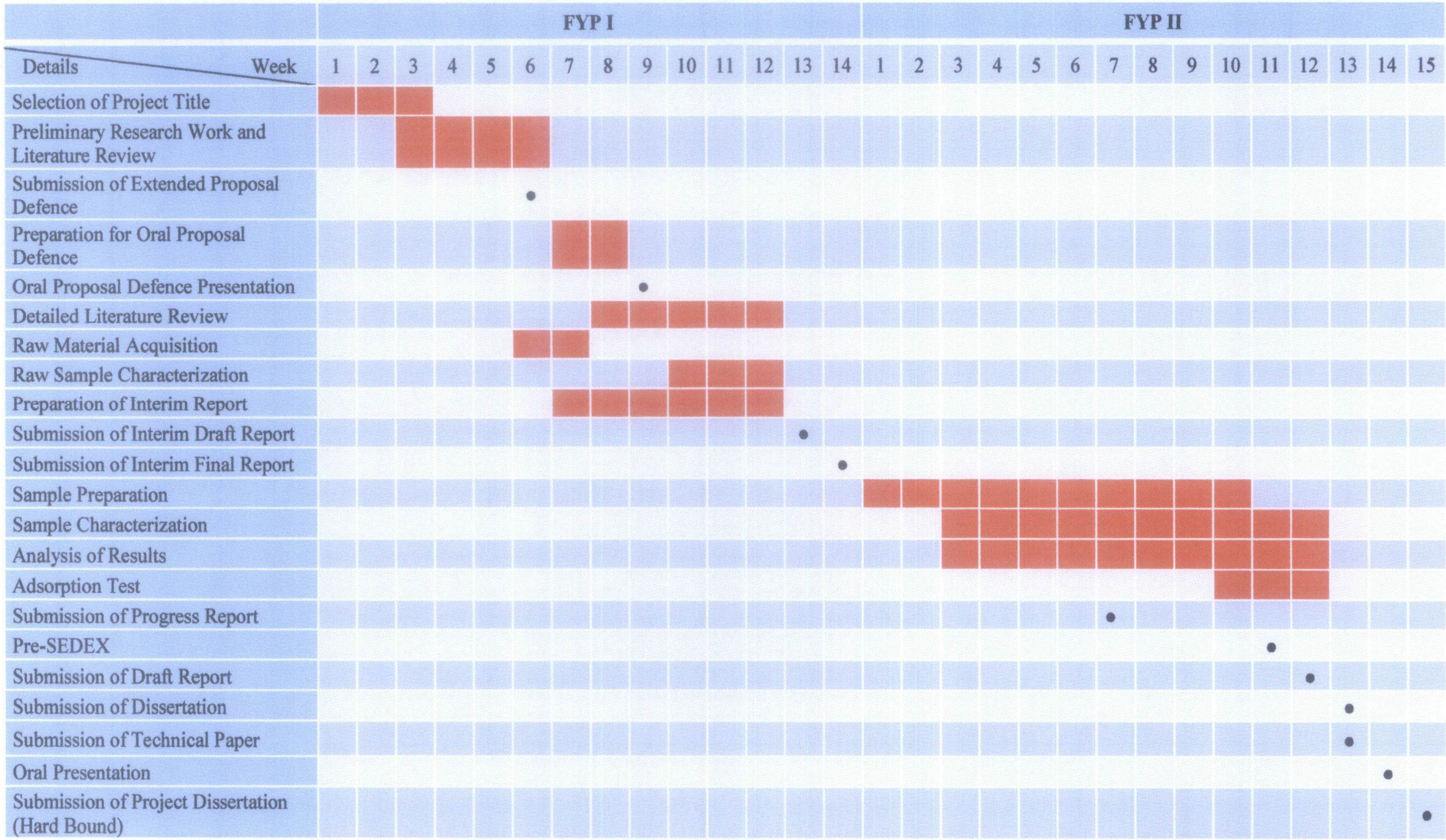


Figure 9: Process flow chart

## 3.4 Gantt Chart and Key Milestone



| | FYP I | | | | | | | | | | | | | | FYP II | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Details Week | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 |
| Selection of Project Title | 🟥 | 🟥 | 🟥 | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Preliminary Research Work and Literature Review | | | 🟥 | 🟥 | 🟥 | 🟥 | | | | | | | | | | | | | | | | | | | | | | | |
| Submission of Extended Proposal Defence | | | | | | ● | | | | | | | | | | | | | | | | | | | | | | | |
| Preparation for Oral Proposal Defence | | | | | | | 🟥 | 🟥 | | | | | | | | | | | | | | | | | | | | | |
| Oral Proposal Defence Presentation | | | | | | | | | ● | | | | | | | | | | | | | | | | | | | | |
| Detailed Literature Review | | | | | | | | 🟥 | 🟥 | 🟥 | 🟥 | 🟥 | | | | | | | | | | | | | | | | | |
| Raw Material Acquisition | | | | | | 🟥 | 🟥 | | | | | | | | | | | | | | | | | | | | | | |
| Raw Sample Characterization | | | | | | | | | | 🟥 | 🟥 | 🟥 | | | | | | | | | | | | | | | | | |
| Preparation of Interim Report | | | | | | | 🟥 | 🟥 | 🟥 | 🟥 | 🟥 | 🟥 | | | | | | | | | | | | | | | | | |
| Submission of Interim Draft Report | | | | | | | | | | | | | ● | | | | | | | | | | | | | | | | |
| Submission of Interim Final Report | | | | | | | | | | | | | | ● | | | | | | | | | | | | | | | |
| Sample Preparation | | | | | | | | | | | | | | | 🟥 | 🟥 | 🟥 | 🟥 | 🟥 | 🟥 | 🟥 | 🟥 | 🟥 | 🟥 | | | | | |
| Sample Characterization | | | | | | | | | | | | | | | | | 🟥 | 🟥 | 🟥 | 🟥 | 🟥 | 🟥 | 🟥 | 🟥 | 🟥 | 🟥 | | | |
| Analysis of Results | | | | | | | | | | | | | | | | | 🟥 | 🟥 | 🟥 | 🟥 | 🟥 | 🟥 | 🟥 | 🟥 | 🟥 | 🟥 | | | |
| Adsorption Test | | | | | | | | | | | | | | | | | | | | | | | | 🟥 | 🟥 | 🟥 | | | |
| Submission of Progress Report | | | | | | | | | | | | | | | | | | | | | ● | | | | | | | | |
| Pre-SEDEX | | | | | | | | | | | | | | | | | | | | | | | | | ● | | | | |
| Submission of Draft Report | | | | | | | | | | | | | | | | | | | | | | | | | | ● | | | |
| Submission of Dissertation | | | | | | | | | | | | | | | | | | | | | | | | | | | ● | | |
| Submission of Technical Paper | | | | | | | | | | | | | | | | | | | | | | | | | | | ● | | |
| Oral Presentation | | | | | | | | | | | | | | | | | | | | | | | | | | | | ● | |
| Submission of Project Dissertation (Hard Bound) | | | | | | | | | | | | | | | | | | | | | | | | | | | | | ● |

# CHAPTER 4

# RESULT AND DISCUSSION

## 4.1 Surface area and porosimetry measurements

Table 8 below shows the preparation condition and BET results of 250μm sawdust activated carbon. All the samples were prepared under different impregnation ratio and temperature condition, which makes it likely for them to show different extent of pore development. Impregnation was done with three different ratios: 1:1, 2:1 and 3:1. Since this is the ratio between dry weight of acid and sawdust, calculation is needed to determine the volume of acid required. The amount of acid used for each impregnation ratio is calculated as shown in Table 7. Samples were continuously heated in a rotary kiln at varying temperature and period of time. However, the samples cannot be removed immediately from the oven before they are completely cooled down, which means that the samples are still being heated when the oven is taking time to cool down to room temperature. This could be a contributing source of error and uncertainty.

Table 8: Preparation of phosphoric acid solution for impregnation process

| Sample | IR | Dry weight of acid, $wt_{dry}$ (g) | Volume of acid required, V (mL) |
|---|---|---|---|
| A6 | 1:1 | $\frac{5\text{g of acid}}{0.85} = 5.9\text{ g}$ | $V = \frac{wt_{dry}}{\rho_{acid}} = \frac{5.9\text{ g}}{1.88\text{ g/cm}^3} = 3.1\text{ mL}$ |
| A7 | 2:1 | $\frac{10\text{g of acid}}{0.85} = 11.8\text{ g}$ | $V = \frac{wt_{dry}}{\rho_{acid}} = \frac{11.8\text{ g}}{1.88\text{ g/cm}^3} = 6.3\text{ mL}$ |
| A8 | 3:1 | $\frac{15\text{g of acid}}{0.85} = 17.6\text{ g}$ | $V = \frac{wt_{dry}}{\rho_{acid}} = \frac{17.6\text{ g}}{1.88\text{ g/cm}^3} = 9.4\text{ mL}$ |

*Conditions applied:*

*i. Each sample is prepared with 5g of sawdust.*
*ii. 85 wt% of orthophosphoric acid solution is used for impregnation process.*
*iii. The density of phosphoric acid, $\rho_{acid}$, is 1.88 g/cm$^3$.*

Table 9: Preparation condition and BET results of 250µm sawdust activated carbon

| Sample | IR | Activation temperature (°C) | Activation time (min) | Specific surface area,$S_{BET}$ ($m^2/g$) | Total pore volume, $V_T$ ($cm^3/g$) | Average pore diameter, D (nm) |
|---|---|---|---|---|---|---|
| Raw | - | - | - | 1.304 | 0.002 | 6.328 |
| A6 | 1:1 | 400 | 30 | 474.483 | 0.253 | 2.134 |
| A7 | 2:1 | 400 | 30 | 199.333 | 0.107 | 2.153 |
| A8 | 3:1 | 400 | 30 | 1.161 | - | - |
| B9 | 1:1 | 500 | 30 | 1135.624 | 0.565 | 1.992 |
| B10 | 2:1 | 500 | 30 | 878.880 | 0.551 | 2.507 |
| B11 | 3:1 | 500 | 30 | 399.013 | 0.261 | 2.616 |
| C12 | 1:1 | 600 | 30 | 539.708 | 0.290 | 2.153 |
| D15 | 1:1 | 700 | 30 | 58.581 | 0.036 | 2.573 |
| F21 | 1:1 | 500 | 60 | 1213.786 | 0.662 | 2.180 |
| J33 | 1:1 | 500 | 90 | 1176.079 | 0.634 | 2.158 |
| N45 | 1:1 | 500 | 120 | 941.242 | 0.495 | 2.105 |

From the results obtained, it is clear that Sample F21 which was prepared at IR of 1:1, activation temperature of 500°C and activation time of 60 minutes yields the highest value of specific surface area, $S_{BET}$ 1213.786 m2/g with average pore diameter equals 2.180 nm and total pore volume as high as 0.662 cm3/g. In Sample B9, B10 and B11, as the impregnation ratio increases, the samples show decreasing $S_{BET}$ value with similar trend observed in Sample A6, A7 and A8. Impregnation ratio is a critical parameter in formation of pores because it signifies the amount of ions available for intercalation to take place. An optimum impregnation ratio of 1:1 to 4:1 has been reported to yield highest surface area carbon (Srinivasakannan & Bakar, 2004), and the result obtained shows that highest value is achieved at 1:1 IR. High impregnation ratio favours more pore formation as it intensify the action of acid with more aggressive physico-chemical effect and dehydration which inhibits the contraction or collapse of the precursor particle. The washing after heat treatment will evacuate and free this internal porosity leaving behind an extensive microporous structure (Girgis & El-Hendawy, 2002). Nevertheless, the outcome of the analysis confirms that there is a maximum amount of ions that can be uptake beyond which would reduce pore development. In fact, Girgis & El-Hendawy (2002) in their report also stated the reason why additional acid does not lead to further action. It is because too much acid forms an insulating layer (or skin) covering the particles, thus reducing the activation process and the contact with surrounding atmosphere. This phenomenon is particularly observed in Sample A8 and B11 where most likely activation is hindered, resulting in negligible surface area and undetected pore.

As for activation temperature, the optimum temperatures have been reported to be between 400 and 500°C by most of the earlier researchers (Srinivasakannan & Bakar, 2004). Hence the experiments were conducted by varying temperature from 400°C to 700°C, and it turned out that the recommended temperature is reliable due to verification provided by Sample B9 at 500°C. The increase in temperature from 600°C to 700°C for Sample C12 and D15 undoubtedly demonstrated the collapse of porous structure due to excessive heat energy intake, which results from knocking and breaking of some porous wall (Borhan, Taha & Hamzah, n.d.). While maintaining a constant impregnation ratio at 1:1 and activation temperature at 500°C, the influence of activation time is examined. The results obtained from Sample B9, F21, J33 and N45 show that the optimum time for carbonization is 60 minutes. Prolonged heat exposure would only cause rupture in porous wall. Since the porous structure has already been well developed at temperature of 500°C, the increase in activation time simply causes the break of the cross-links between carbon structures, with a consequent collapse of pores (Teng, H. et. al., 1998). All the samples that have been analyzed show average pore diameter of around 2 nm, indicating that the pores formed are mesopores.

The existence of mesopores is further proven with the identified isotherms. Figure 8 shows the nitrogen adsorption-desorption isotherm of some selected samples. The isotherm is plotted as quantity of nitrogen gas adsorbed against the relative pressure. Based on the six principal types of adsorption isotherms, it is stated that all isotherms produced should fit at least one or a combination of two or more of the shapes (Borhan, Taha & Hamzah, n.d.). Referring to the graph in Figure 8, it can be seen that all selected samples exhibit trends with combination of Type-I and Type-II isotherms except Sample D15 which shows Type-I isotherm. Literature presents that Type-I isotherm is normally observed on microporous solid whose pore sizes are not exceedingly large when compare to the molecular diameter of the adsorbate, whereas Type-II isotherm is found in adsorbents with pore diameters larger than micropores. A combination of these two could be viewed as the effect of mixed micropores and mesopores structure.

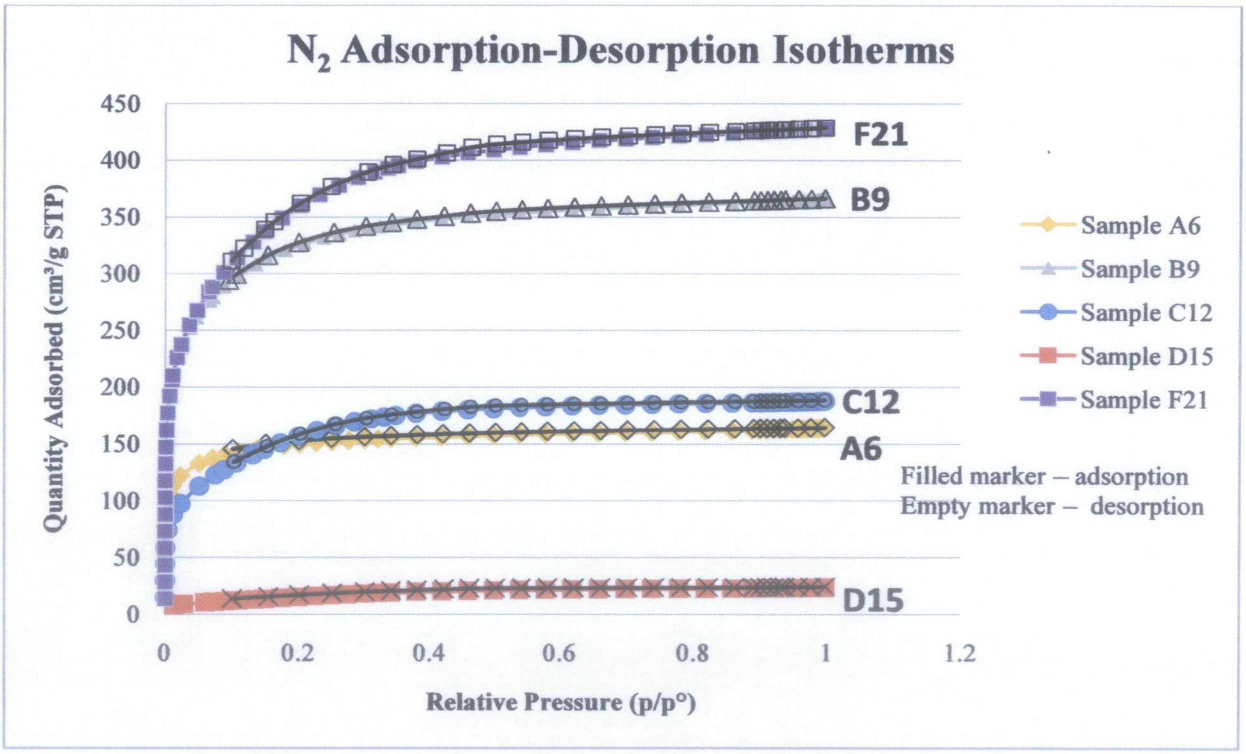
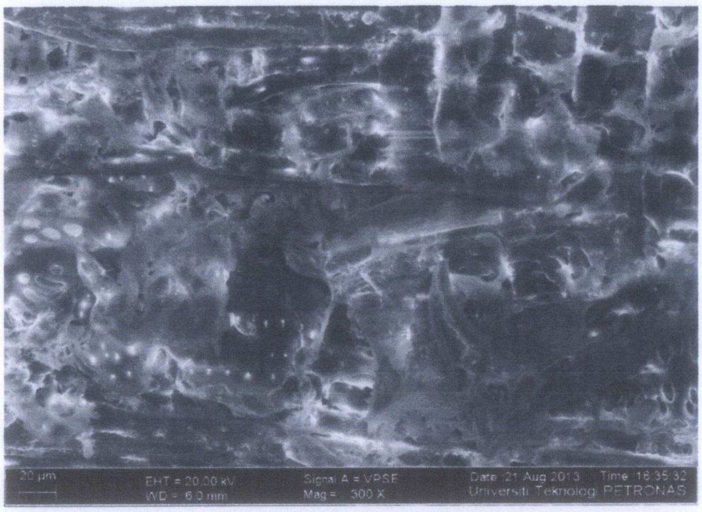


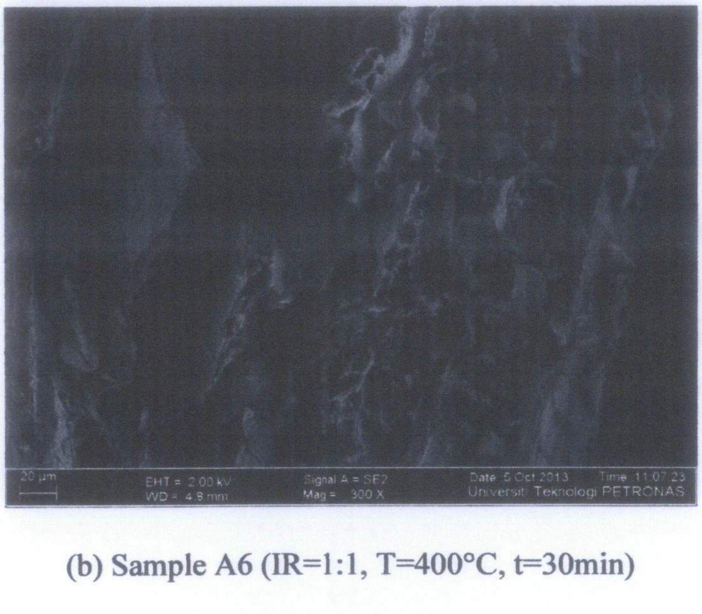
Figure 10: $N_2$ adsorption-desorption isotherms

## 4.2 Morphology

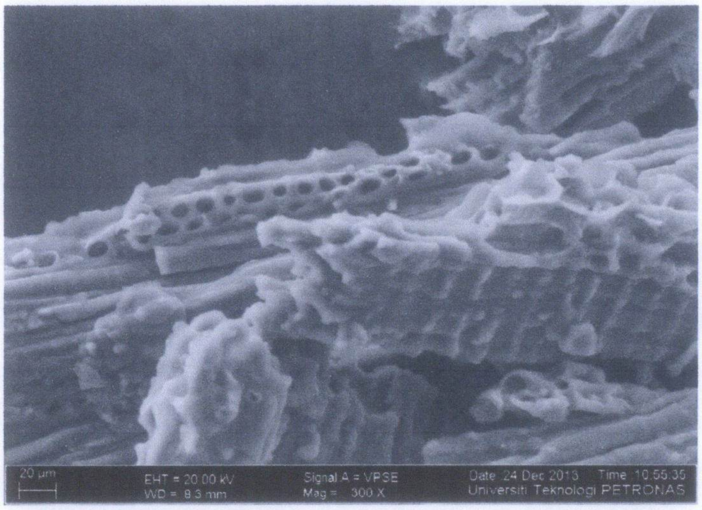
Figure 9 shows the microscopic structure of the raw sawdust and Sample A6 which is prepared at IR of 1:1, activation temperature of 400°C and activation time of 30 minutes. By using Field Emission Scanning Electron Microscopy (FESEM), structural images with magnification up to 300 times are taken. The structural image of fresh sawdust in Figure 9(a) points up that the raw material before undergoing activation shows no noticeable pores. However, the image clearly shows the existence of fine pores on the surface, which is one of the important characteristics for manufacturing activated carbon. After activation, a greater distribution of pores emerged to become active sites for adsorption to take place more readily. The difference in pore structure before activation and after activation is clearly illustrated through comparison made between Figure 9(a) with Figure 9(b) and 9(c). As shown in Figure 9(c), Sample B9 has the most even distribution of pores. On the other hand, collapse of porous wall due to excessive heat exposure is observed in Figure 9(d) with Sample D15 being activated at highest temperature.



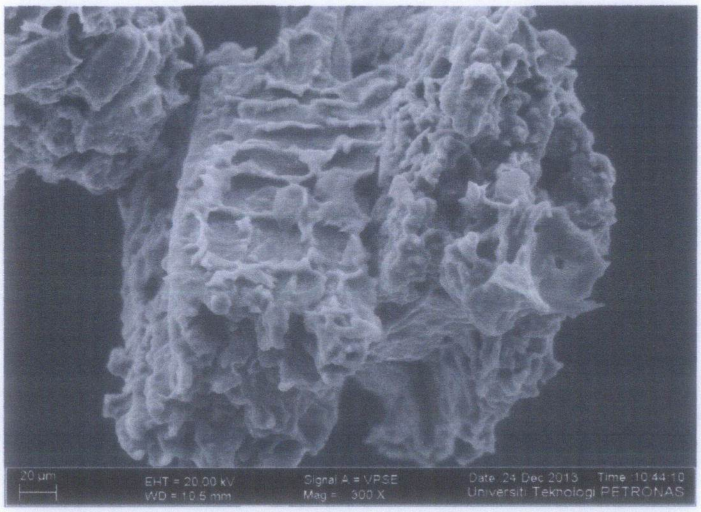
(a) Fresh sawdust



(b) Sample A6 (IR=1:1, T=400°C, t=30min)



(c) Sample B9 (IR=1:1, T=500°C, t=30min)



(d) Sample D15 (IR=1:1, T=700°C, t=30min)

Figure 11: FESEM images of selected samples

## 4.3 Energy-Dispersive X-ray (EDX) Spectroscopy

Aside from examining the surface morphology of the samples, FESEM is also equipped with EDX spectroscopy for detecting the elemental composition. Table 9 below shows the comparison of elemental composition before and after activation. Two elements were detected on the sample before activation: carbon and oxygen. Theoretically, most organic matter with high carbon content could be activated to improve its sorptive characteristics. As a matter of fact, it was reported in specific that suitable range of carbon content should lie between 50 to 80%. The result shows that *Nyatoh* wood species sawdust fulfills the criterion of producing activated carbon. An additional element identified as Phosphorus, P was detected in the sample after activation. Presence of phosphorus element is due to the use of phosphoric acid as chemical activating agent during the impregnation process. Repetitive washing can further reduce the phosphorus element but complete elimination is hardly possible.

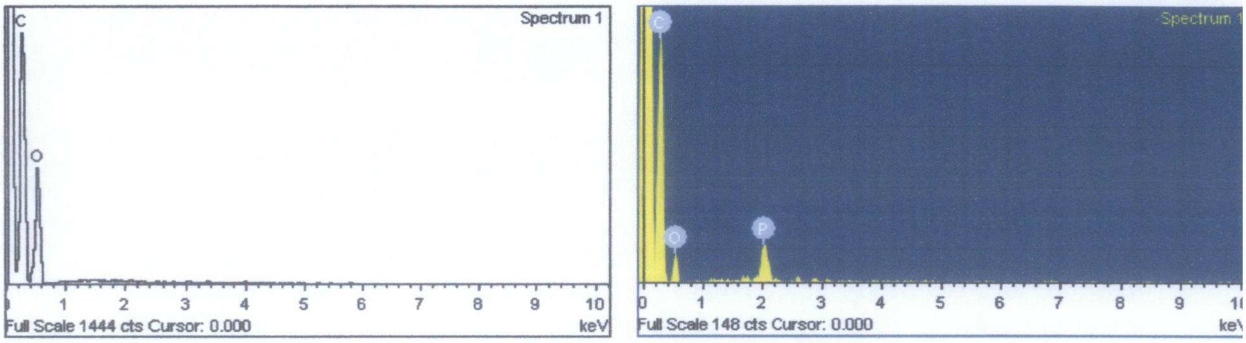


Figure 12: EDX analysis results (left: before activation; right: after activation)

Table 10: Comparison of elemental composition before and after activation

| | **Before Activation** | | **After activation** | |
|---|---|---|---|---|
| **Elements** | Weight % | Atomic % | Weight % | Atomic % |
| Carbon, C | 54.98 | 61.93 | 76.86 | 82.45 |
| Oxygen, O | 45.02 | 38.07 | 20.36 | 16.39 |
| Phosphorus, P | 0.00 | 0.00 | 2.78 | 1.16 |
| **TOTAL** | 100.00 | | 100.00 | |

## 4.4 Adsorption Test

The adsorption test on selected activated carbon samples was conducted using synthetic MEA wastewater produced from diluting MEA with distilled water. In order to measure the rate of adsorption, UV-Vis Spectrophotometer was used to detect the change in MEA concentration throughout the experiment. Sample B9 having the highest value of specific surface area and pore volume, was selected as one of the test subjects along with the fresh sawdust to show contrast. To construct the calibration curve, at least two different concentrations of the compound are required, but for a more accurate curve, three standard solutions with concentrations of 100ppm, 300ppm and 500ppm were prepared to perform the calibration. Table 11 below shows the absorbance intensity obtained by each standard solution at wavelength of 195nm, and the standard calibration curve was plotted as shown in Figure 11.

Table 11: Absorbance intensity of standard solutions

| Sample ID | Type | Concentration (ppm) | Absorbance Intensity |
|---|---|---|---|
| A | Standard | 100 | 1.471 |
| B | Standard | 300 | 2.991 |
| C | Standard | 500 | 5.000 |

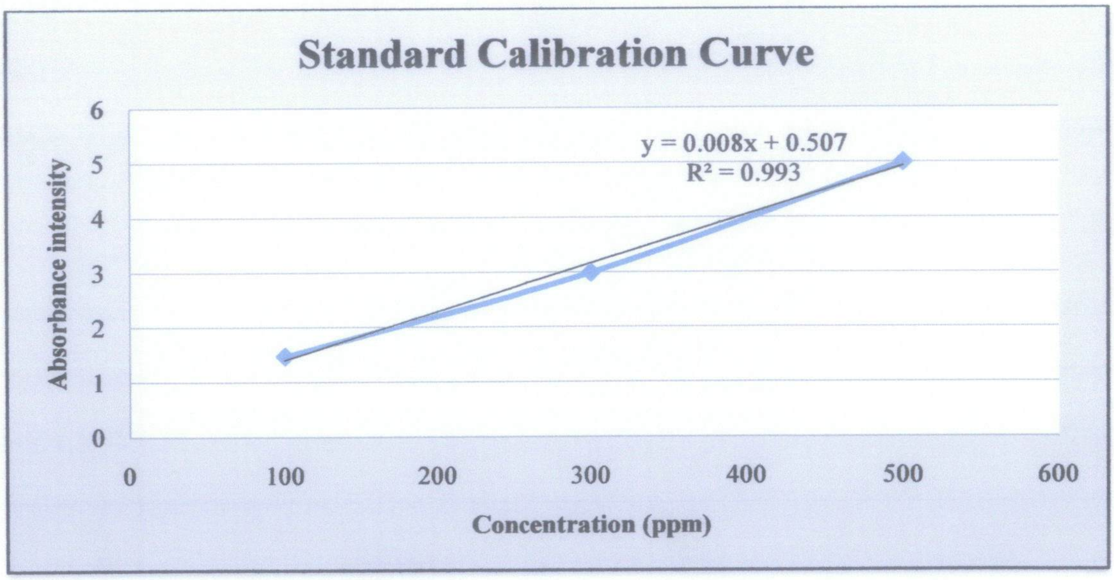


Figure 13: Standard calibration curve

Referring to the plot in Figure 11, the standard calibration curve gives a linear equation:

$$y = 0.0088x + 0.5073$$

The equation was plotted with a R-squared value equals to 0.9936. R-squared known as the coefficient of determination, is a statistical measure of how close the data are to the fitted regression line. In general, the higher the R-squared, the better the model fits the data. Given $R^2 = 0.9936$, it proves that the calibration performed was successful and valid. Hence, as long as the absorbance intensity is provided, it can be substituted into the equation above to find out the concentration of MEA presents in the sample extracted from the synthetic MEA wastewater. The adsorption test was conducted with sample mixture taken for readings at 10 minutes interval. The data collected from the ultraviolet-visible spectroscopy is tabulated in Table 12, Table 13, Table 14 and Table 15. Fresh sawdust and Sample A8 with comparatively low specific surface area, were selected to compare their adsorptive performance with Sample B9 and Sample F21 which possess high specific surface area.

In order to determine the rate of adsorption and measure the adsorption capacity possessed by each sample, the graph of MEA concentration against time was plotted as shown in Figure 12. According to the graph plotted in Figure 12, no sign of adsorption was taking place in the mixture added with fresh sawdust. The unchanged MEA concentration in the mixture proves that fresh sawdust without activation is not capable of adsorbing MEA at all. As for Sample A8, negative values on concentration indicate that the concentration went out of range. This error might be due to presence of impurities affecting the high sensitivity readings of ultraviolet-visible spectroscopy. Since Sample A8 is impregnated with highest amount of acid, the presence of impurities is most likely due to the residual acid remained on the sample which is not cleaned thoroughly. On the other hand, Sample B9 took 90 minutes to reach a near steady state and the concentration of MEA decreased as much as 79% of the initial concentration. Nonetheless, the result was surpassed when Sample F21 which has relatively high specific surface area and pore volume, exhibited higher rate of adsorption. It was found that the concentration of MEA in the synthetic wastewater reduced as much as 93% from its initial concentration. The performance demonstrated by both Sample F21 and Sample B9 confirms that activated carbon produced from sawdust has high capability of adsorbing MEA from aqueous solution and it is indeed a promising adsorbent in MEA wastewater treatment.

Table 12: Absorbance intensity and MEA concentration of mixture tested with activated carbon Sample B9

| Sample ID | Time (min) | Absorbance Intensity | Concentration (ppm) |
|---|---|---|---|
| 1 | 0 | 5.000 | 509.220 |
| 2 | 10 | 2.132 | 184.135 |
| 3 | 20 | 1.811 | 147.759 |
| 4 | 30 | 1.682 | 133.198 |
| 5 | 40 | 1.631 | 127.362 |
| 6 | 50 | 1.537 | 116.752 |
| 7 | 60 | 1.512 | 113.923 |
| 8 | 70 | 1.49 | 111.394 |
| 9 | 80 | 1.456 | 107.550 |
| 10 | 90 | 1.435 | 105.191 |
| 11 | 100 | 1.423 | 103.839 |

Table 13: Absorbance intensity and MEA concentration of mixture tested with activated carbon Sample F21

| Sample ID | Time (min) | Absorbance Intensity | Concentration (ppm) |
|---|---|---|---|
| 1 | 0 | 5.000 | 509.220 |
| 2 | 10 | 1.219 | 80.648 |
| 3 | 20 | 1.074 | 64.290 |
| 4 | 30 | 0.897 | 44.250 |
| 5 | 40 | 0.870 | 41.114 |
| 6 | 50 | 0.834 | 37.035 |
| 7 | 60 | 0.829 | 36.517 |
| 8 | 70 | 0.822 | 35.725 |
| 9 | 80 | 0.818 | 35.354 |
| 10 | 90 | 0.810 | 34.450 |
| 11 | 100 | 0.808 | 34.206 |

Table 14: Absorbance intensity and MEA concentration of mixture tested with activated carbon Sample A8

| Sample ID | Time (min) | Absorbance Intensity | Concentration (ppm) |
|---|---|---|---|
| 1 | 0 | 5.000 | 509.220 |
| 2 | 10 | 0.181 | -36.960 |
| 3 | 20 | 0.157 | -39.616 |

Table 15: Absorbance intensity and MEA concentration of mixture tested with fresh sawdust

| Sample ID | Time (min) | Absorbance Intensity | Concentration (ppm) |
|---|---|---|---|
| 1 | 0 | 5.000 | 509.220 |
| 2 | 10 | 5.000 | 509.220 |
| 3 | 20 | 5.000 | 509.220 |
| 4 | 30 | 5.000 | 509.220 |
| 5 | 40 | 5.000 | 509.220 |
| 6 | 50 | 5.000 | 509.220 |
| 7 | 60 | 5.000 | 509.220 |
| 8 | 70 | 5.000 | 509.220 |
| 9 | 80 | 5.000 | 509.220 |
| 10 | 90 | 5.000 | 509.220 |
| 11 | 100 | 5.000 | 509.220 |

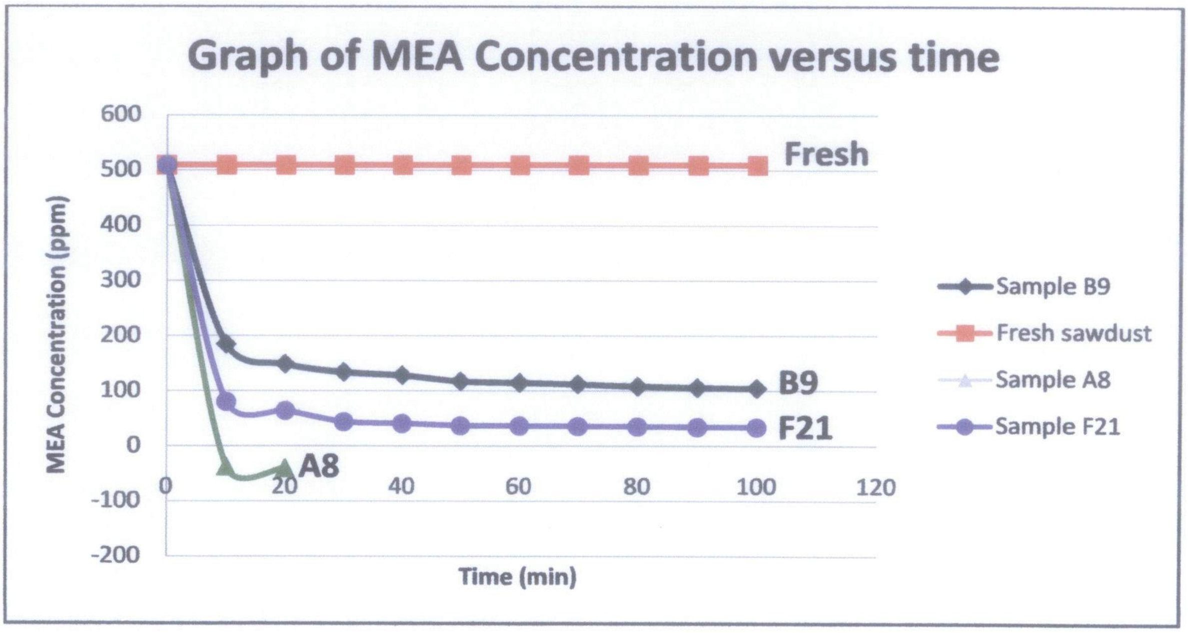


Figure 14: Graph of MEA concentration against time

# CHAPTER 5

# CONCLUSION AND RECOMMENDATIONS

## 5.1 Recommendations for Short-term

To ensure a good project's progression, project planning is of utmost importance. After mapping out the list of sample preparation, a total of 65 samples are to be prepared in order to cover all operating variables. With this much of samples pending for preparation and analysis, getting all the samples ready for characterization test within the specified timeframe is hardly possible. Thus, there is a need to cut down on the number of sample without leaving out assessment on any of the operating variables involved.

Reduction of samples is achievable through one-factor-at-a-time (OFAT) method. It is a method of designing experiments involving the testing of factors, or causes, one at a time instead of all simultaneously. In order to implement OFAT method, the design of experiments (DOE) can be set in such a way that only one variable is manipulating the experiment while the rest acting as constant variables. For example, in set A, samples are prepared under similar activation temperature and activation time of 400ºC and 30 minutes with impregnation ratio varies from 1:1, 1:2 to 1:3. In this case, activation temperature and activation time are the constant variables while impregnation ratio acting as the only manipulating variable. After all three samples have undergone characterizations, if the results obtained confirm that impregnation ratio of 1:1 produces better activated carbon in terms of surface area and pore volume, then impregnation ratio will be omitted as a variable to be assessed in the following sets of samples. In other words, impregnation ratio of 1:1 will be set fixed throughout the experiment since it is able to produce higher quality of activated carbon. Subsequently, the experimental work will continue to evaluate next variable in the similar way as described above, hence reducing the overall number of samples need to be prepared.

## 5.2 Future Recommendations for Long-term: Project Continuation and Expansion

Due to the short time frame given for this research, a detail study on the research could not be carried out. Nevertheless, there are certain areas for future improvements in this research. The suggested recommendations are as follows:

- **Soxhlet extraction technique for sample washing process**
    - Instead of simple washing method, soxhlet extraction technique can be employed to wash the residual chemical remained on the carbon samples after heat treatment. The technique places a specialised piece of glassware in-between a flask and a condenser. The refluxing solvent repeatedly washes the solid carbon samples extracting the residual chemical into the flask. Not only repetitive washing is achievable, the extent of chemical removed from the sample can be examined through checking the pH of the water condensed in the flask.

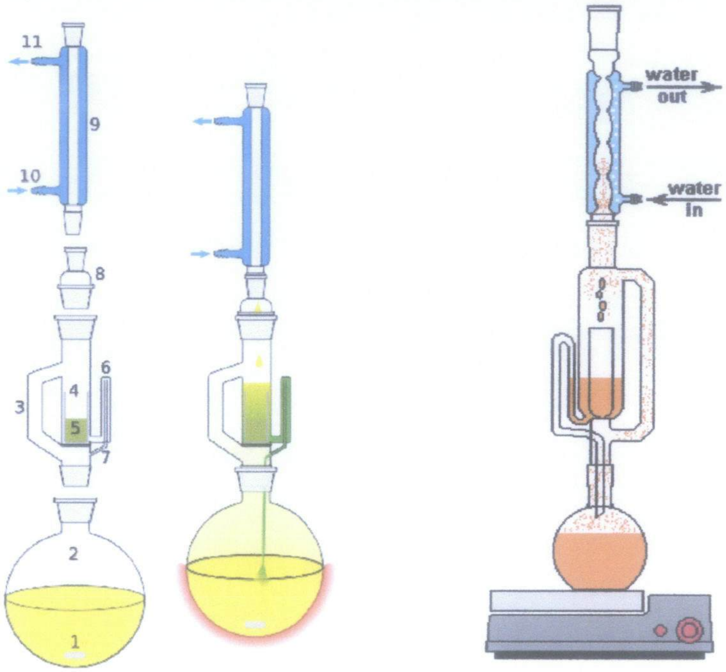


Figure 15: Schematic representation of soxhlet extractor setup

- **Types of raw material used in manufacturing activated carbon**
    - In the case of types of raw material used, different species of wood can be tested for workability. Looking at the fact that each material has its unique properties, activated carbon produced from different raw materials might exhibit different adsorbent qualities.

- **Chemical activation versus physical activation**
    - In the process of manufacturing activated carbon, there are two methods of activation, namely physical and chemical activation. Present study employs only chemical activation because of the lower temperature used and shorter time needed in activating the material. Although chemical activation seems to be preferred over physical activation, both the methods can be made into comparison because each has its pros and cons respectively. Unlike chemical activation, physical activation does not require the use of chemical reactants. Absence of chemical reactant itself can provide a number of benefits as it saves up the cost of reactant, eliminates the need of washing off the remaining reactant and avoids the environmental unfriendly properties of toxic reactant.

- **Batch or continuous mode of adsorption test**
    - As for the adsorption test, a more systematic approach can be introduced in conducting the experiment. The experimental setup could be in the form of batch mode or even continuous flow. Instead of manual sampling, the closed system can be installed with probes to detect the concentration of MEA and examine the rate of adsorption. With the equipment connected to a computerized system, readings can be taken at a shorter time of interval and data can be collected in a more efficient way. This would help to increase the reliability and accuracy of the results.

- **Desorption study for regeneration**
    - Desorption study can be conducted to regenerate the used activated carbon as a way to cut down on the frequency of replacing new batch activated carbon into the system.

## 5.3 Conclusion

The result of this study clearly demonstrated that activated carbons having high surface area and great distribution of microscopic pores can be prepared from sawdust by chemical activation with phosphoric acid. The optimal preparation process of activated carbon from sawdust was successfully achieved by using one-factor-at-a-time (OFAT) method. With an impregnation ratio of 1:1, activation temperature of 500°C and activation time of 60 minutes, activated carbon with highest specific surface area, $S_{BET}$ (1213.786 $m^2/g$), pore volume, $V_T$ (0.662 $cm^3/g$) and pore diameter, D (2.18 nm) can be produced. By judging on the characterization results, there is a high potential for sawdust to become promising adsorbent in treating MEA wastewater. The hypothesis was further verified when adsorption test was carried out using synthetic MEA wastewater. The significant reduction in MEA concentration indicates that this material is suitable to be used in the adsorption of MEA from industrial wastewater.

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