Adsorption of Lead from Aqueous Solution using Activated Carbon from Sawdust as Adsorbent.

by

Wan Muhamad Adib bin Wan Saberi

Dissertation submitted in partial fulfillment of

the requirements for the

Bachelor of Engineering (Hons)

(Chemical Engineering)

JANUARY 2014

Universiti Teknologi PETRONAS

Bandar Seri Iskandar

31750 Tronoh

Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

Adsorption of Lead from Aqueous Solution using Activated Carbon from Sawdust as Adsorbent

by

Wan Muhamad Adib bin Wan Saberi

A project dissertation submitted to the
Chemical Engineering Programme
Universiti Teknologi PETRONAS
in partial fulfillment of the requirement for the
BACHELOR OF ENGINEERING (Hons)
(CHEMICAL ENGINEERING)

Approved by,

(En. Azry Borhan)

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
JANUARY 2014

CERTIFICATION OF ORIGINALITY

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

Produced by,

…………………………………………

(Wan Muhamad Adib Bin Wan Saberi)

ABSTRACT

Activated carbon is a well known as porous material, with large specific surface area use for adsorption purposes. The preparation of activated carbon from agricultural by-products such rice-husk, yam peels, cassava peels, orange peels, to remove and recover metal ions namely lead, cadmium, zinc, selenium from the waste water is one of the most environmental friendly solutions and economical (Akissi, Adouby, Wandan, Yao, & Kotchi, 2010). Wood sawdust from Meranti was used to prepare activated carbon using potassium hydroxide (KOH) and phosphoric acid (H_3PO_4) as activating agent. From FESEM characterization, results showed that the sawdust activated by KOH exhibit fine smaller pores at 1000 times magnification which can be the mesopores. While the sawdust activated using H_3PO_4 has irregular surface with fewer pores. Thus, KOH promote the formation of pores inside activated carbon better than H_3PO_4. This is supported by the EDX spectroscopy that analyzed the carbon content after activation done using KOH is 78.48% while for H_3PO_4 is 69.47%. By using N_2 adsorption-desorption isotherm analysis, Sample E which is prepared at IR of 1:3 with KOH solution, activation temperature of 500°C and activation time of 30 minutes yields the highest value of S_{BET} (2.5613 m^2g^{-1}), total pore volume, V_T (0.005280 cm^3g^{-1}) and pore diameter, D (8.246 nm). Lead adsorption study also been done and it was found that the material is capable to removing up to 89.3% of lead in aqueous solution, suggesting that it can be effectively used as an adsorption material.

ACKNOWLEDGEMENT

I would like to express my highest gratitude and appreciation to all parties that have involved, whether directly or indirectly, in contributing for this final year project until its success. Throughout the whole schedule of the project, valuable knowledge and experience have been learned that will be a strong guidance for my future career.

First and foremost, I would like to thank Chemical Engineering Department and my supervisor for assisting and guiding me in selecting my FYP title. With their strong support, I have been able to select a new gap for a research area that is related to my background of study. I would like to dedicate a special thanks to my supervisor, En. Azry Borhan for his actions and supports in assisting me with ideas and knowledge for my FYP project schedules and experimental works. Not to forget, to all lab technologist that have supported me for the whole project period, by giving guidance in the basic part of the project.

Last but not least, many thanks to my family and friends, and all people that have been supporting me for all four years of experience in my degree, especially in Chemical Engineering Department. As for the support and encouragement from these people, I am able to perform my study and project to the best of my ability. Thank you and Allah may reward for all your kindness.

TABLE OF CONTENT

LIST OF FIGURES

LIST OF TABLES

CHAPTER 1

INTRODUCTION

1.1 Background Of Study

The project will cover about the preparation of low-cost adsorbent, activated carbon from Meranti wood sawdust to remove heavy metal, lead from aqueous solution by adsorption process. The purpose of the research is to find the optimal parameters to maximize the percentage adsorption of lead by varying the parameters during experiments. The wood sawdust was chemically activated first with two different activating agents; Potassium Hydroxide (KOH) and Phosphoric Acid (H_3PO_4) to find which activating agents will promote the pores formation inside activated carbon better.

There are 3 different variables will tested such as activation temperature, time and impregnation ratio (IR). The best preparation condition for adsorbents will produced the activated carbons with the highest values of S_{BET}, specific surface area and average pore diameter. All the samples will be characterized by nitrogen adsorption-desorption isotherms measured in Micrometrics ASAP 2020 and Field Emission Scanning Electron Microscope (FESEM). After get the result, the project will continue by mass production of sawdust adsorbent. Finally the last stage is to test the adsorbents with lead aqueous solution for evaluation.

1.2 Problem Statement

Heavy metal pollution occurs in many industrial wastewaters such as those in manufacturing process for example, storage battery, printing, paints, fuels, photographic materials and glass production industry. The main threats to human health from heavy metals are associated with exposure to lead, cadmium, mercury and arsenic (Jarup, 2003). The increase of awareness of hazard of heavy metals gave a lot concern for researches to come out with methods to treat these wastewaters.

The most commonly used methods for removing metals are chemical or electrochemical precipitation, both of which pose significant problems in terms of disposal of the precipitated waste and ion-exchanged treatments, which is not economical (Argun, Dursun, Ozdemir, & Karatas, 2007). Hence, attention has been devoted to the study of removal of heavy metal ions from solution by adsorption using agricultural materials for example sawdust as it is by products produced large quantities at sawmills, economical, and environmental friendly.

1.3 Objectives And Scope Of Study

1.3.1 Objective

The aim of the project is to find the optimal parameters in preparation of the sawdust as the adsorbents and maximize the percentage adsorption of lead. In addition, the characterization of produced activated carbon also is analyzed using Field-emission Scanning Electron Microscope (FESEM) and Micrometrics ASAP 2020. The parameters investigated for the adsorbents preparation are types of activating agents, activation temperature, activation time and impregnation ratio (IR).

1.3.2 Scope of Study

The project is focusing on the following scope of study:

I. The modification of sawdust using KOH and H_3PO_4 to enhance the adsorption capacity.
II. The activation of sawdust using Fixed Bed Activation unit at activation temperature 500^oC and 600^oC.
III. The characterization of activated carbon using Field-emission Scanning Electron Microscope (FESEM) and Micrometrics ASAP 2020
IV. The adsorption test by mixing a specified amount of activated carbon with 50 ml of 50 ppm concentration lead aqueous solution synthesized from lead nitrate chemicals over period of time.
V. Batch experiments in laboratory scale are carried out to obtain all data.

CHAPTER 2

LITERATURE REVIEW

2.1 Lead

In cooperation with the U.S. Environmental Protection Agency, the Agency for Toxic Substances and Disease Registry (ATSDR) has compiled a Priority List for 2011 called the ASTDR 2011 Substance Priority List. From the list, arsenic is the most hazardous heavy metal followed by the lead on second rank. (ASTDR, 2011).

Lead, one of the most toxic heavy metals, is attracting wide attention of environmentalist due to its acute and chronic toxic effects in animal and human health. The symptoms of acute lead poisoning are headache, irritability, abdominal pain and various symptoms related to the nervous system. Long-term lead exposure may also give rise to kidney damage (Jarup, 2003). Exposure to lead over a lifetime may also increase the risk of developing cancer. The International Agency for Research on Cancer (IARC) has recently classified lead as probably carcinogenic to humans.

In Canada, the Guidelines for Canadian Drinking Water Quality limit the lead content of drinking water to a maximum acceptable concentration (MAC) of 0.010 mg/L in drinking water (10 parts per billion), measured at the tap. The guideline for drinking water was established to be protective of the most vulnerable population, children. Consuming water over the course of a lifetime (i.e., 70 years) with lead levels at or near the guideline value is considered to be protective of human health.

Lead is widely used in many important manufacturing processes such as storage battery, manufacturing, printing, pigments, fuels, photographic materials and explosive manufacturing. Therefore, the appropriate techniques are important to process wastewater containing of metal ions before discharging it to protect human and environment health.

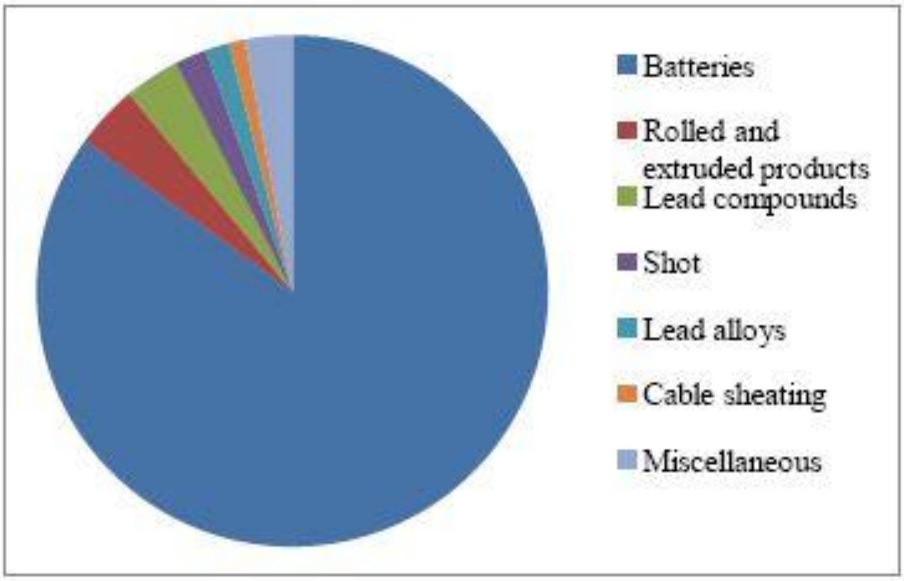


Fig 1: Lead Usage in Industries

From the Figure 1, lead is enormously used in batteries manufactured industry

2.2 Lead Removal Methods

Methods for removing lead metal ions from aqueous solution mainly consist of physical, chemical and biological technologies. Conventional methods for removing lead metal ions from aqueous solution have been suggested, such as chemical precipitation, filtration, ion exchange, electrochemical treatment, membrane technologies, adsorption on activated carbon, evaporation etc.

Chemical precipitation methods are trustworthy to remove lead metal ions, however it require large settling tanks for the precipitation of voluminous alkaline sludge and need subsequent treatment. However, chemical precipitation and electrochemical treatment are ineffective, especially when lead metal ion concentration in aqueous solution is among 1 to 100 mg/L. While, ion exchange, membrane technologies and activated carbon adsorption process are extremely expensive when treating large amount of water and wastewater containing lead metal in low concentration, they cannot be used at large scale.

The adsorption process is favorable compare to other methods to treat industrial waste effluents because it is low cost, availability of adsorbents, profitability, ease of operation and efficient to compare with conventional methods. To apply adsorption techniques, suitable adsorbents must be chosen. Numerous approaches have been studied for the development of low-cost adsorbents. Many researches showed effective adsorption of heavy metals using agricultural products and by-products such as peanut skins, wool, tea leaves, pecan shell-based granular activated carbons, modified rice husk, rice husk activated carbon and maize husk. Hence, adsorption process has been chosen in this project as it is simpler and can be conducted in small scale experiment.

2.3 Activated Carbons

Activated carbon has the unique ability to absorb a wide range of compounds from both the liquid and gas phase. This adsorptive feature is responsible for removing contaminants from water and other substances where the adsorbent material is added.

Activated Carbon features a highly crystalline form with a wide surface area and extensively developed internal pore structure. Surface area is used as a primary indicator of the activity level, based on the principle that the greater the surface area, the higher the number of adsorptive sites available. Application of high temperatures in the presence of a controlled flow of steam used as the oxidizing medium is what “activates” carbon and produces pore structure. Pore size distribution defines the performance of the material; micropores, mesopores and macropores. For the adsorption, adsorbent with micropores structure is more preferred.

Different types of Activated Carbons can be produced with specific characteristics depending upon the raw material and activation technique used in their production.

Table 1: Activation Techniques

Steam activation	**Chemical activation**
• Activation is carried out at high temperatures of 800 - 1000°C in the presence of steam.	• The raw material is impregnated with a strong dehydrating agent, typically phosphoric acid (H3PO4).
• Activated carbons produced by steam activation generally exhibit a 'fine' pore structure, ideal for the adsorption of compounds from both the liquid and vapor phase.	• Activated carbons produced by chemical activation generally exhibit a very 'open' pore structure, ideal for the adsorption of large molecules

2.4 Agricultural Adsorbent

Agricultural by-products such as rice-husk, yam peels, cassava peels, orange peels, banana peels, corn cobs, sawdust, potato peels among others have been used by researches as adsorbents to remove and recover metal ions namely lead, cadmium, zinc, selenium from the waste water environments. This method also called as bio-sorption technique (Okoro & Okoro, 2011).These agricultural byproducts are cheap, eco-friendly and abundant for use in the metal-ions adsorption. The main mechanism involved in the sorption of biomass is ion exchange. There was a strong ionic balance between adsorbed (H^+ and M^+) and released ions (Ca^+, Mg^{2+}, K^+ …) from the biomass (Akissi, Adouby, Wandan, Yao, & Kotchi, 2010).

Malaysia is one of the major wood timber suppliers worldwide, therefore, producing huge amount of sawdust as the byproducts of the process. Thus, the availability of sawdust can be used for other good purposes. It is suggested one of the most practical way is to convert these residue by converting it into activated carbon adsorbents. In this project, Meranti wood sawdust has been chosen as the raw material for chemical activation into activated carbon.

2.5 Sawdust As An Adsorbent

The research task concerning the use of sawdust or byproducts of the agriculture for the purification of wastewater are numerous (Akissi et al 2010, Ghani et al 2007, Adouby et al 2007, Argun et al 2007, Baral et al 2006, Ansari et al 2006). Some of them showed the performance of these adsorbents for the recovery of metal ions in aqueous solution.

(Ghani, Hefny, & El-Chagaby, 2007) investigated the influence of pH, contact time, metal ions concentration, adsorbent concentration on the selectivity and sensitivity of the heavy metal removal process. From the result, he found that the removal of lead from the synthetically prepared wastewater increase with increasing contact time and attains equilibrium at about 90-120 min. For the pH condition, lead removal recorded its minimum values at pH 2.5 and maximum at pH 6.5. This is supported by another research conducted by (Baral, Das, & Rath, 2006)says that the percentage adsorption is reaching maximum at pH values in range 4.5-6.

The amount of adsorbents use also gives effect on the adsorption percentage. The dependence of lead sorption on adsorbents dose was studied by varying the amount of adsorbents from 0.25 to 2g, while keeping other parameters (pH, concentration, and contact time constant). The result show that the percent removal of lead increases with increasing adsorbents doses (Ghani et al 2007, Baral et al 2007, Ansari et al 2006). This may be attributed to the increase of the sites of adsorption.

Next, the size of the adsorbents also gives effect on the percent of lead removal in solution. (Adouby, Akissi, Wandan, & Yao, 2007) studied the effect of particle sizes on the removal of lead ion by sawdust. Two particle sizes, less than 0.5 mm (sawdust A) and ranging between 0.5 and 1mm (sawdust B) have been directly used without any chemical modification, as an adsorbent while keeping other parameters constant. Thus with size < 0.5mm, the maximum rates 63.99% were obtained while for the size >0.5 mm the maximum rates is 44.31% for the removal of lead. Thus, the removals of lead ion by the sawdust increases while the particle size of the adsorbent decreases.

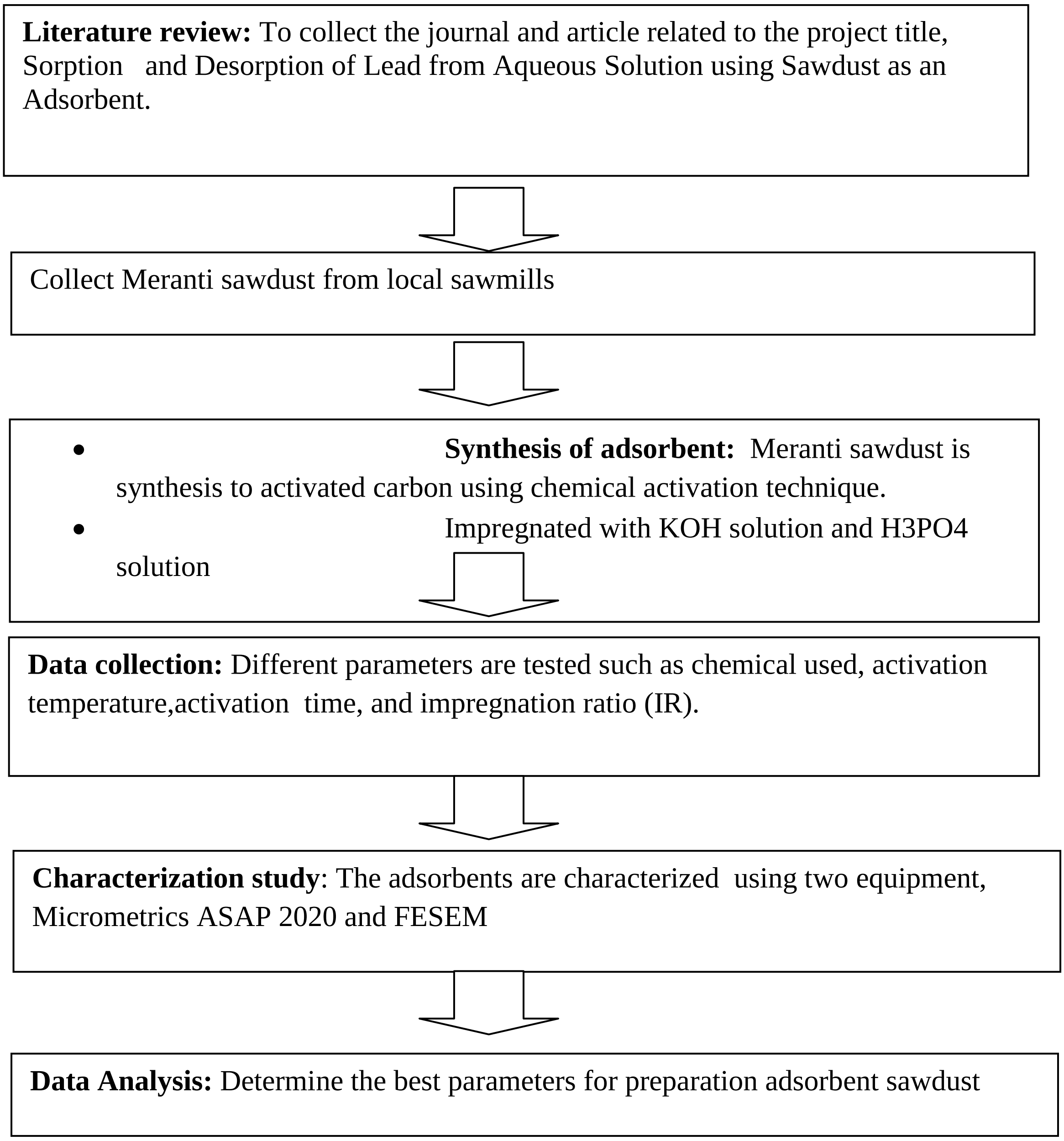
The initial lead concentration in aqueous solution also gives effect on the adsorption process. (Ghani et., al 2007) and (Saroj et., al 2007) investigated that the increase in initial concentration of lead (II) from 5 to 50ppm decreased its percentage of adsorption. This may be resulted; higher initial adsorbate concentrations will have limit space for the adsorption sites with adsorbents. However, the result is contradicted with another research conducted on previous year before. (Ansari & Raofie, 2006) indicate that the adsorption of lead ion by sawdust increases with increasing the initial concentration of metal ion.

CHAPTER 3

METHODOLOGY

3.1 Flow Chart of Project Activities

The list of work of the entire project need to be carried out thus a proper activities planning can be made. Figure below shows the process flows of works need to be implemented in this project.



Literature review: To collect the journal and article related to the project title, Sorption and Desorption of Lead from Aqueous Solution using Sawdust as an Adsorbent.

Collect Meranti sawdust from local sawmills

- **Synthesis of adsorbent:** Meranti sawdust is synthesis to activated carbon using chemical activation technique.
- Impregnated with KOH solution and H3PO4 solution

Data collection: Different parameters are tested such as chemical used, activation temperature,activation time, and impregnation ratio (IR).

Characterization study: The adsorbents are characterized using two equipment, Micrometrics ASAP 2020 and FESEM

Data Analysis: Determine the best parameters for preparation adsorbent sawdust

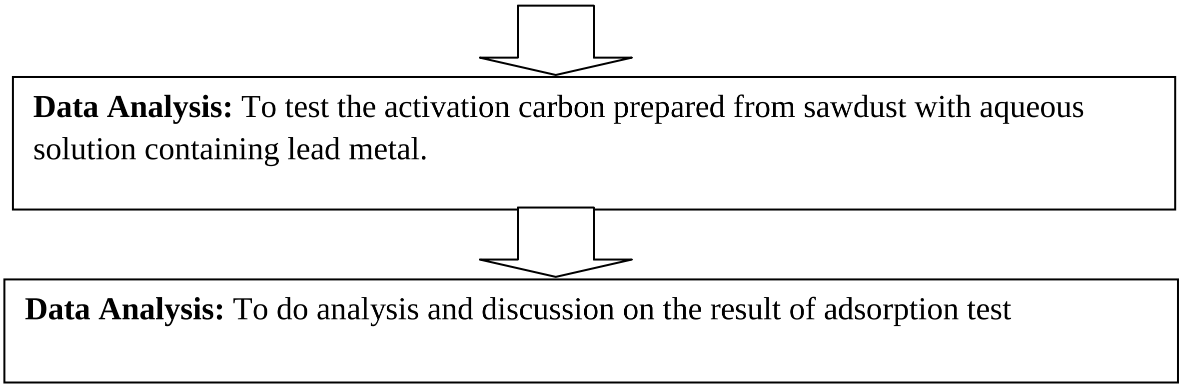


Fig. 2: Flow chart of project

3.2 Experimental Procedure

The synthesis procedure is outlined as follows:

1. The Meranti sawdust collected from a local sawmills washed with distilled water and dried under sunlight until almost all the moisture evaporated.
2. The impregnation solution was prepared by dissolving specific amount of KOH pellets in deionised water. The impregnation ratio (IR) is determined by using Eq (1):

   $$IR = \frac{\text{dry mass KOH}}{\text{dry mass sawdust}}$$
3. The temperature of the impregnation solutions was allowed to stabilize at 23°C before the dried sawdust is added to the solutions.
4. The impregnation process is left for overnight to allow chemical fully absorbed.
5. The treated sawdust then is carbonized in a Fixed Bed Activation Unit at different operating activation temperatures 500°C , 600°C and activation time 30min and 60 min.

6. The activated carbon produced is left to sit in ambient temperature and washed with distilled water to remove remaining KOH.
7. The activated carbon is dried in an oven at 70°C overnight and stored in airtight container.
8. The steps 2-8 are repeated using different impregnation chemicals phosphoric acid.

Sample characterization

To determine the best operating parameter for preparing activated carbon from sawdust, several steps characterization were carried out.

FESEM. This equipment allows investigating molecular surface structure near-atomic resolution. With ultra-high resolution imaging, it can fulfill the requirements of analyzing up to nano scale surface structure and morphology of solids.

MICROMETRICS ASAP 2020. This equipment specialized to determine the specific surface are, pore size and pore volume of the activated carbon produced. This characterization is determined by using nitrogen adsorption-desorption isotherms. Here, the nitrogen gas is used as the adsorbate that is set to flow at 200°C for 2 hours.

Lead adsorption study

1. Batch adsorption experiments were performed at room temperature 30°C in 100 mL beaker flask.
2. Accurately weighed amounts (0.4 g) of adsorbent (sawdust) were agitated at 300 rpm with 50 mL of (50ppm) lead solution for 20, 30 and 60 minutes.
3. At the end of the equilibrium period, sawdust was separated by filter paper.
4. The concentrations of lead adsorbed were obtained from the difference between the initial and the final concentration of the metal in filtrate.
5. The amount of lead adsorbed in mg/g at a given time was computed by using the following equation:

$$q_t = \frac{(C_o - C_t)V}{m}$$

   Co metal concentrations initially
   Ct are the metal concentrations (in mg/L) and at a given time
   V is the volume of the solutions in L
   m is the mass of adsorbent in g

6. The treated lead samples were sent to AAS analyzer to determine its concentration.

3.3 Tools, Equipments and Materials

These are the chemicals/materials that will be use in this project:

i) Sawdust
ii) Potassium Hydroxide, KOH
iii) Phosphoric Acid, H_3PO_4
iv) Lead nitrate, $Pb(NO_3)_2$
v) Distilled water

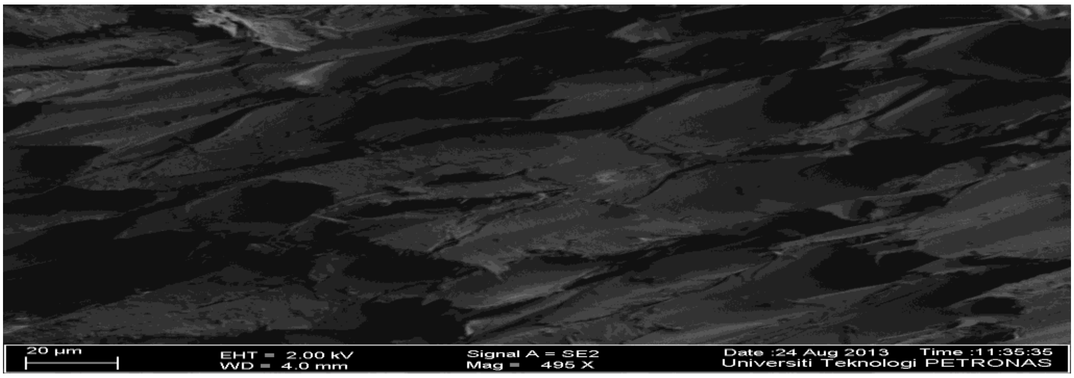
These are the equipment or tools that will be use in this project:

i) Field Emission Scanning Electron Microscope, FESEM
ii) Micrometrics ASAP 2020
iii) Atomic Absorption Spectroscopy analyzer, AAS
iv) Fixed Bed Activation Unit
v) Digital mass balance
vi) 50 ml measuring cylinders
vii) Magnetic stirrer, 100 ml beakers, 1L filter funnel, filter paper.

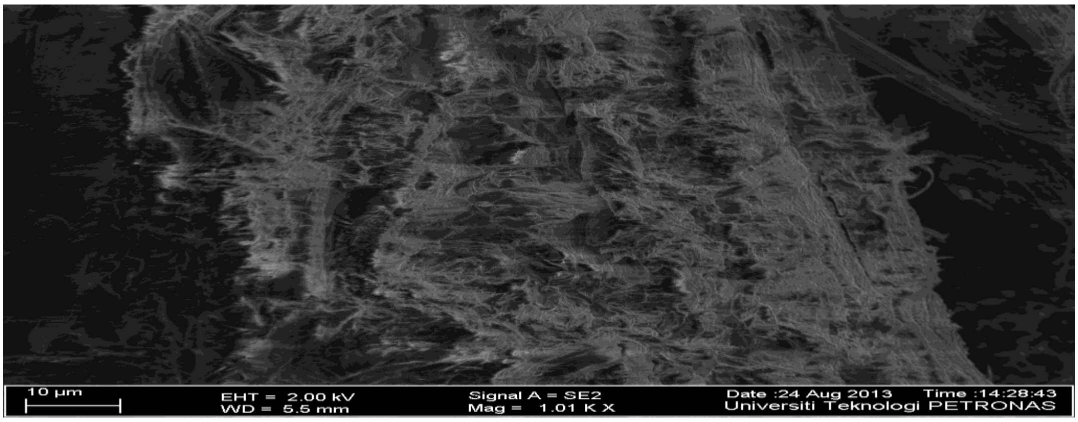
CHAPTER 4

RESULT AND DISCUSSION

4.1 Morphology



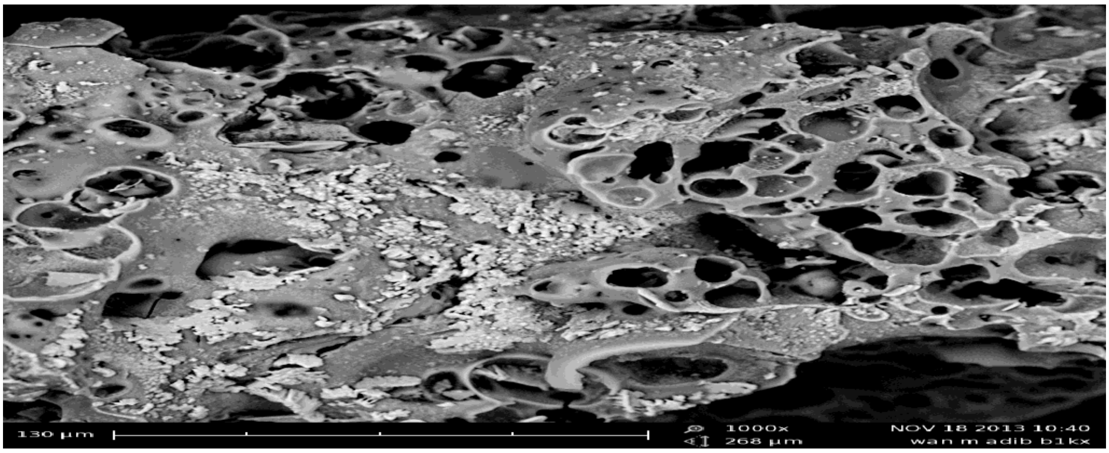
(a) fresh sawdust at 495x magnification



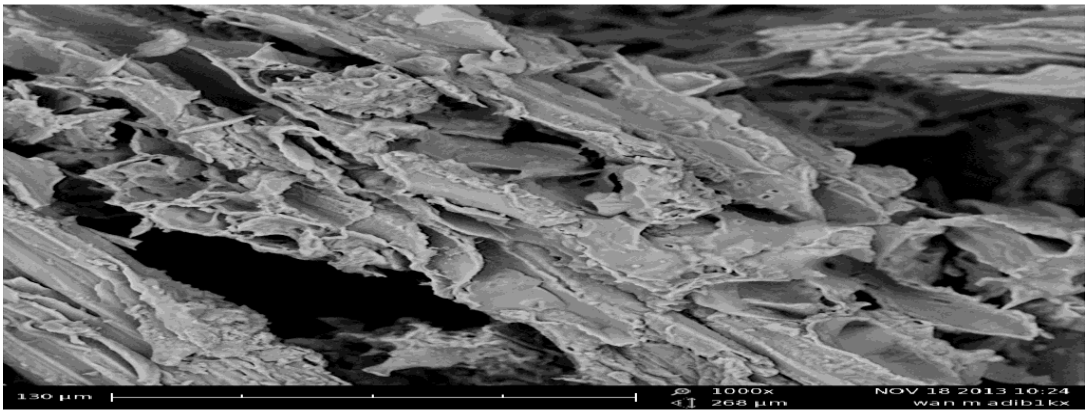
(b) fresh sawdust at 1000x magnification

Fig.3: FESEM image before chemical activation

The microstructure of the raw sawdust before chemical activation is as in Figure 3 (a-b). From figures above, it shows the structural image of fresh sawdust at 495 times and 1000 times magnification has not yet develop any pore or undergo any reaction that resulted in none pores seen. However, the image clearly showed that the sawdust before activation has canal structure, which is one important feature for preparing activated carbon. The canal structure that exists in the raw sawdust will enable the sawdust to fully adsorb the chemical reagent that will activate the carbon content inside it.



sample C: impregnated with KOH



sample D: impregnated with H_3PO_4

Fig.4, FESEM image after chemical activation

The microstructure of the raw sawdust after chemical activation is as in Fig.4: (c-d). FESEM image for sample C shows the existence of pores after being activated with potassium hydroxide at ratio 1:1, activation temperature 500^oC for 30 minutes. At 1000 times magnification, we can see activated carbon fibers having different pore size distribution which can be mesopores were formed. While for Sample D, the sawdust was activated with H_3PO_4 at ratio 1:1, activation temperature 500^oC for 30 minutes have irregular surface structure and fewer pores. Thus, KOH activating agent promotes better pores structure compared to H_3PO_4 activating agent.

4.2 EDX Spectroscopy

FESEM equipment that is used to investigate molecular surface structure of the activated carbon is also used in detecting the element compositions in samples. Table 2 shows the comparison of composition element for the sawdust that activated by two different activation agent while keeping other variables same;

Table 2: Comparison of elemental composition using H3PO4 and KOH activation agent.

Chemical	H_3PO_4		**KOH**		
Elements	Weight %	Atomic %	**Elements**	Weight %	Atomic %
Carbon, C	69.47	80.16	**Carbon, C**	78.48	84.17
Oxygen, O	14.74	12.77	**Oxygen, O**	18.37	14.79
Phosphoric, P	15.79	7.06	**Potassium, K**	3.15	1.04
Total	100		**Total**	100	

Thorough investigation of the literature dealing with carbon in wood, (Wenzl, 1970) stated that all species had similar elemental composition; absolutely dry wood of any species containing about 50% carbon. From table 2, whereas after activation regardless of activation agent, it shows carbon content inside the sawdust is increased. Thus chemical activation is proved to increase carbon percentage in wood. Carbon content is detected to be highest at 78.48% when activated using KOH, while for activation using H_3PO_4 it is recorded 69.47%. So, we deduce that KOH is a better activation agent for activated carbon.

4.3 Surface Area Analyzer And Porosimetry System (SAP)

Figure 3 shows the nitrogen adsorption-desorption isotherm of fresh sawdust. The isotherm is plotted based on the amount of nitrogen gas adsorbed versus the relative pressure P/Po (P=absolute pressure, Po=saturation pressure). From the figures, it shows the Type III of isotherm curve which indicate the presence of mesopores within in range from1 to 25nm. This is further proved by the result obtained from the analysis of Micrometrics ASAP 2020.

Sample	Characteristic
Fresh sawdust	• BET Surface Area: 809.82m^2/g • Pore Volume: 0.651cm^3/g • Pore Size: 3.2 nm

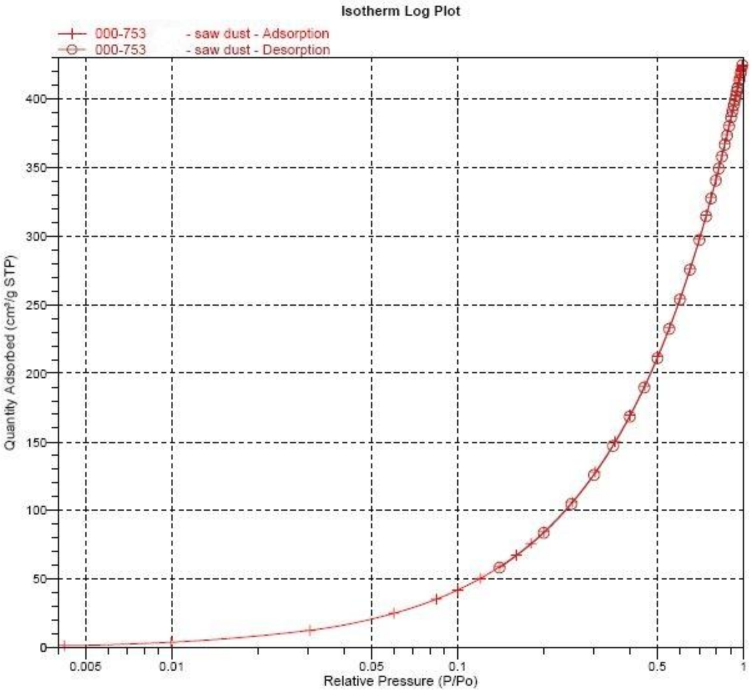


Figure 5: N_2 adsorption desorption isotherm plot

Table 3: Preparation condition and results of 250µm sawdust activated carbon

Sample	**IR (KOH)**	**Act. temp (°C)**	**Act. time (min)**	**Specific surface area, S_{BET} (m^2g^{-1})**	**Total pore volume, V_T (cm3g-1)**	**Average pore diameter, D (nm)**
A	1:1	500	30	1.0956	0.002626	8.409
B	1:1	500	60	0.8825	0.001810	1.296
C	1:1	600	30	2.5583	0.001814	2.835
D	1:2	500	30	1.0049	0.001445	5.753
E	1:3	500	30	2.5613	0.005280	8.246
Sample	**IR (H_3PO_4)**	**Act. temp (°C)**	**Act. time (min)**	**Specific surface area, S_{BET} (m^2g^{-1})**	**Total pore volume, V_T (cm^3g-1)**	**Average pore diameter, D (nm)**
F	1:1	500	30	1.1256	0.001643	5.836
G	1:2	500	30	0.6179	0.000010	1.979

Table 3 above; shows the preparation condition and analysis results of 250µm sawdust activated carbon using Micrometrics ASAP 2020. Two different chemicals have been used for chemical activation sawdust which is KOH and H_3PO_4. Other chemicals, which frequently used are K_2CO_3 and NaOH (Hayashi, Horikawa, Muroyama, & Gomes, 2002). Result showed that Sample E which is prepared at IR of 1:3, activation temperature of 500°C and activation time of 30 minutes yields the highest value of S_{BET} (2.5613 m^2g^{-1}) , total pore volume, V_T (0.005280 cm^3g^{-1}) and pore diameter, D (8.246 nm).

The surface area of activated carbon increases with increasing impregnation ratio from 1:1 to 1:3 and decreased slightly for ratios 1:2 (Adinata, Wan Daud, & Aroua, 2007) Thus, the impregnation ratios also play an important role for the surface area of activated carbon. The surface area of activated carbon is related to the pore development that occurs during intercalation of potassium into the carbon structure during activation period. However, higher impregnation ratio also may result to decrease yield and density of activated carbon. When higher impregnation was used, the weight losses were due to the increasing release of volatile products as result of intensifying dehydration and elimination reactions (Evans, Halliop, & MacDonald, 1999). The excessive KOH molecules also may decompose into moisture during degassing period for BET analysis, which can results inaccurate data. This theory is supported by the comparisons of Sample D that have relatively small specific surface area compare to Sample A.

Sample A, B, C which is prepared at IR of 1:1 are also analyzed to find the effect of controlling parameters that is activation temperature and activation time. The result showed that the specific surface areas increased with increase in activation temperature from 500^{o}C to 600^{o}C. This carbonization temperature increased the C-KOH reaction rate, resulting in increasing "burn-off" (Adinata, Wan Daud, & Aroua, 2007) This theory is supported by the comparison of sample C and A. However, the specific surface areas decreased with increase in the activation time from 30 to 60 minutes. This is probably due to the excessive heat energy that was given at longer period of time, causes in knocking and breaking of some porous wall.

A comparison also been done to compare which activation agent is good for chemical activation. From the result, Sample A sawdust activated by KOH has higher total pore volume and average pore diameter compared to Sample F which is activated by H_3PO_4 while maintaining same controlling parameters. Thus, KOH generates better pores formation compared to H_3PO_4 which is previously proved from FESEM results before. All samples that have been analyzed showing the pore diameter that ranges from 1-9 nm, which clearly indicates that, the pores are mesopores. This is based from IUPAC, which classified that the pores ranges are macro (>59 nm), meso (50- nm), and micro (<2 nm). For lead adsorption test comparison, two promising wood sawdust activated carbon samples (E and G) along with sample fresh sawdust were chosen for further analysis.

4.4 Adsorption Lead Test

Adsorption is the process whereby the molecules of gases or liquids or the solutes in solutions get adhered to the surface of the solids. In adsorption process two substances are involved. One is the solid or liquid on which adsorption occurs to the surface and it is called adsorbent. The second is the adsorbate, which is the gas or liquid or the solute from a solution which gets adsorbed on the surface.

Adsorbate + Adsorbent ----------> Adsorption

Lead + Activated carbon

The studies on adsorption of lead by the selected activated carbon samples were conducted using lead solution synthesized from lead nitrate chemical. Three different samples were used to show the comparison for lead adsorption which is sample E, having the highest value specific surface area, pore volume and size along sample G, having the lowest pore volume and size; and also fresh saw dust. In order to measure adsorption capacity, we used Atomic absorption spectroscopy (AAS) technique to determine the concentration of lead ion in tested samples.

First of all, a calibration curve was constructed using 5 standard solutions with concentrations of 20ppm, 30ppm, 40ppm, 50ppm and 80ppm. Table 4 below shows, absorbance intensity for each of the standard solutions.

Table 4: Absorbance intensity of standard solutions

SAMPLE ID	TYPE	ABSORBANCE INTENSITY	CONCENTRATION (PPM)
1	Standard	0.142	20
2	Standard	0.245	30
3	Standard	0.283	40
4	Standard	0.360	50
5	Standard	0.550	80

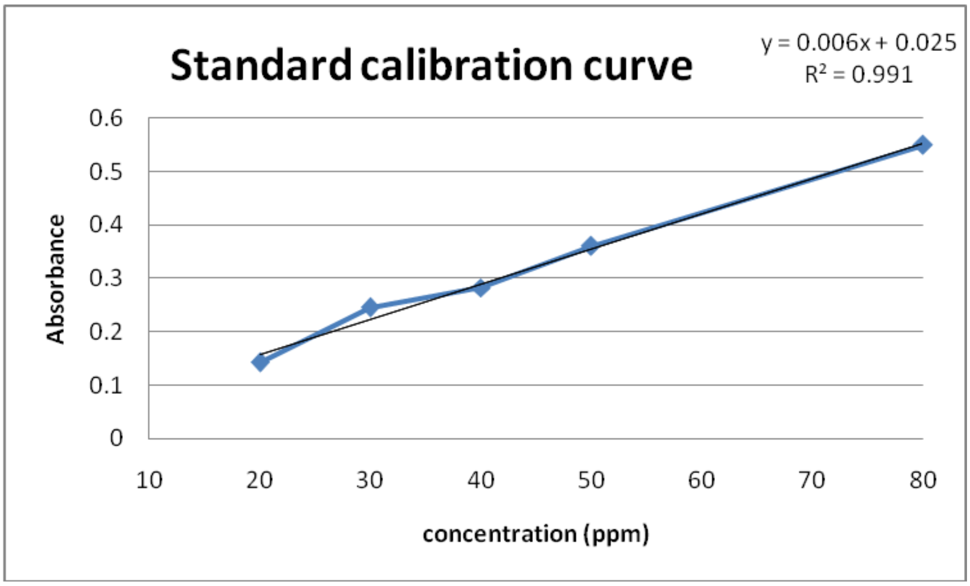


Figure 6: Standard calibration curve of lead

The adsorption test was conducted for 20, 30, 60 and 70 minutes. The treated lead solution sample was sent to AAS to determine the concentration of lead ion samples. Thus, to analyze the feasibility of the activated carbon in adsorption test; a graph of lead concentration versus time is plotted (Figure 7).

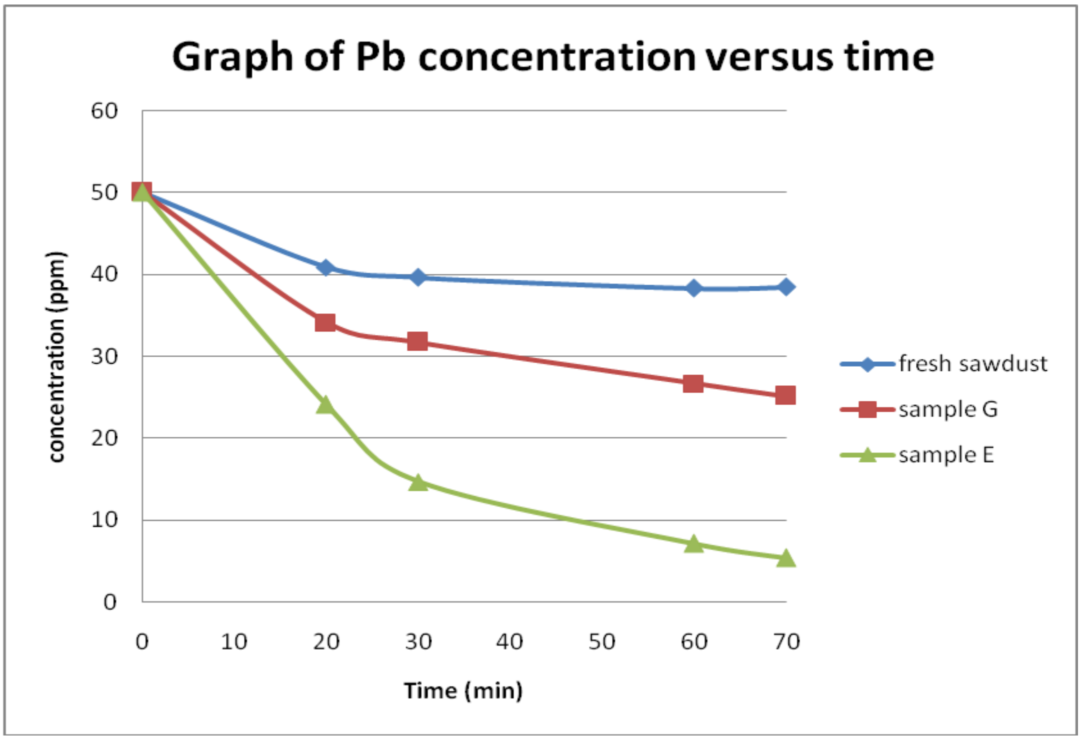


Figure 7: Graph of Pb concentration versus time

Figure 7, shows the plot of lead concentration using the best sample E, poor sample G and fresh sawdust sample. Sample E which is prepared at IR of 1:3 with KOH solution, activation temperature of 500^{o}C and activation time of 30 minutes yields the highest value of S_{BET} (2.5613 m^2g^{-1}), total pore volume, V_T (0.005280 cm^3g^{-1}) and pore diameter, D (8.246 nm). From the graph above, it was found that the initial Pb concentration is decrease from 50ppm up to 5.347ppm when it is treated using sample E. Thus, activated carbon sample E is capable to reduce the initial lead concentration up to 89.3% with lead uptake capacity 5.58mg/g.

While for lead solution tested using sample G, the final lead concentration is reduce to 49.7% of its initial concentration. Since, it has the lowest value specific surface area and pore therefore, limited pore volume are available for adsorption of lead to take place. Last but not least, for fresh sawdust the lead concentration is decrease to 18.24% of its initial concentration which is not feasible for lead adsorption purposes. As the conclusion, the best parameters for activated carbon from Meranti wood sawdust is by impregnated it with potassium hydroxide at ratio 1:3, activation temperature 500^{o}C for 30 min.

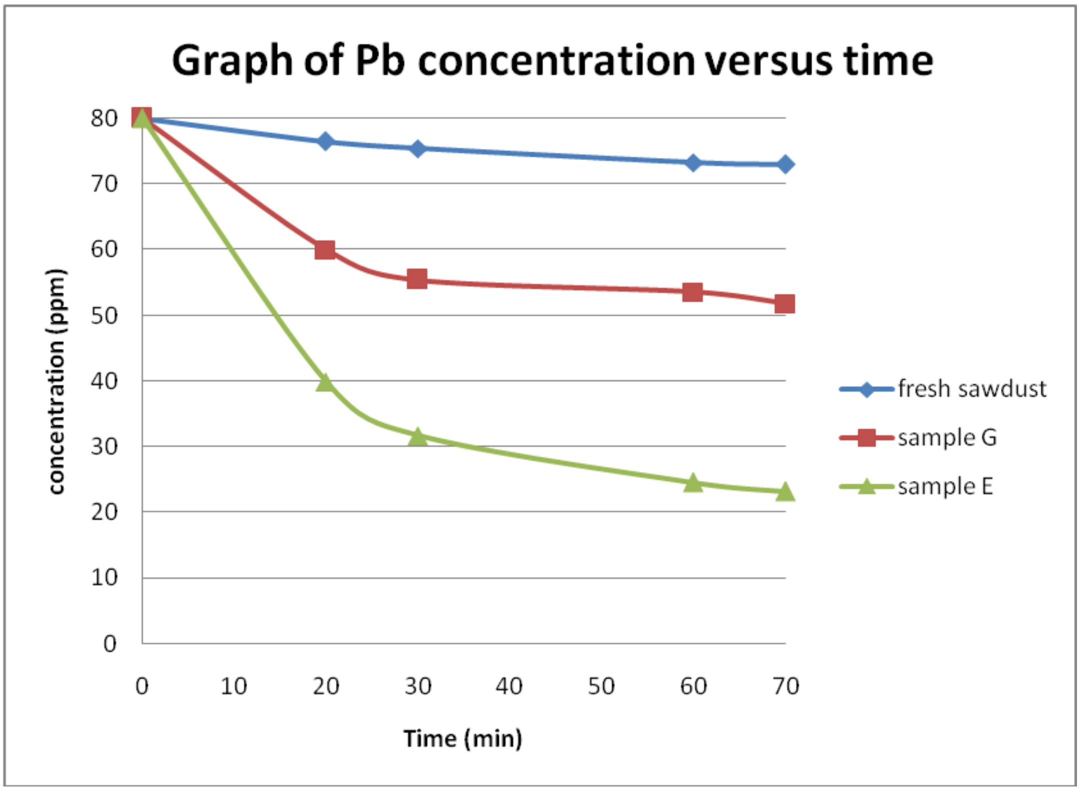


Figure 8: Graph of Pb concentration versus time

Figure 8, shows the plot of lead concentration at 80ppm using the best sample E, poor sample G and also fresh sawdust sample. From the above graph, the analysis of percentage adsorption with initial lead adsorbate concentration was studied at varying contact time. For sample E, the Pb concentration is gradually decreased and reaches equilibrium after 70 minute. The final Pb concentration is reduced to 71.06% of its initial concentration with lead uptake capacity 7.1mg/g. Then again, for lead sample tested using sample G, the final Pb concentration is reduced to 35.78% of its initial concentration.

Next for fresh sample sawdust, the final lead concentration is decreased to 8.73% of its initial concentration. By comparing the result from Figure 7 and Figure 8, it was found that the percentage adsorption decreased with increase in initial Pb concentration. However, lead uptake capacity is increased with increase in initial concentration which may be due to the availability of more number of Pb ions in aqueous solution for sorption.

Adsorption isotherms

The adsoption data of the Pb(II) metal ions by activated carbon Sample E sawdust also has been analyzed with Langmuir models.

Langmuir isotherm

The linear Langmuir equation may be described as:

$$\frac{Ce}{qe} = \frac{1}{qm.b} + \frac{Ce}{qm}$$

Where Ce is the Pb equilibrium concentration (mg/l),
qe is the amount lead adsorbed at equilibrium (mg/g),
qm and b are treated as empirical constant.

Table 5: The adsorption data for isotherm model.

SAMPLE	CONC. Ce	qe (mg/g)	Ce/qe (g/L)
1	24.154	3.23	7.47
2	14.707	4.41	3.33
3	7.153	5.35	1.38
4	5.347	5.58	0.958

Using the data from Table 5, the linear plots of Ce/qe versus Ce show that the adsorption of lead follows the Linear Langmuir isotherm model (Figure 9). qm and b were determined from the slope and intercept of the plot; there are equal to 3.521 mg/g and 2.088 l/mg respectively.

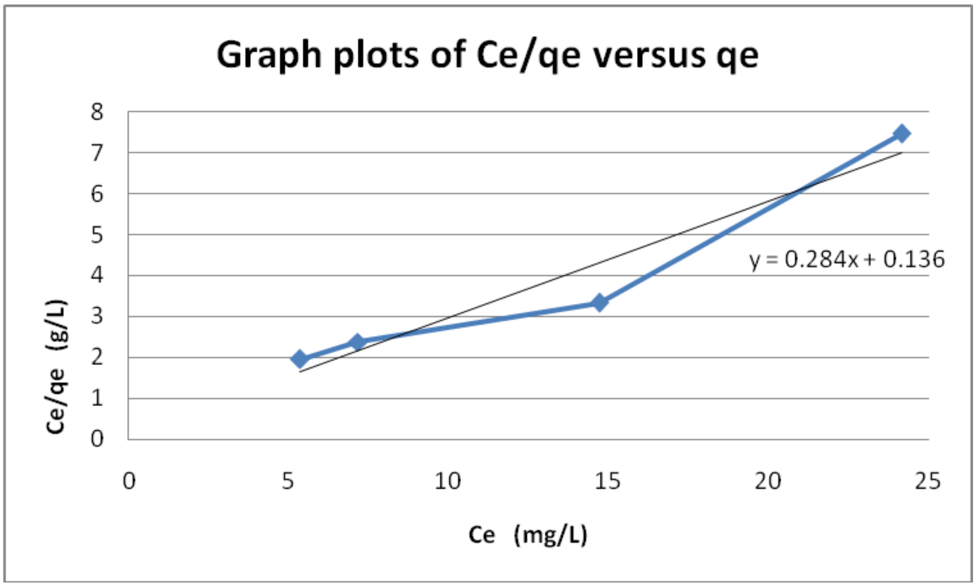


Fig. 9: Linear Langmuir isotherm graph.

The characteristics of the Langmuir isotherm can be expressed using dimensionless separation factor denoted by, $R_{L,}$ which described the type of the isotherm as below:

$$R_L = 1/ (1 + b. C_o)$$

Where b is the Langmuir constant and C_o is the initial concentration of Pb(II).

Table 6: R_L value and type of isotherm

R_L value	Type of isotherm
$R_L > 1$	unfavorable
$R_L =1$	linear
$0 < R_L < 1$	favorable
$R_{L\,=}\ 0$	irreversible

From the equation in Figure 9, b is 2.088. Hence, the calculated of R_L value is equal to 0.0094. Thus according to the table 6, R_L value between 0 and 1 indicate favorable adsorption of lead.

CHAPTER 5

CONCLUSION

In this project, Meranti sawdust is synthesized to activated carbon for lead removal in aqueous solution. The resulting adsorbent will be characterized using FESEM and Micrometrics ASAP 2020. By using N_2 adsorption-desorption isotherm analysis, Sample E which is prepared at IR of 1:3 with KOH solution, activation temperature of $500^{o}C$ and activation time of 30 minutes yields the highest value of S_{BET} (2.5613 m^2g^{-1}), total pore volume, V_T (0.005280 cm^3g^{-1}) and pore diameter, D (8.246 nm). Lead adsorption study will carried out to analyze the feasibility of activated carbon from the sawdust to be used as commercialized adsorbent in the future.

From the lead adsorption study, it was found that the sorption is favorable and follows the Linear Langmuir isotherm model. The result shows that the activated carbon is capable to removing up to 89.3% of initial lead concentration in solution. Hence, from the adsorption test it clearly indicates that this material is highly feasible to be utilized in the adsorption of heavy metal from waste water factory industries.

REFERENCES

Adinata, D., Wan Daud, W. M., & Aroua, M. K. (2007). Preparation and characterization of activated carbon from palm shell by chemical activation with K2CO3. *Bioresource Technology* , 145-149.

Adouby, K., Akissi, K. L., Wandan, E., & Yao, B. (2007). Removal of Heavy Metal Ions (Pb,Cu) in Aqueous Solutions by Pterygota macrocarpa Sawdust. *Applied Sciences* , 1864-1872.

Akissi, K. L., Adouby, K., Wandan, E., Yao, B., & Kotchi, K. (2010). Sorption and Desorption of Pb(II) from Aqueous Solution using Triplochiton scleroxylon Sawdust as Sorbent. *Applied Sciences* , 1536-1544.

Ansari, R., & Raofie, F. (2006). Removal of Lead Ion from Aqueous Solutions Using Sawdust Coated by Polyaniline. *E-Journal of Chemistry* , 49-59.

Argun, E. M., Dursun, S., Ozdemir, C., & Karatas, M. (2007). Heavy metal adsorption by modified oak sawdust: Thermodynamics and kinetics. *Hazardous Material* , 77-85.

Baral, S. S., Das, S. N., & Rath, P. (2006). Hexavalent chromium removal from aqueous solution by adsorption on treated sawdust. *Biochemical Engineering* .

Djamila, H., & Zoubida, B. *Equilibrium Sorption Isotherm for Pb(II) Ions on Sawdust.* Algeria: Bab Ezzouar Algiers.

Evans, M., Halliop, E., & MacDonald, J. (1999). The Production of Chemically-Activated Carbon. *Carbon* , 269-274.

Ghani, A. N., Hefny, M., & El-Chagaby, G. (2007). Removal of lead from aqueous solution using low cost abundantly available adsorbents. *Int. J. Environ. Sci. Tech.* , 67-73.

Hayashi, J., Horikawa, T., Muroyama, K., & Gomes, V. G. (2002). Activated carbon from chickpea husk by chemical activation with K2CO3: preparation and characterization. *Microporous and Mesoporous Materials* , 63-68.

Jarup, L. (2003). Hazards of heavy metal contamination. *British Medical Bulletin* , 167-182.

M., K., & Surchi, S. (2011). Agricultural Wastes as Low Cost Adsorbents for Pb Removal: Kinetics, Equlibrium and Thermodynamics. *International Journal of Chemistry* .

Raymundo-Pinero, E., Azais, P., Cacciaguerra, T., Cazorla-Amoros, D., Linares-Solano, A., & Beguin, F. (2005). KOH and Naoh activation mechanism of multiwall carbon nanotubes with different structural organization. *Carbon* , 786-795.

Wenzl, H. (1970). *The chemical technology of wood.* New York: Academic Press.

Zahra, N. (2012). Lead Removal from Water by Low Cost Adsorbents: A Review. *Pak.J.Analy.Environ.Chem.* , 01-08.

APPENDICES

Appendices 1: Gant chart for FYP 1

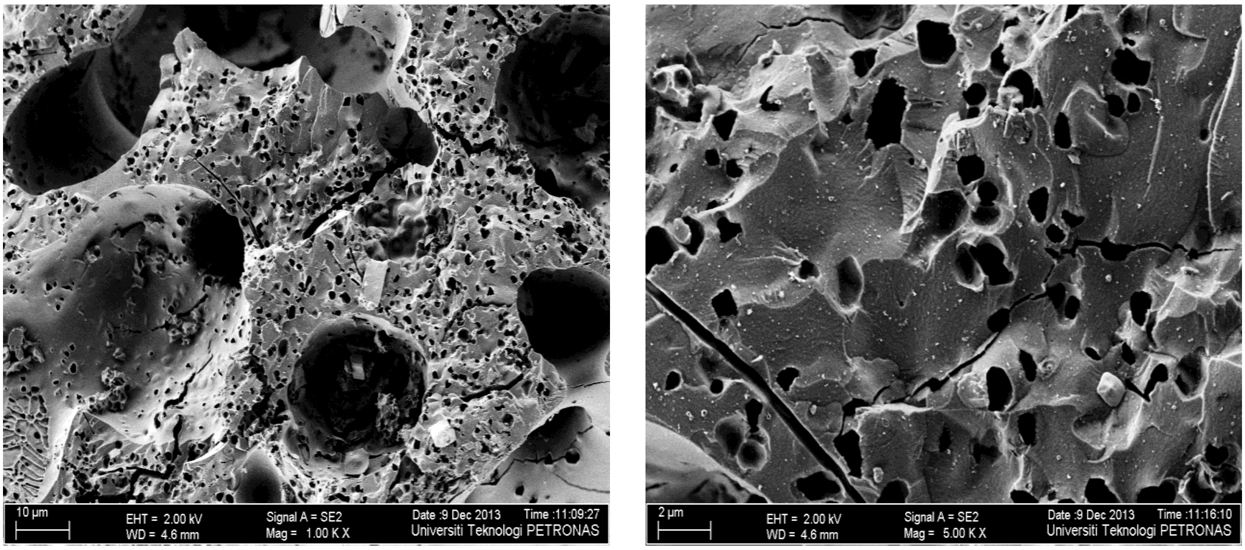
No.	**Project Activities**	**Weeks**													
		1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**
Final Year Project I															
1	Selection of the project title	🟨	🟨	🟨									Aidilfitri Holiday		
2	Literature review from journals and research paper			🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨		🟨	🟨
3	To collect the raw materials				🟨	🟨	🟨								
4	To do lab sample preparation					🟨	🟨	🟨	🟨	🟨	🟨	🟨			
5	Submission of extended proposal							●							
6	Viva: Proposal defense and Progress Evaluation								●						
7	Project progress					🟨	🟨	🟨	🟨	🟨	🟨	🟨		🟨	
8	Draft Report										🟨	🟨		🟨	
9	Interim Report														●

● **Key Milestone**

Appendices 2: Gant chart for FYP 2

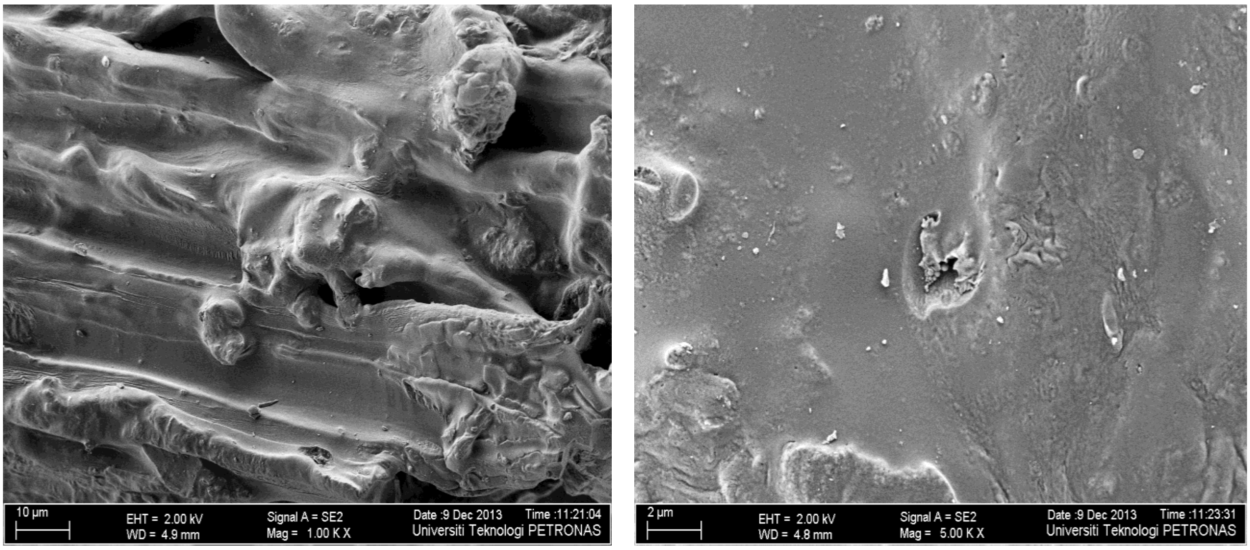
Project Activities	**Weeks**															
	1	**2**	**3**	**4**	**5**	**6**	**7**		**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**
Lab work continues	🟨	🟨	🟨	🟨	🟨	🟨	🟨	Mid-Sem Break								
Submission of Progress report									●							
Lab work continues									🟨	🟨	🟨	🟨	🟨			
Pre-SEDEX												●				
Submission of Draft Report													●			
Submission of Dissertation (soft bound)													●			
Submission of Technical Paper													●			
Oral Presentation														●		
Submission of Project Dissertation (Hard Bound)																●

Appendices 3: FESEM IMAGES



1000x magnification 5000x magnification

Impregnated with KOH, 1:3 at 500^{o}C for 30 min.



1000x magnification 5000x magnification

Impregnated with H3PO4, 1:2 at 500^{o}C for 30 min.

Appendices 4: EDX SPECTROSCOPY

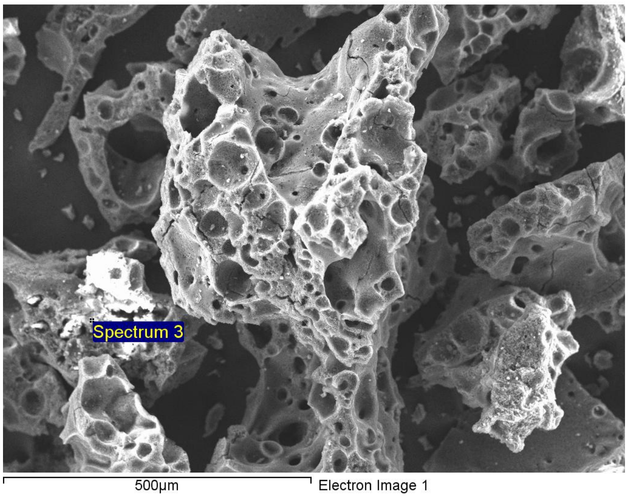
Spectrum processing: (IR with KOH)

C CaCO3 1-Jun-1999 12:00 AM

O SiO2 1-Jun-1999 12:00 AM

K MAD-10 Feldspar 1-Jun-1999 12:00 AM

Element	Weight %	Atomic %
C	78.48	84.17
O	18.37	14.79
K	3.15	1.04
Totals	100.00	



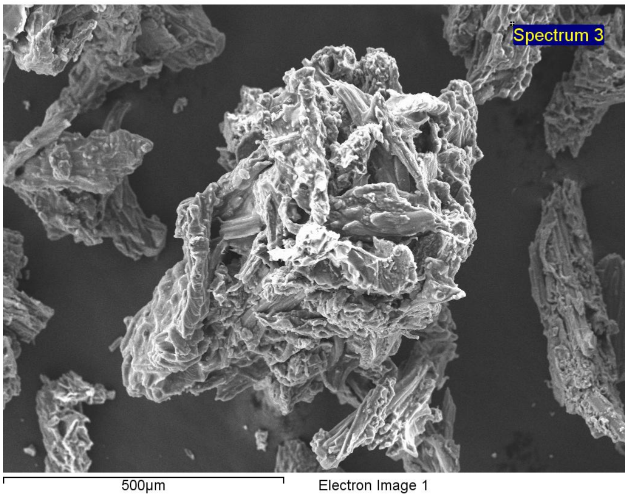
Spectrum processing: (IR with H3PO4)

C CaCO3 1-Jun-1999 12:00 AM

O SiO2 1-Jun-1999 12:00 AM

P GaP 1-Jun-1999 12:00 AM

Element	Weight %	Atomic %
C	69.47	80.16
O	14.74	12.77
P	15.79	7.06
Totals	100.00	



Appendices 5: AAS (Pb)Standard Solution