Biosorption of Heavy Metal Ions from Industrial Waste Water by Banana Peel Based Biosorbent

by

Phoon Kok Hoong

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

MAY 2013

Universiti Teknologi PETRONAS
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CERTIFICATION OF APPROVAL

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

Approved by,

(Mr. Azry bin Borhan)

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

May 2013

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.

PHOON KOK HOONG

ABSTRACT

The main purpose of this project is to study the potential of using banana peel (BP) as biosorbent in removing heavy metal ions and oil/grease particles from industrial waste water. The study emphasizes on the parameters involved in the preparation phase of the BP adsorbent, such as particle sizes, activating agent, impregnation ratio, carbonization temperature and duration. The dried BP is first grinded into two different particle sizes (0.25mm and 3.00mm), then chemically activated using either zinc chloride or phosphoric acid and carbonized at different sets of temperature and duration into activated carbon, which is a popular type of adsorbent used in industrial waste water treatment. The characterization of BP based activated carbon is carried out using the surface area analyzer (Micromeritics ASAP 2020) and the Field Emission Scanning Electron Microscope (FESEM) to determine which set of parameters produces the largest surface area estimated using the BET theory (S_{BET}) which is directly related to the effectiveness of that particular adsorbent. Based on the characterization results, sample A20 which is of particle size of 0.25mm, activated using H3PO4 at 1:1 impregnation ratio, carbonized at 400°C for 2 hours, is found to have the largest S_{BET} (256.63m2/g). The total pore volume (V_T) of sample A20 is 0.01356cm^3/g while its average pore diameter (D) is 0.247nm. The produced BP based activated carbon samples are also tested for their adsorption capacity with typical pollutants found in industrial waste water such as heavy metal ions as well as oil and grease (O&G) particles. Three heavy metal ions are studied in this project, which are copper (Cu^{2+}), zinc (Zn^{2+}) and lead (Pb^{2+}). The adsorption capacity of sample A20 is specifically studied while being compared to another sample A32. Sample A20 yields higher percentage removal for all tested waste water pollutants, which are 81.6% for crude oil particles, 59.6% for Cu^{2+}, 44.33% for Zn^{2+} and 84.46% for Pb^{2+}.

ACKNOWLEDGEMENT

First of all, I would like to express my sincere gratitude to my supervisor from University Teknologi PETRONAS (UTP), Mr. Azry bin Borhan for his guidance during the duration of this Final Year Project (FYP). He has always been helpful and is very willing to share his expertise on the subject by guiding me to the right direction whenever I have doubts or questions pertaining to the project.

Besides that, my honest appreciation goes to all lab technicians from the Chemical Engineering Department and Centralized Analytical Laboratory (CAL) in UTP who greatly assisted me in the process of sample characterization and analysis. My deepest gratitude to them for providing me with the best service in operating those technologically advanced analytical equipment.

Apart from that, I would like to thank my parents for their deep understanding and support in me when I am involved in this project. Their moral support gives me the motivation necessary to complete the study on the subject and finish the project.

Last but not least, special appreciation to the coordinators of this course, Dr. Anis Suhaila Binti Shuib for FYP I and Dr. Nurhayati Binti Mellon for FYP II. Thanks to their coordination, the project is carried out and completed smoothly.

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CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

Adsorption is a greatly preferred method for the removal of heavy metal ions in waste water treatment, generally due to its high efficiency, simplicity in handling, high availability of raw materials as well as its cost effectiveness. Besides, adsorption technology also has the ability to remove and then recover and recycle some of the useful waste material (e.g. metals) from the waste water which can help to reduce cost (Philomina & Enoch, 2012). As such, the demand for adsorbents are increasing as more industries are required to produce their waste water under a stricter condition as regulated by law.

Activated carbon is one of the most common type of adsorbent used in waste water treatment. It is highly porous (average pore diameter of 10 Å to 60 Å), therefore possessing large surface area, which ranges from 300 to 1200 m^2/g. (Geankoplis, 2003), (Marsh & Rodriguez-Reinoso, 2006). The large surface area of the activated carbon will contribute to the adsorption process itself, since there are more reactive sites for the adsorbates to bind on the surface of the activated carbon. As illustrated in Figure 1.1, the graph shows a steady increase in the exports of adsorbent (activated carbon) from China to Japan, which is one of the largest consumer of water treatment adsorbent in the world, due to the country’s strict policy on their water cleanliness (Marsh & Rodriguez-Reinoso, 2006). From the steady increase of activated carbon consumption in the graph, the study on this subject is imminently important.

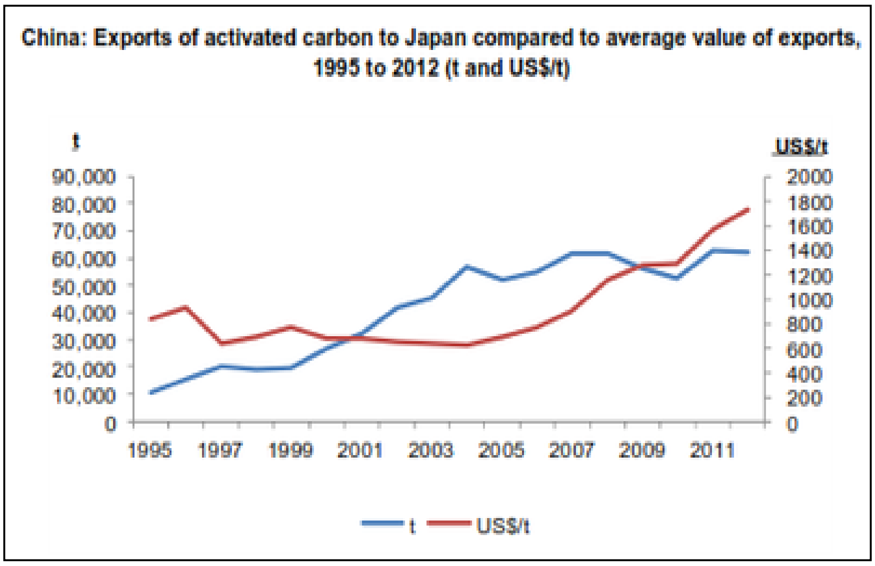

Figure 1.1: Trend of China Exports of Activated Carbon to Japan from 1995 to 2012 (Retrieved March 12, 2013,

from http://www.roskill.com/reports/industrial-minerals/activated-carbon)

Activated carbon can be produced from a wide range of raw materials (precursors). Recent studies on activated carbon seems to emphasize on using precursors from otherwise worthless waste materials, particularly agriculture wastes and industrial by-products. As long as the waste material contains enough carbon content, it can be qualified as the precursor for activated carbon production. These adsorbents produced from agriculture wastes or biomass are known as 'biosorbent' (Ahalya, Ramachandra, & Kanamadi, 2003), (Nilanjana, Vimala, & Karthika, 2008). Although using biomass in environmental cleanup has been in practice for quite some time already, further studies on biosorption shows a lot of its potential in providing an economical alternative for treating industrial waste water.

One of the agriculture wastes that received attention in the study of this particular subject is banana peel (BP). Based on a study conducted by the Department of Agriculture, Malaysia, there are about 250,000 Mt/yr – 290,000 Mt/yr of banana being produced in Malaysia from the year of 2005 – 2009 and the numbers have been increasing annually (Mokhtarud-din & William, 2010). Typically, the flesh of the banana fruit is being consumed as food while the banana peel is treated as unwanted parts of the banana that normally will be discarded as wastes. However, BP is an agriculture waste that is extremely reusable in many areas, such as being used as shoe polish, wart removal and itch relief from bug bites (R.W. Thompson, 2009).

Figure 1.2: Banana Peel as Household Waste

In the field of chemical engineering, BP has the potential to be used as cheap biosorbent to remove harmful particles such as heavy metal ions and oil/grease particles from industrial effluents. The reason of this is because BP is easily available in Malaysia due to banana being one of the common fruits planted commercially in the country. BP is low cost material as it is normally discarded as wastes, thus making the production of activated carbon from BP very cost effective in terms of raw material costing. Besides, BP is organic in nature, thus 100% biodegradable and environmental friendly, as well as being parallel with the concept of sustainability and truly practicing ‘reuse and reduce’ of waste material. Most importantly, BP itself has considerably high carbon content, which qualifies as precursors for producing activated carbon that can be used in the removal of heavy metal ions and oil/grease particles in industrial waste water (Memon, et al., 2008). Practically, raw BP (without chemical and physical activation) can already be used as biosorbent in waste water treatment. However, studies show that, by including activation process in the preparation of BP based biosorbent, the adsorption capacity will be greatly improved due to the formation of new pores which increase the total surface area and the adsorptive sites of the adsorbent. (Ademiluyi & David-West, 2012), (Diao, Walawender, & Fan, 2002).

1.2 PROBLEM STATEMENT

In recent years, heavy metal pollution has become one of the most serious environmental problems due to the rapid development and expansion of many industries (mining, energy and fuel producing, fertilizer, pesticide, leather, metal surface treating, aerospace, etc.). Presence of heavy metals, even in minute traces, is highly toxic and detrimental to both flora and fauna to the point of upsetting the whole ecosystem in the polluted location. When effluent waste containing heavy metals are directly or indirectly being discharged into the environment, it will cause serious environmental pollution and even threatening human life (Volesky, 1990a). When living organisms are exposed to excessive amount of heavy metal, the organisms' body system will be greatly affected, effects ranging from damage of central nervous system to corrosion of living tissue.

These are some of the common heavy metal ions that are known to cause harmful effects when come into contact with human. For example, cadmium ions (Cd^{2+}) is known to cause tubular and glomerular damage, proteinuria, anemia, kidney damage. On the other hand, lead ions (Pb^{2+}) can cause kidney damage, renal tubular damage, abdominal pain and lead encephalopathy. Meanwhile, arsenic ions (As^{3+}) is commonly associated with metabolic disorders, various cancers (skin, liver, lung) and dermal pigments (Blackfoot disease). Another common heavy metal ions in industrial wastewater is copper ions (Cu^{2+}). Copper ions are known to cause severe mucosal irritation, hepatic and renal damage, gastrointestinal irritation and widespread capillary damage (L. Järup, 2003). Apart from heavy metal ions, oil & grease (O&G) particles also often been illegally discharged into wastewater. O&G particles will affect aquatic lives and as well as impair the birds flying ability if the feathers on the birds' wings are soaked with oily water (Dunnet et al., 1982). The industrial effluents which contain different derivatives of heavy metals such as Cadmium (Cd), Lead (Pb), Nickel (Ni), Chromium (Cr), Arsenic (As), Copper (Cu), Iron (Fe) etc, when continuously discharged, will produce a significant toxic impact on aquatic environment (Brewer, 2010). Figure 1.3 shows the harmful effects of heavy metal and grease particles that affect human and aquatic organisms.

Figure 1.3: Effects of Heavy Metal and Grease Particles in Wastewater

Removal of heavy metals has always been a challenge to engineers and scientists of this field. Traditional heavy metal treatment includes chemicals and processes in surface chemistry such as precipitation, adsorption, membrane processes, ionic exchange, floatation, and others (Selatnia *et al.*, 2004), (Rosangela *et al.*, 2007). However, these techniques are rather expensive and are not selective enough to allow the recovery of very dilute heavy metals present in the effluent (Mohammad *et al.*, 2000). These disadvantages, coupled with the need for more economical and effective methods for the recovery of metals from waste water, have resulted in the development of alternative separation technologies (Saikaew. & Kaewsarn, 2009).

Biosorption is potential to become a good alternative for the removal of heavy metal ions in industrial wastewater. It is economically feasible and the precursor materials are easily available. However, the problem that exists with biosorption is that there are so many materials as options, ranging from fruit peel to saw dust, it is hard to determine that which biosorbent is suitable for the removal of a selected heavy metal ion. Therefore, extensive characterization study has to be carried out on each one of precursor material, in this case banana peel (BP), in order to determine the best preparation condition of converting the precursor to activated carbon which is effective in removing harmful substances (heavy metal and oil & grease particles) from industrial effluent.

1.3 OBJECTIVES

The main objective of this project is to evaluate the potential of using banana peel (BP) as biosorbent in removing heavy metal ions and oil/grease particles from industrial waste water. Apart from that, the relationship between different preparation condition of the BP and the resulting adsorption capabilities of the biosorbent is investigated so that the best preparation condition of converting BP to useful biosorbent (activated carbon) could be determined. The effectiveness of using BP as adsorbent in the removal of heavy metal and oil & grease (O&G) particles could also be determined from this project of study.

By and large, the objectives can be summarized into the following:

i) To evaluate the feasibility of using banana peel as biosorbent in waste water treatment.

ii) To determine the best preparation condition (set of manipulated parameters) of converting BP into activated carbon.

iii) To study and evaluate the potential using BP based activated carbon in removal of heavy metal ions and O&G particles through adsorption.

1.4 SCOPE OF STUDY

This study focuses on determining the best preparation condition to convert banana peel (BP) into activated carbon which can be used as adsorbent in treating waste water, targeting the removal of heavy metal ions and oil & grease (O&G) particles. The activation method used for the adsorbent in this study is chemical activation which will be justified later in the report. The chemical agents used in this study is phosphoric acid (H_3PO_4) and zinc chloride ($ZnCl_2$) for comparison purposes. The scope of the activation temperature is limit to only from 400℃ to 600℃ and the activation time for the adsorbent is 1 hours to 2 hours. The impregnation ratio and the particle size are also among the parameters that are under study in order to determine their effect on the adsorption effectiveness of BP based adsorbent. Nonetheless, this project also explores the effectiveness of the BP based adsorbent in terms of removing harmful substances from waste water. The target substances in this study are heavy metal ions (Cu^{2+}, Pb^{2+} and Zn^{2+}) and O&G particles since they are among the few commonly found pollutants in industrial waste water (Järup, 2003). Ionic solution of individual heavy metal ions and crude oil mixed with water are prepared to be used as test solution for the BP based biosorbent samples in order to simulate the condition of actual industrial waste water. The time frame for this project work is about 28 weeks. According to the Gantt Chart, the study should be completed and all results obtained by week 26 (FYP II Week 12). Thus, this project is completely achievable within the provided time frame.

CHAPTER 2

LITERATURE REVIEW

Adsorption is defined as the process of the adhesion of one or more component of a gas or liquid stream on the surface of a solid adsorbent to accomplish a separation process. The film of components in which adsorbed to the adsorbent surface is known as the adsorbate (Geankoplis, 2003). The process continues until equilibrium is established between the amount of solid-bound adsorbate and the remaining portion in the solution. Adsorption can be categorized in to two types, namely physisorption and chemisorption. Physisorption typically involves weaker bonding forces among the molecules (e.g. Van der Waals force). It usually occurs between the adsorbed molecules and the adsorbent internal pore surface. Another trait of physisorption is that it is readily reversible, which means that desorption can be achieved easier. On the other hand, chemisorption usually involves strong chemical bonding (e.g. covalent bond). The process is also more selective and highly specific on the adsorbate molecules and it usually occurs in monolayer (Geankoplis, 2003).

Adsorption process can be studied through various methods. The parameters that are often studied in the subject of adsorption are the effects of solution pH, contact time, adsorption temperature, adsorbent dosage and adsorbate concentration present in the solution (Philomina & Enoch, 2012), (Kaewsarn, Saikaew, & Wongcharee, 2008), (Hossain, Ngo, Guo, & Nguyen, 2012). These studies show that the adsorption is most conducive in pH around 4 to 5, contact time of about 30 to 40 minutes and higher temperature. Higher amount of adosrbate concentration and adsorbent dosage will also contribute to the faster time take for the adsorption to reach equilibrium. Another important description of adsorption process is the isotherm. Adsorption isotherm describes the equilibrium of the sorption process of a material at the surface boundary at constant temperature. The isotherm curve represents the amount of adsorbate bound at the surface of the adsorbent in the function of the amount of adsorbate present in the gas phase or solution. There are several existing adsorption isotherm, such as the Linear, Freundlich, Langmuir and the Brunauer, Emmett and Teller (BET) isotherm. (Geankoplis, 2003), (Marsh & Rodriguez-Reinoso, 2006). BET theory is commonly used to explain and estimate the adsorption of gas molecules on a solid surface by assuming multilayer adsorption. Figure 2.1 depicts the IUPAC classification of adsorption isotherm according to the shape of the curves. The reversible Type I isotherm are given by microporous solids having relatively small external surfaces, such as molecular sieve zeolites and activated carbon whereby the limiting uptake is being governed by the accessible micropore volume rather than by the internal surface area. Type II isotherm is the common form of isotherm obtained with a non-porous or macroporous adsorbent which represents unrestricted monolayer-multilayer adsorption. Type III isotherm are found with water vapor adsorption on pure non-porous carbons or when the adsorbent-adsorbate interaction is weak compared to the adsorbate-adsorbate interaction. Type IV isotherm has characteristics feature that is its hysteresis loop, which is associated with capillary condensation taking place in mesopore, and limiting the uptake over a range of high p/p°. Type V isotherm is related to Type III isotherm in that the adsorbate-adsorbate interaction is weak. Lastly, type VI isotherm represents stepwise multilayer adsorption on a uniform non-porous surface (Sing, 1982).

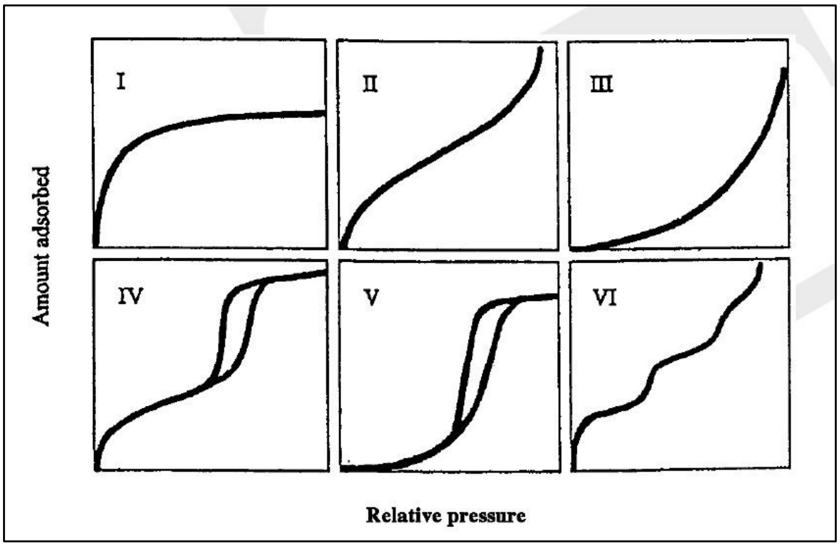

Figure 2.1: IUPAC Classification of Adsorption Isotherms

(Retrieved July 31, 2013, from http://www.nippon-bel.co.jp/tech/seminar02_e.html)

Activated carbon is a widely used adsorbent in waste water treatment, especially in removal of heavy metal ions due to its high specific surface area and affinity to metals. It is highly porous with average pore diameter of 10 Å to 60 Å, therefore possessing very large surface area, which ranges from 300 to 1200 m^2/g. (Geankoplis, 2003). The large surface area of the activated carbon will contribute to the adsorption process itself, since there are more reactive sites for the adsorbates to bind on the surface of the activated carbon. Activated carbon can be manufactured from a variety of precursors via physical or chemical activation. Physical activation is usually carried out in two steps: firstly, carbonization of raw material is done in an inert atmosphere at a temperature below 700°C, and the second step is the activation in the presence of steam, carbon dioxide, and/or air at temperatures between 800 and 1000°C. Chemical activation is generally carried out in one step, which consists of the impregnation of the raw material with a strong dehydrating agent, such as H_3PO_4, $ZnCl_2$, K_2CO_3, NaOH or KOH, and then heating the mixture to temperatures of 400-800°C to simultaneously form and activate the carbon (Marsh & Rodriguez-Reinoso, 2006). Chemical activation provides a few advantages over physical activation which include single step activation, low activation temperatures, shorter activation time, higher yields and better porous structure. The chemical agents used are usually substances with dehydrogenation properties that inhibit the formation of tar and reduce the production of other volatile products. The disadvantage of chemical activation process is the need for an important washing step, which is time consuming due to number of washings required to completely remove the activation agent from the carbon (Lim, Srinivasakannan, & Balasubramanian, 2010).

Of the several activating agents reported, the most important and commonly used activating agents are phosphoric acid, zinc chloride and alkaline metal compounds. Phosphoric acid and zinc chloride are used for the activation of lignocellulosic materials that have not been carbonized previously; whereas metal compounds such as KOH are commonly used for the activation of coal precursors or chars (D.Lazano-Castello, Lillo-Rodenas, Cazorla-Amoros, & Linares-Solano, 2001). Several studies of chemical activation have been conducted with zinc chloride, which has been found to maximize the adsorptive capacity and the bulk density of activated carbons produced from lignocellulosic materials such as peach stones (Molina-Sabio, Rodriguez-Reinoso, Caturla, & Selles, 1996). However, as compared to zinc chloride, phosphoric acid is most preferred due to problems of corrosion, inefficient chemical recovery and the environmental disadvantages associated with zinc chloride (Molina-Sabio, Rodriguez-Reinoso, Caturla, & Selles, 1996), (Adinata, Daud, & Aroua, 2007), (Guo, Xu, Chen, & Lua, 2005). Furthermore, activated carbons prepared using phosphoric acid has better acceptance in food, fine chemical and pharmaceutical applications due to its non-contaminating nature. Phosphoric acid activation has been applied to coconut shell (Laine, Calafat, & Labady, 1994), peach stones, coals and hardwoods (Jagtoyen & Derbyshire, Activated Carbons from Yellow poplar and white oak by phosphoric acid activation, 1998), (Jagtoyen & Derbyshire, Some considerations of the origins of porosity in carbons from chemically activated wood., 1993), and shells of nuts like almond, pecan, English walnut, black walnut and macademia nut (Toles, Marshall, Johns, Wartelle, & McAloon, 2000). These precursors are of cellulosic or lignocellulosic origin.

Activated carbon with suitable pore structure having high surface area has good value realization, commercial acceptance and hence it is of the utmost importance to utilize processes that maximize the yield with good pore characteristics. Majority of the study reports only the pore structure and pore characteristics of the activated carbon, without mentioning the yield of activated carbon. The yield as well as the pore structure of the activated carbon is widely reported to be influenced by the activation temperature (Adinata, Daud, & Aroua, 2007), (Hu & Srinivasan, 2001), (Guo & Lua, 2003), activation time (Hu & Srinivasan, 2001) and the impregnation ratio (Adinata, Daud, & Aroua, 2007), (Hu & Srinivasan, 2001), (Patnukao & Pavasant, 2008), (Girgis & Ishak, 1999). Generally the yield of activated carbon decreases with increase in activation temperature, activation time and impregnation ratio, while the pore characteristic improves with increase in the above stated parameters, mostly to an optimum value and decreases beyond (Adinata, Daud, & Aroua, 2007), (Guo & Lua, 2003). It has been shown that the impregnation ratio, which is the weight ratio of impregnator to precursor and the activation temperature govern the properties of the resultant activated carbons (Diao, Walawender, & Fan, 2002). However, there is a limit to the positive effects of temperature and the impregnation ratio to the activated carbon. Excessive heat energy given at high temperature or long duration to the carbon is known to reduce the overall surface area of the activated carbon because of the knocking and breaking of some porous wall (Borhan & Kamil, 2012). Overly high impregnation ration can also cause excessive reaction between the activating chemical and the activated carbon, thus hindering the formation of pores (Cao, Xie, Liv, & Bao, 2006). It is also reported that the suitable range of carbon content in raw material, must be in between 50-80% so that the yield of activated carbon can be maintained at reasonable range after the carbonization phase (Wu, Tseng, & Hu, 2005), (Rengaraj, Arabindoo, & Murugesan, 1998) . Besides, the pore size of the BP biosorbent must be at least of mesopores level ($20Å < D < 500Å$) according to the IUPAC classification (Marsh & Rodriguez-Reinoso, 2006), (Borhan & Kamil, 2012).

Table 2.1: IUPAC Classification of Pore Size (Mays, 2007)

IUPAC Classification of Pores	Pore Diameter
Macropore	Larger than 50 nm
Mesopore	50 – 2 nm
Micropore	Smaller than 2 nm
Super-micropore	0.7 – 2 nm
Ultra-micropore	0.7 – 0.4 nm
Sub-micropore	Smaller than 0.4 nm

Biosorption is a process that utilizes inexpensive dead biomass to sequester toxic heavy metals and is particularly useful for the removal of contaminants from industrial effluents. These adsorbents produced from agriculture wastes or biomass are known as ‘biosorbent’ (Ahalya, Ramachandra, & Kanamadi, 2003). Using biomass in waste water treatment is nothing sort of ground-breaking, but further studies show promising results that biosorption is potential of providing a cost effective alternative in waste water treatment. The major advantages of biosorption over conventional treatment methods include low cost, high efficiency, minimization of chemical and biological sludge, and regeneration of biosorbent and possibility of metal recovery (Philomina & Enoch, 2012). Numerous researches on the subject of biosorption has been carried out using various agricultural wastes or industrial by-products such as sawdust (Larous, Meniai, & Lechocine, 2005), rice husk (Wong, Lee, Low, & Haron, 2003), pomelo peel (Saikaew. & Kaewsarn, 2009), bamboo (Hameed, Din, & Ahmad, 2007), pecan shells (Shawabkeh, Rockstraw, & Bhada, 2002), etc.

The potential of using banana peel to remove heavy metal is documented in many studies. Past studies has shown that banana peel is capable of removing arsenic, copper, cadmium, chromium and iron contaminants (Memon, Bhanger, & Memon, 2008), (Kaewsarn, Saikaew, & Wongcharee, 2008), (Philomina & Enoch, 2012), (Memon, et al., 2008), (Hossain, Ngo, Guo, & Nguyen, 2012). However, most of these studies are more related to the factors that affect the adsorption process rather directly such as effect of dosage, temperature, pH, concentration and agitation (Philomina & Enoch, 2012), (Hossain, Ngo, Guo, & Nguyen, 2012), while others are studying on the kinetics and the thermodynamics of the adsorption isotherm using banana peel as adsorbent (Memon, et al., 2008), (Kaewsarn, Saikaew, & Wongcharee, 2008). Chemical activation of banana peel based biosorbent is rarely studied extensively. However, comparison between thermally activated carbon, chemically activated carbon and microwave activated carbon with banana peel as precursor has been studied (Philomina & Enoch, 2012). From the study, it shows that chemically activated and microwave activated carbon has shorter optimum contact time than thermally activated carbon. In another case, banana peel is also capable of being regenerated and reused for copper removal till seven times without reducing the adsorption efficiency (Hossain, Ngo, Guo, & Nguyen, 2012). Energy Dispersive X-ray (EDX) Spectroscopy analysis on banana peel biomass shows that the carbon content in it is about 49.60% (Suantak, Chandrajit, & Shri, 2012), close enough for being qualified to be commercially converted into activated carbon (Wu, Tseng, & Hu, 2005) . Nevertheless, all these studies on the application of banana peel based biosorbent verify the potential of using banana peel in waste water treatment.

CHAPTER 3

METHODOLOGY

3.1 LIST OF MATERIALS REQUIRED

The materials needed for this project are the raw material (precursor) for the activated carbon which is banana peel (BP). Peels from banana are of the Cavendish group bananas which is a subgroup of the triploid (AAA) cultivars of the *Musa acuminata* species. This type of banana is used because it is very common and often commercially produced in Southeast Asia. Other materials needed are the chemicals required for the impregnation of the BP sample as well as the stock solution for the adsorption capacity test. Solution of the targeted heavy metal (Cu, Pb and Zn) and crude oil mixed with diluted water are prepared to simulate the pollutants present in industrial waste water. The materials needed are tabulated in Table 3.1.

Figure 3.1: Cavendish Group of Bananas

Table 3.1: List of Materials Required for the Experiment

No	Materials	Purpose
1.	Banana Peel *(Musa acuminata)*	To be used as raw material for producing adsorbent (activated carbon) in the biosorption of wastewater treatment.
2.	Phosphoric Acid (H_3PO_4)	To impregnate the banana peel as means of chemical activation to increase the overall pore volume for adsorption process.
3.	Zinc Chloride ($ZnCl_2$)	
4.	Heavy Metal Stock Solution/ Crude Oil Mixed With Water	To determine the percentage removal of the targeted substance when tested with the biosorbent sample in batch adsorption process (adsorption capacity test).

3.2 LIST OF EQUIPMENT REQUIRED

The equipment used in this study are mostly for the sample analysis except for the drying oven and the furnace which are used in the sample preparation phase. The analytical equipment are operated by highly trained technicians to ensure that the results obtained are accurate and reliable. Table 3.2 lists all the equipment used in this project.

Table 3.2: List of Equipment Required

No	Equipment	Purpose
1.	Field Emission Scanning Electron Microscope (FESEM)	To provide magnified view (10 – 100,000 times) of the structure of the activated carbon produced from the Banana Peel (BP). EDX function can also determine the composition of the elements present in the sample.
2.	Surface Area Analyzer and Porosimetry System (Micromeritics ASAP 2020)	To determine the pore size distribution, specific surface area and porosity of the BP biosorbent by nitrogen adsorption-desorption isotherms.

No	Equipment	Purpose
3.	Atomic Absorption Spectrophotometer (AAS)	To determine the concentration of heavy metal ions in the sample solution before and after the adsorption capacity test.
4.	InfraCal TOG/TPH Analyzer	To determine the concentration of crude oil particles in the water sample before and after the adsorption capacity test.
5.	Drying Oven	To dry the banana peel sample overnight and remove all the moisture from the banana peel before experiment.
6.	Tubular Furnace	To carbonize the BP into activated carbon by heating it to the required temperature.

3.3 EXPERIMENTAL APPROACH & PROCEDURE

The experimental procedure of this project will be divided into three phases. The first one is the biosorbent sample preparation whereby the samples are prepared according to certain sets of parameters, such as segregating the sample into different particle sizes, impregnating the sample with different activating agent at different weight ratio, carbonizing the sample at various sets of duration and temperature. The next phase of the experiment is the characterization of the biosorbent sample, whereby analysis will be carried out on the samples to determine the pore size distribution of the samples, the adsorption isotherm, the total pore volume as well as obtaining the microscopic images of the biosorbent sample to prove the existence of pore formation at different stages of sample preparation. Lastly, the project will enter the final phase which is to test the adsorption capacity of the biosorbent sample in order to investigate the effectiveness of removing heavy metal ions and oil/grease particles contained in industrial wastewater. Each experimental procedure will be further elaborated in the next part of the report.

3.3.1 Preparation of Raw Material

Banana peel (BP) is massively collected from fried banana stalls and cafeterias. After collecting sufficient BP (~ 7.0kg), they are roughly cut into small pieces so that they can be thoroughly washed with tap water to remove external dirt. Then, the wetted banana peel are kept in air for removing the water from the surface and dried in oven at 100°C overnight to remove excessive moisture. The dried banana peel are then grinded into powder form and then segregated into different particle sizes using sieves, and then kept in an air tied container for further activation (Hossain, Ngo, Guo, & Nguyen, 2012). Figure 3.2 shows the comparison of photos taken for each BP powder after segregated into different particle sizes.

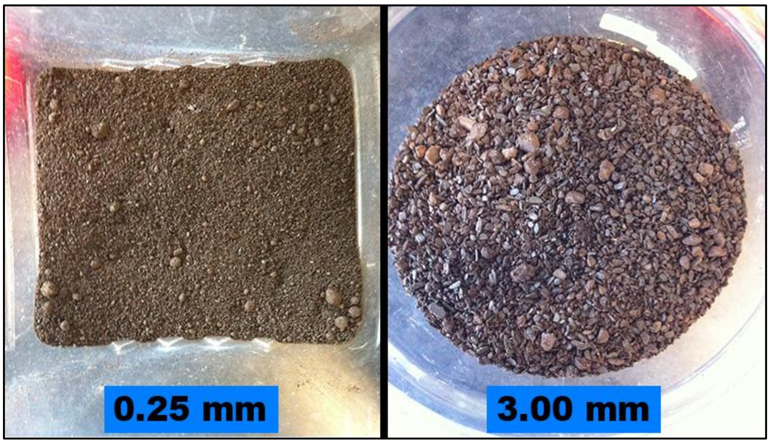

Figure 3.2: Photo of Grinded BP for Both Particle Sizes

3.3.2 Chemical Activation of Adsorbent

Chemical activation is used in this study due to the lower temperature requirement and ability to gain higher yield with better porous structure in the activated carbon produced (Lim, Srinivasakannan, & Balasubramanian, 2010). The parameters which are manipulated in the activation phase of the BP based adsorbent are the types of activating agent, impregnation ratio, carbonizing temperature and duration. The activating agents being used in this study are zinc chloride ($ZnCl_2$) and phosphoric acid (H_3PO_4). These activating agents are chosen in this study based on the past researches conducted on similar lignocellulosic precursor and the results of using these chemicals show better pore formation in the activated carbon compared to others (Ademiluyi & David-West, 2012), (Borhan & Kamil, 2012), (Diao, Walawender, & Fan, 2002), (Toles, Marshall, Johns, Wartelle, & McAloon, 2000). The range of the impregnation ratio studied in this project is 1:1, 1:2 and 1:3. The impregnation ration (IR) is defined as the dry weight of the grinded BP powder (W_{BP}) to the dry weight of activating agent (W_{ZnCl2} or W_{H3PO4}).

$$IR = \frac{W_{BP}}{W_{ZnCl_2}\ or\ W_{H_3PO_4}} \tag{3.1}$$

10g of BP biosorbent will be soaked in 100ml activating chemical overnight to make sure that the reagents are fully adsorbed into the banana peel powder. The beaker containing the mixture is covered with aluminum foil to prevent contamination or evaporation of chemical agent.

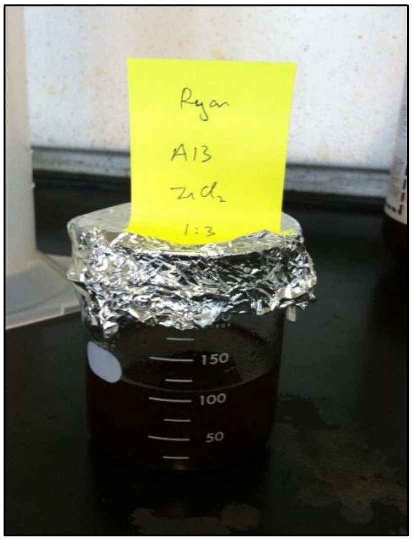

Figure 3.3: Photo of BP Powder Soaked in Activating Agent

The soaked BP powder is then filtered from the chemical. The residue from the filtration which is the impregnated BP powder is then carbonized in a furnace (tubular furnace) under steady flow of nitrogen gas that act as the carrier gas which promotes the pore formation in the samples. Different sets of temperature (400°C, 500°C and 600°C) and duration (60 min and 120 min) are used for the carbonization process. At this stage, the BP powder has turned into activated carbon.

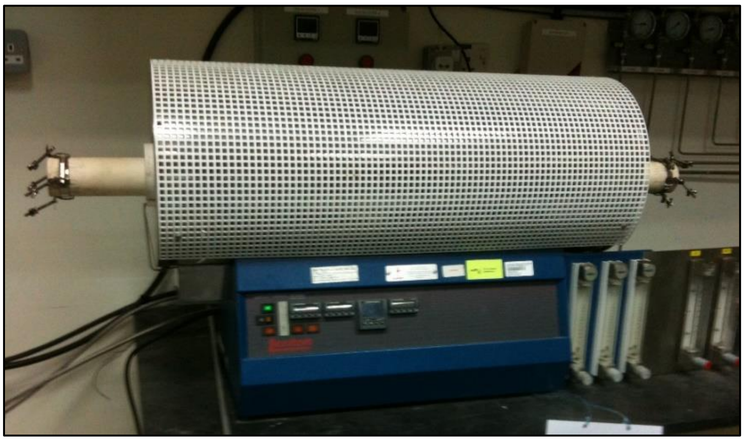

Figure 3.4: Tubular Furnace Used for Carbonization

After the samples are cooled down to room temperature, they are washed repeatedly to remove any remaining traces of the activating chemicals from the impregnation phase. The BP based activated carbon are continuously washed until the filtrate presents a neutral pH when tested with a pH paper (for H_3PO_4 impregnation) or the filtrate presents as clear liquid (for $ZnCl_2$ impregnation).

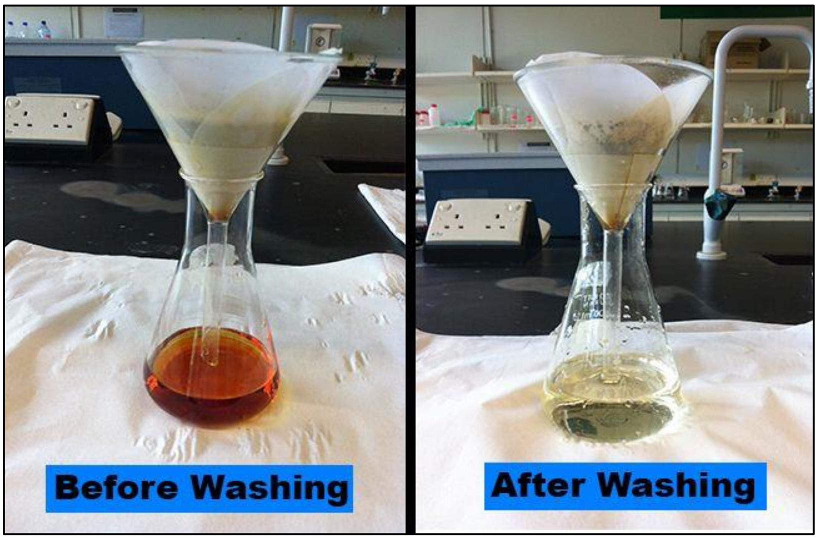

Figure 3.5: Filtrate Presents Clearer After Repeated Washing

Lastly, the samples are stored in separate containers with their respective labels and placed inside a desiccator with moisture absorbing crystals to prevent the samples from being contaminated by atmospheric moisture.

Figure 3.6: Sample Storage in Desiccator

Each set of parameters is used for two particle sizes of BP powder, which are 0.25mm and 3.00mm. In total, there are 72 samples to be prepared for all the combination of parameters under study. The preparation condition and the status of each sample can be found in Appendix I while the breakdown of sample preparation is illustrated in the figure below:

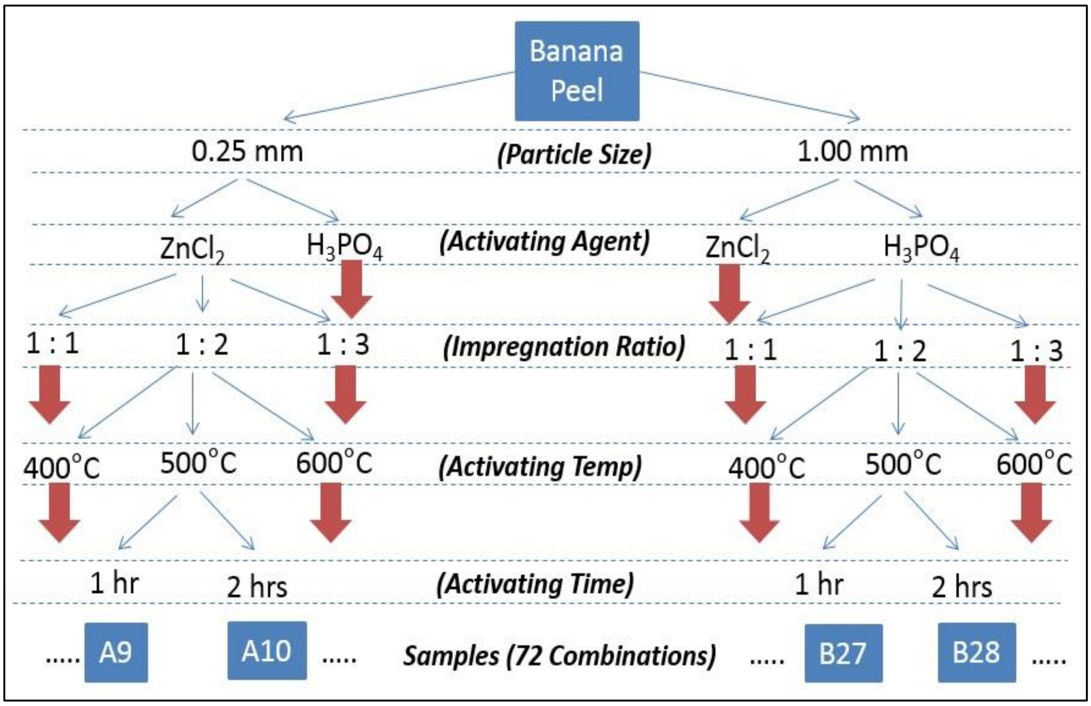

Figure 3.7: Breakdown of Samples to be Prepared

3.3.3 Characterization of Sample

There are several equipment involved in the characterization of sample. First and foremost, FESEM is used to provide magnification (10 – 100,000 times) to the view for the surface morphology of the BP biosorbent in ultra-high resolution images in order to confirm the formation of adsorption pores (macropores, mesopores and micropores) by comparing with the FESEM images obtained for the BP biosorbent prior to activation. The Energy Dispersive X-ray Spectroscopy (EDX) in the FESEM equipment is also used to detect the element composition in the samples before and after activation in order to study whether the carbon content in raw BP is sufficient for commercial production of activated carbon.

Figure 3.8: FESEM Facility in University Teknologi PETRONAS (UTP)

The pore size distribution, specific surface area and the porosity of the samples are determined by the nitrogen adsorption-desorption isotherms characterized by the Micromeritics ASAP 2020, using nitrogen gas as adsorbate while being degassed at 350°C for 4 hours. The specific surface area of the biosorbent samples is estimated by the Brunauer-Emmett-Teller (BET) method using the N_2 adsorption isotherm data while for the pore size distribution, the Barett-Joyner-Halenda (BJH) adsoprtion model is used (Borhan & Kamil, 2012). The formation of mesopores or smaller is strongly desired in the sample to be qualified as activated carbon (Borhan & Kamil, 2012).

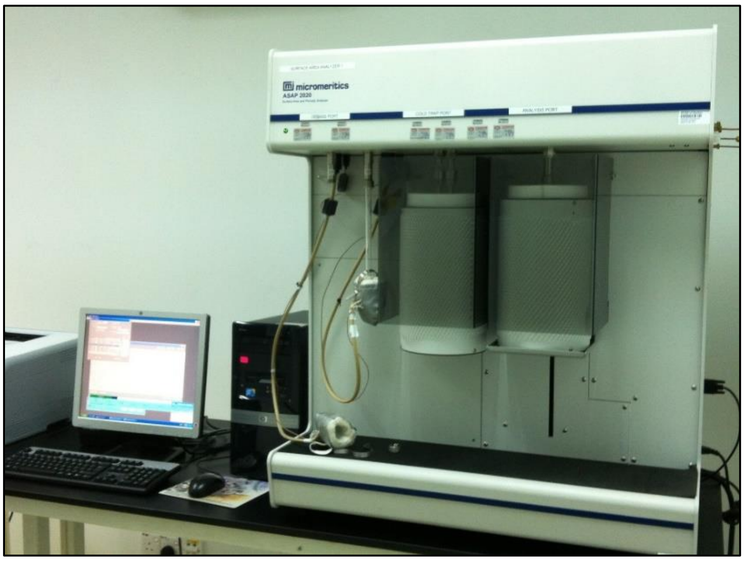

Figure 3.9: Surface Area Analyzer (Micromeritics ASAP 2020) in UTP

3.3.4 Adsorption Capacity Test

Three heavy metal, copper (Cu), lead (Pb) and zinc (Zn) are frequently found in industrial waste water (Järup, 2003), therefore are chosen for this study. Copper is a common heavy metal discharged in industries such as electroplating and mining while lead is commonly found in manufacturing industries of battery, fertilizer and leather products. Zinc is very often used in anti-rust coating as well as motor oil and tire manufacturing. The potential of using BP based activated carbon to remove oil and grease (O&G) particles is also explored in this study. O&G particles is a common contaminant found in refinery water discharge which often cause perish of aquatic lives.

The heavy metal test solution is prepared by dissolving the salt crystal containing that particular heavy metal in distilled water. Batch adsorption is then carried out by soaking 0.1g of BP based activated carbon in 20mL of heavy metal test solution for 16 hours. The activated carbon sample that has the largest specific surface area (S_{BET}) based on the results of the characterization analysis is selected for this test while another sample of activated carbon with almost similar parameters is used to act as an experiment control and to provide comparison of performance between the two samples. The mixture is then filtered and the filtrate which is the test solution after adsorption is collected and sent for quantitative analysis. For the analysis of heavy metal removal, the Atomic Absorption Spectrophotometer (AAS) is used. Spectroscopy is the use of the absorption, emission or scattering of electromagnetic radiation by atoms or molecules to qualitatively or quantitatively study the atoms/molecules. The interaction of radiation with matter can cause redirection of the energy levels in these atoms/molecules. By comparing the composition of heavy metal in the test solution with and without adsorption, the percentage removal of each heavy metal could be known, thus the effectiveness of the BP based activated carbon towards various heavy metal (selectivity) could be determined from this test.

Figure 3.10: Atomic Absorption Spectrophotometer (AAS) in UTP

For the O&G removal test, the InfraCal TOG/TPH Analyzer is used. Approximately 1.0g of laboratory crude oil is mixed with 60mL of distilled water to prepare the test solution for O&G removal test. Then, 0.1g of BP based activated carbon is added to 20mL of the crude oil test solution and the mixture is allowed to sit for 16 hours. Similarly, the activated carbon sample with the largest S_{BET} is chosen for this test and the performance is compared to another sample that has almost similar parameters which also acts as an experiment control. After that, the activated carbon is removed from the crude oil test solution. The crude oil test solution with and without adsorption is then collected in separate vials with proper labels in order to determine the percentage removal of crude oil particles by using both samples of activated carbon.

Hexane (C_6H_{14}) is used as an extracting solvent of the oil particles from the collected test solution. When added with hexane, the test solution will form two separate layers with the hexane layer containing crude oil particles being on top because hexane and oil have a lower density than water. A small amount of this hexane layer is then extracted and dropped on the crystal surface of the TOG/TPH analyser which can be run and determine the concentration of oil and grease in the sample solution.

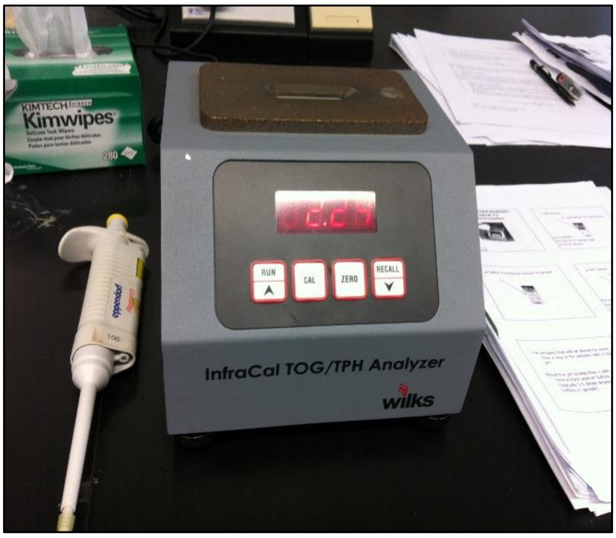

Figure 3.11: InfraCal TOG/TPH Analyzer in UTP

The adsorption capacity of the activated carbon is defined by the percentage removal of the targeted substances (pollutants) in this test. The BP based activated carbon should theoretically show different affinity towards the adsorption of different targeted substances. The percentage removal of the targeted substances is calculated using the following formula (Philomina & Enoch, 2012):

$$\%R = (C_i - C_f) / C_i \times 100\% \qquad (3.2)$$

whereby:

$\%R$ = percentage removal of individual targeted substance

C_i = initial concentration (before adsorption) of the targeted substance (ppm)

C_f = final concentration (after adsorption) of the targeted substance (ppm)

3.4 PROJECT GANTT CHART & MILESTONES

Table 3.3: Gantt Chart for FYP I

No	**Detail/Week**	**FYP 1**													
		1	2	3	4	5	6	7	8	9	10	11	12	13	14
1.	**Selection of Project Topic** - Discussion with supervisor about expectation and future work.	■	■												
2.	**Preliminary Research Work** - Conduct literature review and information gathering.		■	■	■	■									
3.	**Submission of Extended Proposal and Proposal Defense**						■	■	■	■					
4.	**Gathering resources and materials** - Ensure all materials and equipment are ready for project work. - Start preparing samples for analytical research.										■	■	■		
5.	**Submission of Interim Report**													■	■

Table 3.4: Gantt Chart for FYP II

No	**Detail/Week**	**FYP 2**														
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
1.	**Conduct project work** - Send samples to Centralized Analytical Lab for characterization. - Test biosorbent with water sample containing pollutants. - Collect data and analyzed the results.	■	■	■	■	■	■	■	■	■	■	■	■			
2.	**Submission of Progress Report**							■								
3.	**Pre-SEDEX** **-** Presentation to be qualified for Engineering Exhibition.										■					
4.	**Submission of relevant papers** - Complete dissertation and technical paper.											■	■	■	■	■
5.	**Oral Presentation** - Presentation to supervisor and industry professional about the study and draw conclusion based on the results													■		

CHAPTER 4

RESULTS AND DISCUSSION

4.1 DATA GATHERING & ANALYSIS

4.1.1 Activated Carbon Yield

The yield of activated carbon is defined as the ratio of the weight of the resultant activated carbon to that of the original banana peel (BP) with both weights on dry basis. The formula for the calculation of yield (Diao, Walawender, & Fan, 2002) is as below:

$$\text{Yield} = \frac{M_{AC}}{M_{BP}} \text{ x } 100\% \tag{4.1}$$

whereby:

M_{AC} = mass of the activated carbon sample after washing and drying (g)
M_{BP} = original mass of the BP powder prior to carbonization (g)

The average yield based on all the samples that have been converted into activated carbon is **43.24%**. The individual yield and the status of each sample preparation is as tabulated in APPENDIX I. It is noted that although the weight of BP powder used for all samples is fixed at 10g, there are some loss in BP mass during the transfer from the filter paper to the crucible for carbonization after the BP powder is impregnated by the chemical agents. Therefore, the individual M_{BP} as tabulated in APPENDIX I is less than 10g for all samples prepared.

4.1.2 Elemental Composition & Surface Morphology Analysis

Table 4.1: Elemental Composition for Sample ‘RAW’ and Sample ‘A7’

Element	Before Carbonized (RAW)		After Carbonized (A7)	
	Weight %	*Atomic %*	*Weight %*	*Atomic %*
Carbon, *C*	**60.96**	69.58	58.81	73.24
Oxygen, *O*	32.98	28.27	23.24	21.73
Silicon, *Si*	-	-	1.43	0.76
Chlorine, *Cl*	0.73	0.28	1.91	0.81
Potassium, *K*	5.33	1.87	-	-
Phosphorus, *P*	-	-	0.47	0.23
Zinc, *Zn*	-	-	14.13	3.23
Total	100	100	100	100

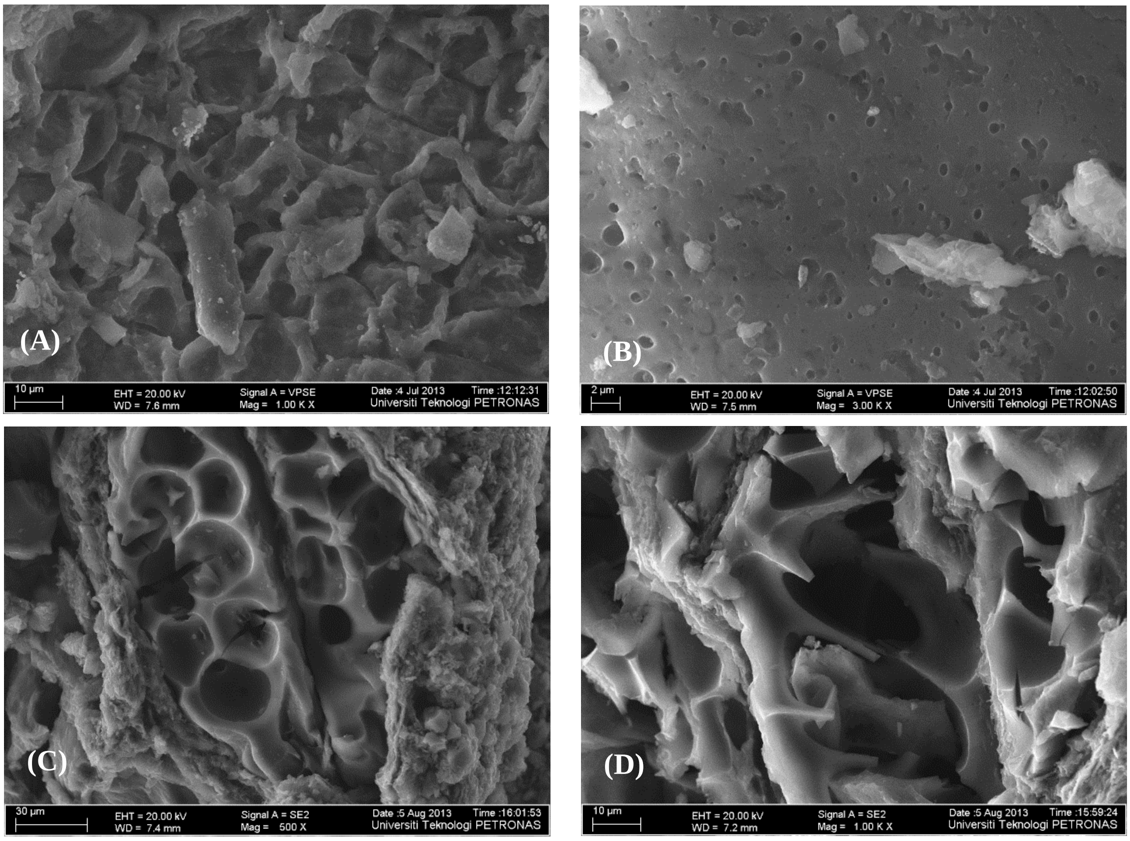

Figure 4.1 (A-D): FESEM Images for Selected Samples; (A) Raw banana peel, (B) Sample A7, (C) Sample A33, (D) Sample B37 – illustration of pore collapse at high carbonization temperature (800°C for 2 hours)

4.1.3 Surface Area & Porosity Analysis

Table 4.2: Surface Area and Porosity Results for Selected Samples

Sample	**Act. Agent**	**IR**	**Car. Temp (°C)**	**Car. Time (min)**	**S_{BET} (m^2/g)**	**V_T (cm^3/g)**	**D (nm)**
A1	$ZnCl_2$	1:1	400	60	28.0863	0.02438	4.1611
A7	$ZnCl_2$	1:2	400	60	12.1171	0.01344	4.7238
A10	$ZnCl_2$	1:2	500	120	38.0080	0.00694	2.7089
A20	**H_3PO_4**	**1:1**	**400**	**120**	**256.6347**	**0.01356**	**0.2470**
B7	$ZnCl_2$	1:2	400	60	7.7014	0.01004	5.9098
B16	$ZnCl_2$	1:3	500	120	2.2814	0.00470	9.1840
B21	H_3PO_4	1:1	500	60	1.3222	0.00138	3.6747
B34	H_3PO_4	1:3	500	120	3.8339	0.00381	1.0012
B35	H_3PO_4	1:3	600	60	2.7250	0.00306	0.8131

***S_{BET}:** Surface Area by BET Theory; **V_T:** Total Pore Volume; **D:** Average Pore Diameter

4.1.4 Adsorption-Desorption Isotherm Analysis

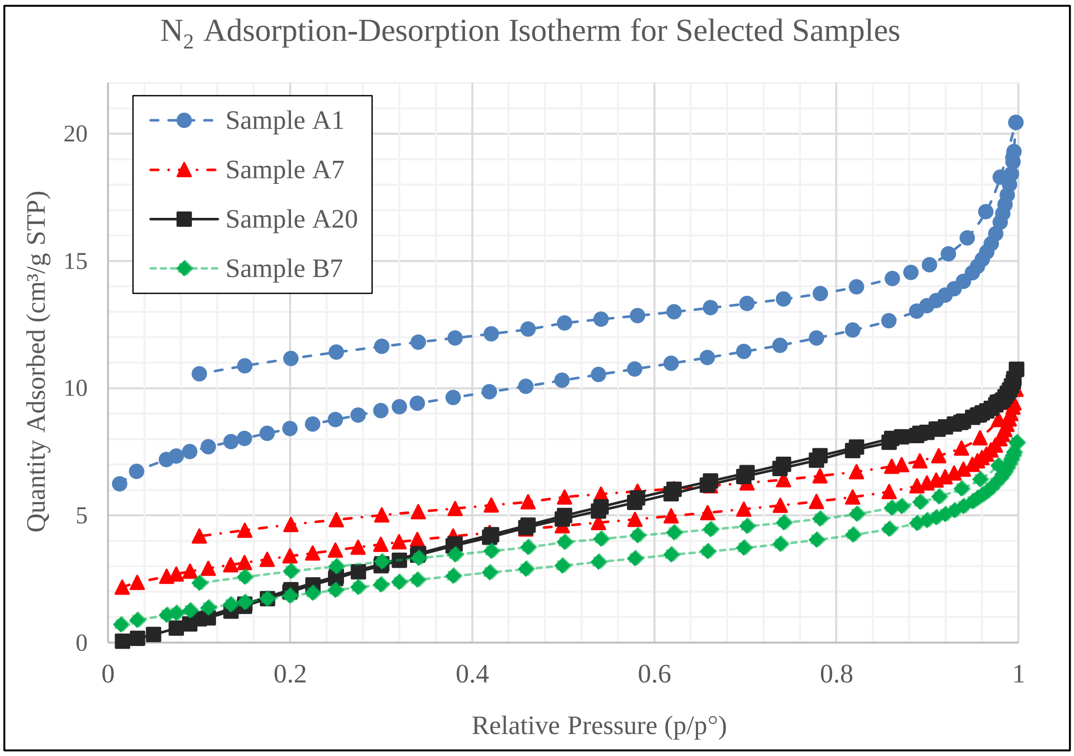

Figure 4.2: Nitrogen Adsorption-Desorption Isotherm for Selected Samples

4.1.5 Adsorption Capacity Test

Table 4.3: Concentration of Pollutants Adsorbed with Selected Samples

Pollutants	**Sample A20**		**Sample A32**	
	Initial Conc. (ppm)	**Final Conc. (ppm)**	**Initial Conc. (ppm)**	**Final Conc. (ppm)**
Crude Oil (O&G)	154	28.33	154	48.67
Lead (Pb)	10.17	1.58	10.17	3.39
Zinc (Zn)	4.85	2.70	4.85	4.12
Copper (Cu)	5.47	2.21	5.47	4.25

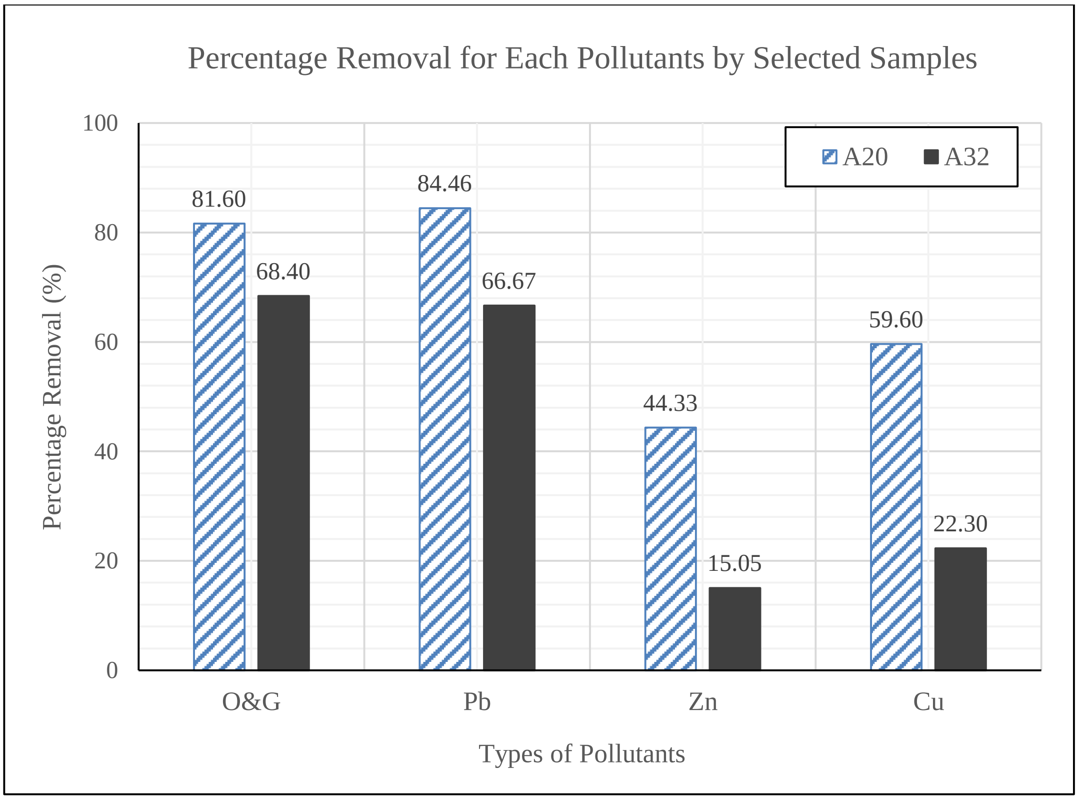

Figure 4.3: Percentage Removal of Each Pollutants by Selected Samples

4.2 RESULTS & DISCUSSION

The activated carbon yield from banana peel (BP) powder is satisfactory, achieving an average of 43.24% out of the samples prepared completely. The position of sample in the furnace during the carbonization phase is the major factor in affecting the individual yield of the sample. As the sample is placed nearer to the heating source, the more heat the sample receives which leads to larger amount of mass loss. Therefore, it is important to place all the samples as close as possible to the heating source in the furnace to ensure all samples receive uniform heating.

For the analysis using the Energy Dispersive X-ray (EDX) Spectroscopy, it is determined that the carbon content (weight) of the fresh BP powder (sample RAW) is 60.96% which indicates that banana peel is suitable to be converted into activated carbon since its carbon content falls within the desirable range (50% – 80%) (Wu, Tseng, & Hu, 2005). There are traces amount of potassium which is consider normal, because potassium is a common element found in banana fruit. On the other hand, sample A7 has been impregnated with zinc chloride ($ZnCl_2$) solution and carbonized. This is portrayed in the EDX analysis for the sample, as zinc content is found among other elements. The chlorine content is also higher in sample A7. Both of these observations can be attributed to the insufficient washing of the samples after the overnight impreganation with chemical reagent. Silicon and phosphorus can be considered as impurities in the sample which possibly originated from the crucible that holds the sample in the furnace during the carbonization process.

Based on the FESEM imaging, figure 4.1(A) which depicts the canal structure in raw banana peel sample, which is crucial to the production of activated carbon since the structure enables the banana peel powder to absorb the chemical reagent which activates the pore formation inside. On the other hand, figure 4.1(B) is the 3000 times magnification on sample A7. The image clearly shows that pores have already been formed on the sample at 400°C and 1 hour of carbonization. More well-structured pores are observed on the surface morphology of sample A33 as shown in figure 4.1(C), but at 500°C of carbonization temperature, the porous wall are broken slightly. This indicates that at 500°C of temperature, the heat is excessive for the sample which results in the knocking and breaking of the porous formation in the sample (Borhan & Kamil, 2012). Lastly, figure 4.1(D) shows the complete collapse of the pore formation in sample B37. This sample is prepared specifically to prove that excessive heat energy and long period of carbonization will lead to the destruction of porous structure in the carbon, which decreses the reactive sites for the adsorption process.

The effect of high carbonizing temperature is also shown in the results obtained from the surface area analyzer. Based on the results, it would appear that 400°C is the upper limit of the carbonization temperature for this BP based activated carbon as any higher than that produces unsatisfactory results. Samples B16, B21, B34 and B35, all carbonized at 500°C and 600°C respectively, yield low S_{BET} with the exception of sample A10, which is carbonized at 500°C for 2 hours, but yields comparitively higher S_{BET}. Besides, samples from group B, which are of the larger particle size (3.0mm), generally yield lower S_{BET} than that of the samples from group A (0.25mm). This could be due to the fact that larger particle size has less surface are for the chemical reagents to activate the sample during the impregnation phase. Besides, by comparing between samples A1 and A7, it can be deduced that high impregnation ratio is not desirable for using $ZnCl_2$ activation unless the adsorbent is carbonized at higher temperature as shown by the results of A10. Pore development occurs in the precursor due to the intercalation of the activating chemical, which is often a dehydarating agent, into the carbon structure (Tan, Ahmad, & Hameed, 2008). Thus, higher impregnation ratio should increase the amount of dehydrating agent that can be intercalated, therefore promoting more pore formation (Sudaryanto, Hartono, Irawaty, Hindarso, & Ismadji, 2006). However, there is a limit to the amount of these dehydating agent that can be uptake which beyond would reduce the pore formation. If there is too much of $ZnCl_2$ or H_3PO_4, it could lead to excessive reaction between the activating chemicals and the carbon, which may hinder the pore formation (Cao, Xie, Liv, & Bao, 2006). The excessive molecules of these activating chemicals may also decomposed into water, which caused gasification process to occur under high temperature. Apart from that, comparison between samples B16 and B34 shows that H_3PO_4 is just a slighly better activating chemical than $ZnCl_2$ since the S_{BET} of sample B34 is just a bit higher than that of B16. It is also worth noting that all the samples analyzed are found to contain pores in at least mesoporosity class and smaller. More importantly, sample A20 yields the largest S_{BET} (256.6347m^2/g) among the samples analyzed which could be attributed to the formation of micropores (pore diameter: 0.247nm) in the sample. The fact that sample A20 produces such significantly good results indicates that the set of parameters in preparing sample A20 is the best among the samples analyzed.

In the adsorption isotherem analysis, isotherm graphs of selected samples are compared. The classification of isotherm in this study is based on the IUPAC classification as shown in Figure 2.1. Based on the six identified isotherms, it is stated that all adsorption isotherm should fit at least one or a combination of the six identified types (Fletcher, 2008). Figure 4.2 shows that samples A1, A7 and B7 resemble closely the combination of Type II and Type III isotherms. These two type of isotherm is related to the gas-solid adsorption of carbon based material with meso- to macro- porosity that has a mixture of strong and weak adsorbate-adsorbent interaction. Although the average pore diameter results of these samples are of the microporostiy range, their surface areas are relatively small, thus affecting their isotherm to follow Type II and Type III which generally describes the adsorption isotherm of adsorbent with larger porosity. Figure 4.2 also depicts the isotherm for sample A20, which has the largest S_{BET} among all the other sample analyzed. Its adsorption isotherm clearly follows Type III which is related to the physical adsorption of gases whereby the adsorbent-adsorbate interaction is weak compared to the adsorbate-adsorbate interaction, a phenomenon that is commonly found in adsorbent with micropores. This is further proved by the results obtained from the BET surface area anlysis of the sample, which shows that the pores formed in it is of microporosity (pore diameter- 0.247nm).

In the adsorption capacity test, sample A20 and A32 are selected to be used in the batch adsorption of crude oil and heavy metals, which are Zn, Pb and Cu. Sample A20 (activated with H_3PO_4 with IR of 1:1 and carbonized at 400°C for 120 min) is selected for this test because of its high S_{BET} result in the porosity and surface area analysis. To act as a control for this test, sample A32 is selected due to its parameters being close to sample A20, since sample A32 is also carbonized at 400°C for 120 min and activated with H_3PO_4 but with IR of 1:3. Using sample A32 in the adsorption capacity test can also provide a comparison in the effectiveness of removing the targeted pollutants to that of sample A20. The result of the test shows that sample A20 is more effective compared to sample A32, in removing oil & grease (O&G) particles and the selected heavy metals from their respective solution, which could be attributed to the high value of S_{BET} in sample A20. Besides, among the three heavy metal, the BP based activated carbon is shown to have higher affinity in the adsorption of lead (Pb) as both samples, A20 and A32 produce the highest percentage removal for Pb, 84.46% and 66.67% respectively, compared to the Zn (44.33% and 15.05%) and Cu (59.60% and 22.30%). The BP based activated carbon is also proved to be effective in removing O&G particles as the percentage removal of crude oil for samples A20 and A32 are as high as 81.6% and 68.4% respectively.

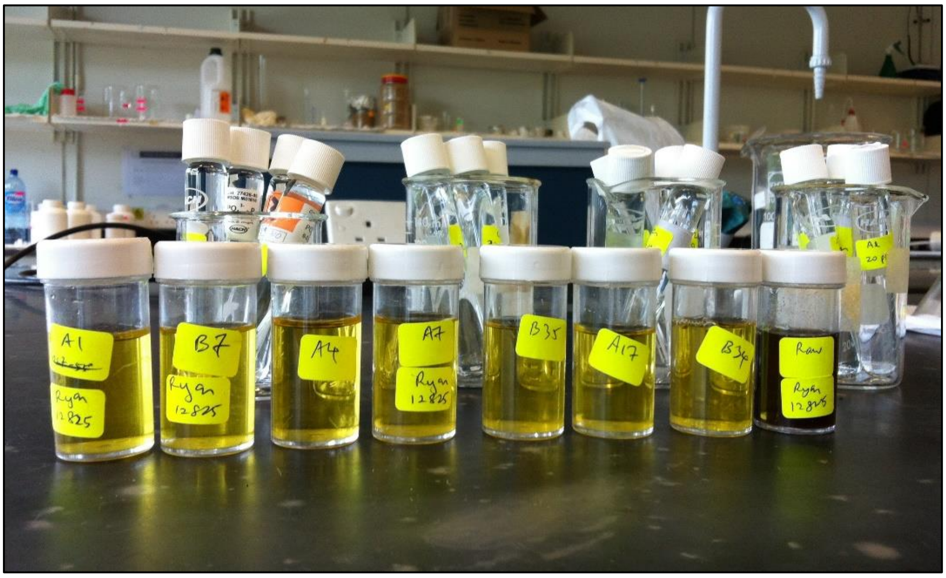

Figure 4.4: Photo of Collected Adsorption Test Solution in Separate Vials

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 CONCLUSION

The study in this project shows that the banana peel (BP) is a suitable precursor to be converted into activated carbon due to its high carbon content. Different parameters directly related to the preparation of the sample are manipulated to study the effects on the surface area and the pore formation of the activated carbon produced. Based on the results, it is proven that smaller particle size of precursor is more effective in getting chemically activated since the surface area of contact with the activating agent is larger. Besides, the impregnation ratio for banana peel based activated carbon should not be too high as it will hinder the pore formation, with better results obtained at IR = 1:1 for zinc chloride ($ZnCl_2$) and phosphoric acid (H_3PO_4) activation. Furthermore, the carbonization temperature for using BP as precursor should not be higher than 400°C as any higher will bring about the breakdown of the porous formation in the activated carbon and cause the reduction of effective surface area for the adsorption process. Chemical activation using H_3PO_4 is only slightly preferred than using $ZnCl_2$ as the S_{BET} for the samples produced with these two chemical agents do not differ much. The preparation condition for sample A20 is proved to be the most effective as supported by the results of the BET surface area analysis as well as the nitrogen adsorption-desorption isotherm of the sample which indicates meso- to micro- porosity in the sample, a trait that is highly desirable in activated carbon. BP based activated carbon is also proved to be particularly effective in removing crude oil particles and lead ions (Pb^{2+}) among other heavy metals such as copper (Cu^{2+}) and zinc (Zn^{2+}).

5.2 RECOMMENDATIONS

The project can enter the next phase of research which is to study on the adsorption process itself using the banana peel (BP) based activated carbon as adsorbent. There are plenty of parameters that can be studied such as the initial concentration of heavy metal ions in the solution, the amount of the adsorbent present, the pH of the solution, the temperature and contact time of the adsorption process. The sample with the highest S_{BET} from this project (sample A20) will be mass produced to conduct this study. The study on the adsorption process itself is important as it determines the most conducive environment for the pollutants to be adsorbed on the reactive sites of the BP based activated carbon which will highly increase the adsorption capacity of the adsorbent. During this study, the time required for the adsorption process to reach equilibrium can also be determined. Adsorption equilibrium is achieved when the rate of adsorption is equal to the rate of desorption, thus making any further adsorption highly unlikely (maximum amount of adsorbate bind on the reactive sites of the adsorbent). It is preferred that the adsorption equilibrium should be achieved as fast as possible while maintaining high percentage of pollutant removal.

Other biomass or agriculture waste can also be studied on the feasibility as precursor to be converted into activated carbon. Activated carbon made from different precursor will have different preference or selectivity in removing the pollutants from industrial effluent. By conducting similar studies on different raw materials, more data can be obtained and the biosorbent produced will be more effective in removing the target pollutants. These studies on biosorbent application, if successful, will be greatly beneficial to the environment since the waste material is reduced and reused in a way that can help preserve the environment while adding economic value to the otherwise worthless waste material.

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APPENIDICES

APPENDIX I:

List of Samples with Parameters & Preparation Status

Group A									
Particle Size : 0.25mm									
No	***Activating Agent***	***Impregnation Ratio***	***Activating Temp (°C)***	***Activating Time (min)***	***Impregnation***	***Carbonization***	***Weight before Carbonized (g)***	***Weight after carbonized (g)***	***Yield (%)***
1	$ZnCl_2$	1:1	400	60	YES	YES	8.27	3.18	38.45
2	$ZnCl_2$	1:1	400	120	YES	YES	9.18	4.82	52.51
3	$ZnCl_2$	1:1	500	60	YES	NO	9.01	-	-
4	$ZnCl_2$	1:1	500	120	YES	YES	8.45	3.14	37.16
5	$ZnCl_2$	1:1	600	60	YES	NO	8.42	-	-
6	$ZnCl_2$	1:1	600	120	YES	NO	8.27	-	-
7	$ZnCl_2$	1:2	400	60	YES	YES	9.64	2.89	29.98
8	$ZnCl_2$	1:2	400	120	YES	NO	8.00	-	-
9	$ZnCl_2$	1:2	500	60	YES	NO	8.34	-	-
10	$ZnCl_2$	1:2	500	120	YES	YES	8.92	3.14	35.20
11	$ZnCl_2$	1:2	600	60	YES	YES	8.32	2.87	34.50
12	$ZnCl_2$	1:2	600	120	YES	YES	8.49	2.92	34.39
13	$ZnCl_2$	1:3	400	60	YES	NO	8.74	-	-
14	$ZnCl_2$	1:3	400	120	YES	YES	8.70	4.91	56.44
15	$ZnCl_2$	1:3	500	60	YES	YES	8.80	3.25	36.93
16	$ZnCl_2$	1:3	500	120	YES	NO	9.24	-	-
17	$ZnCl_2$	1:3	600	60	YES	YES	9.57	2.8	29.26
18	$ZnCl_2$	1:3	600	120	YES	YES	8.21	3.25	39.59
19	H_3PO_4	1:1	400	60	YES	NO	7.92	-	-
20	H_3PO_4	1:1	400	120	YES	YES	9.01	3.99	44.28
21	H_3PO_4	1:1	500	60	YES	NO	9.64	-	-
22	H_3PO_4	1:1	500	120	YES	NO	8.44	-	-
23	H_3PO_4	1:1	600	60	YES	NO	8.45	-	-
24	H_3PO_4	1:1	600	120	YES	NO	8.92	-	-
25	H3PO4	1:2	400	60	YES	NO	8.90	-	-
26	H_3PO_4	1:2	400	120	YES	YES	8.20	3.83	46.71
27	H3PO4	1:2	500	60	YES	NO	8.92	-	-
28	H_3PO_4	1:2	500	120	YES	NO	8.32	-	-
29	H_3PO_4	1:2	600	60	YES	NO	9.57	-	-
30	H_3PO_4	1:2	600	120	YES	NO	8.74	-	-
31	H_3PO_4	1:3	400	60	YES	NO	9.20	-	-
32	H_3PO_4	1:3	400	120	YES	YES	7.99	4.82	60.33
33	H_3PO_4	1:3	500	60	YES	YES	8.34	4.37	52.40
34	H_3PO_4	1:3	500	120	YES	NO	8.32	-	-
35	H_3PO_4	1:3	600	60	YES	NO	9.01	-	-
36	H_3PO_4	1:3	600	120	YES	NO	8.92	-	-

Group B

Particle Size : 3.00mm

No	***Activating Agent***	***Impregnation Ratio***	***Activating Temp (°C)***	***Activating Time (min)***	***Impregnation***	***Carbonization***	***Original Sample Weight (g)***	***Weight after carbonized (g)***	***Yield (%)***
1	$ZnCl_2$	1:1	400	60	YES	NO	9.42	-	-
2	$ZnCl_2$	1:1	400	120	YES	NO	8.49	-	-
3	$ZnCl_2$	1:1	500	60	YES	NO	8.74	-	-
4	$ZnCl_2$	1:1	500	120	YES	NO	8.71	-	-
5	$ZnCl_2$	1:1	600	60	YES	NO	8.84	-	-
6	$ZnCl_2$	1:1	600	120	YES	YES	8.30	3.11	37.47
7	$ZnCl_2$	1:2	400	60	YES	YES	8.82	2.95	33.45
8	$ZnCl_2$	1:2	400	120	YES	YES	9.10	6.94	76.26
9	$ZnCl_2$	1:2	500	60	YES	NO	9.34	-	-
10	$ZnCl_2$	1:2	500	120	YES	NO	8.92	-	-
11	$ZnCl_2$	1:2	600	60	YES	NO	8.30	-	-
12	$ZnCl_2$	1:2	600	120	YES	NO	8.49	-	-
13	$ZnCl_2$	1:3	400	60	YES	NO	7.83	-	-
14	$ZnCl_2$	1:3	400	120	YES	NO	8.78	-	-
15	$ZnCl_2$	1:3	500	60	YES	NO	9.44	-	-
16	$ZnCl_2$	1:3	500	120	YES	YES	8.45	3.46	40.95
17	$ZnCl_2$	1:3	600	60	YES	YES	8.92	1.31	14.69
18	$ZnCl_2$	1:3	600	120	YES	YES	8.90	3.91	43.93
19	H_3PO_4	1:1	400	60	YES	NO	8.34	-	-
20	H_3PO_4	1:1	400	120	YES	YES	8.49	6.72	79.15
21	H_3PO_4	1:1	500	60	YES	YES	8.74	3.31	37.87
22	H_3PO_4	1:1	500	120	YES	NO	8.70	-	-
23	H_3PO_4	1:1	600	60	YES	NO	8.45	-	-
24	H_3PO_4	1:1	600	120	YES	NO	8.92	-	-
25	H3PO4	1:2	400	60	YES	NO	8.90	-	-
26	H_3PO_4	1:2	400	120	YES	NO	8.34	-	-
27	H3PO4	1:2	500	60	YES	NO	8.92	-	-
28	H_3PO_4	1:2	500	120	YES	NO	8.49	-	-
29	H_3PO_4	1:2	600	60	YES	NO	8.74	-	-
30	H_3PO_4	1:2	600	120	YES	NO	7.90	-	-
31	H_3PO_4	1:3	400	60	YES	NO	8.34	-	-
32	H_3PO_4	1:3	400	120	YES	NO	8.32	-	-
33	H_3PO_4	1:3	500	60	YES	YES	8.42	3.04	36.10
34	H_3PO_4	1:3	500	120	YES	YES	8.52	4.95	58.10
35	H_3PO_4	1:3	600	60	YES	YES	8.90	3.4	38.20
36	H_3PO_4	1:3	600	120	YES	NO	8.34	-	-

APPENDIX II:

Elemental Composition Determined by Energy Dispersive X-Ray (EDX)

for Sample RAW & Sample A7

Raw

04/07/2013 12:34:09

Spectrum processing :

No peaks omitted

Processing option : All elements analyzed (Normalised)

Number of iterations = 4

Standard :

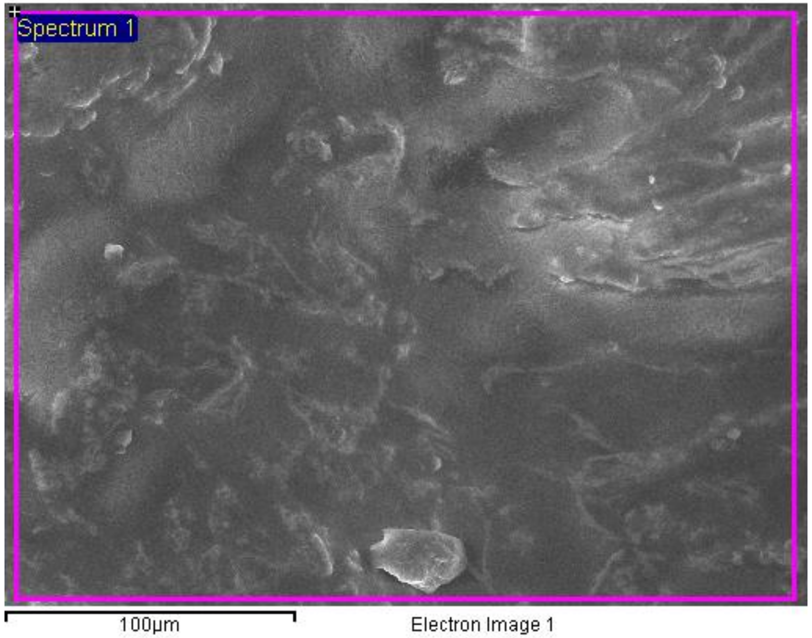
C   CaCO3   1-Jun-1999 12:00 AM

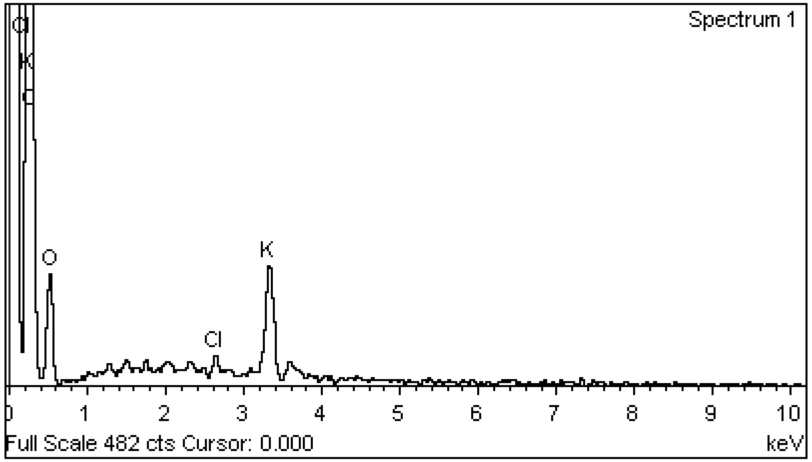
O   SiO2   1-Jun-1999 12:00 AM

Cl   KCl   1-Jun-1999 12:00 AM

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

Element	Weight%	Atomic%
C K	60.96	69.58
O K	32.98	28.27
Cl K	0.73	0.28
K K	5.33	1.87
Totals	100.00	





A7

04/07/2013 12:28:00

Spectrum processing :

No peaks omitted

Processing option : All elements analyzed (Normalised)

Number of iterations = 5

Standard :

C CaCO3 1-Jun-1999 12:00 AM

O SiO2 1-Jun-1999 12:00 AM

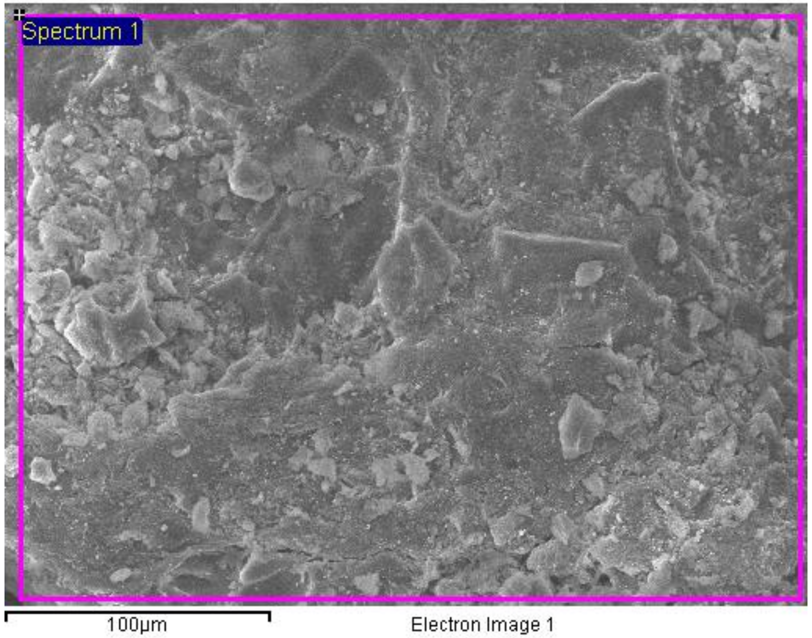
Si SiO2 1-Jun-1999 12:00 AM

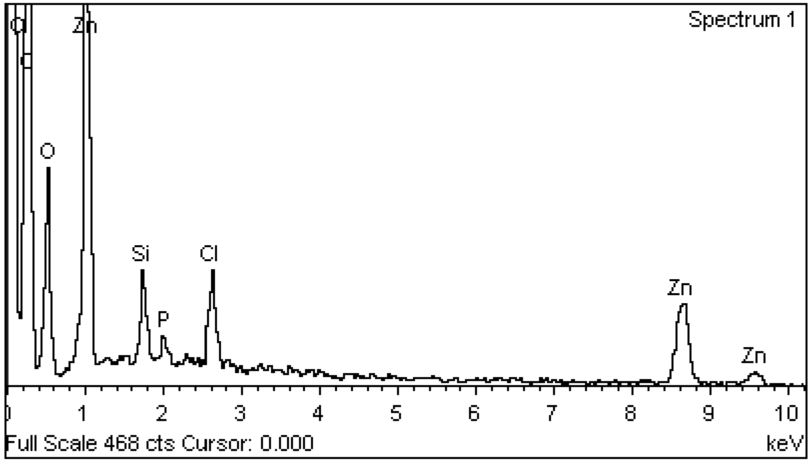
P GaP 1-Jun-1999 12:00 AM

Cl KCl 1-Jun-1999 12:00 AM

Zn Zn 1-Jun-1999 12:00 AM

Element	Weight%	Atomic%
C K	58.81	73.24
O K	23.24	21.73
Si K	1.43	0.76
P K	0.47	0.23
Cl K	1.91	0.81
Zn K	14.13	3.23
Totals	100.00	



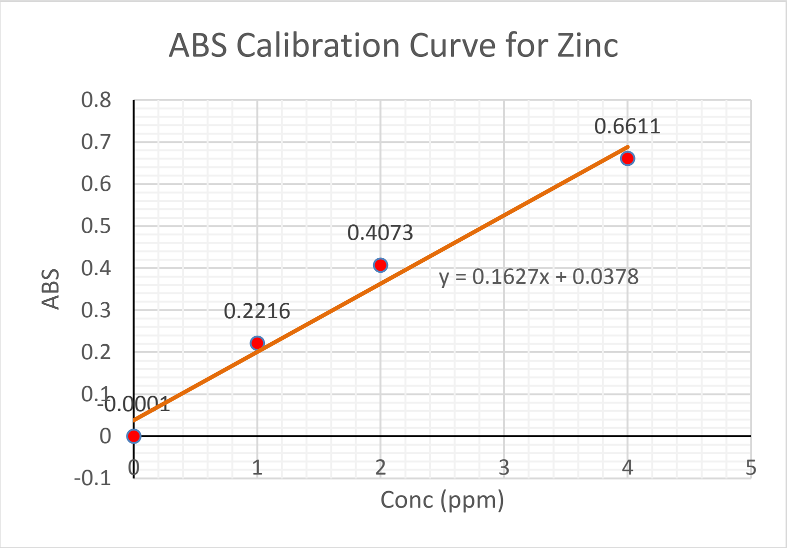


APPENDIX III:

Adsorption Capacity Test Results

(A) Zinc

Conc. (ppm)	ABS
0	-0.0001
1	0.2216
2	0.4073
4	0.6611



Gradient = 0.1627
Y-intercept = 0.0378

Coefficient:
K3 = --
K2 = --
K1 = 1.627 x 10^{-1}
K0 = 3.782 x 10^{-2}

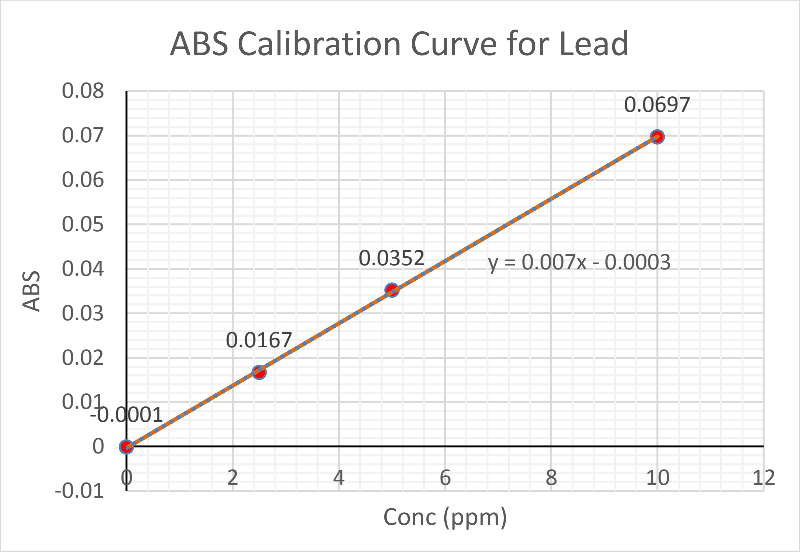
Correction Coefficient: 0.9902

Tabulated Data of ABS of Zinc and the Concentration for Each Sample

Sample	ABS (Initial)	Initial Conc. (ppm)	ABS (Final)	Final Conc. (ppm)	Percentage removal (%)
A20	0.8275	4.85	0.4770	2.70	44.3299
A32	0.8275	4.85	0.7075	4.12	15.0516

(B) Lead

Conc. (ppm)	ABS
0	-0.0001
2.5	0.0167
5	0.0352
10	0.0697



Gradient = 0.007
Y-intercept = -0.0003

Coefficient:
K3 = --
K2 = --
K1 = 7.00686 x 10^{-3}
K0 = -2.8000 x 10^{-4}

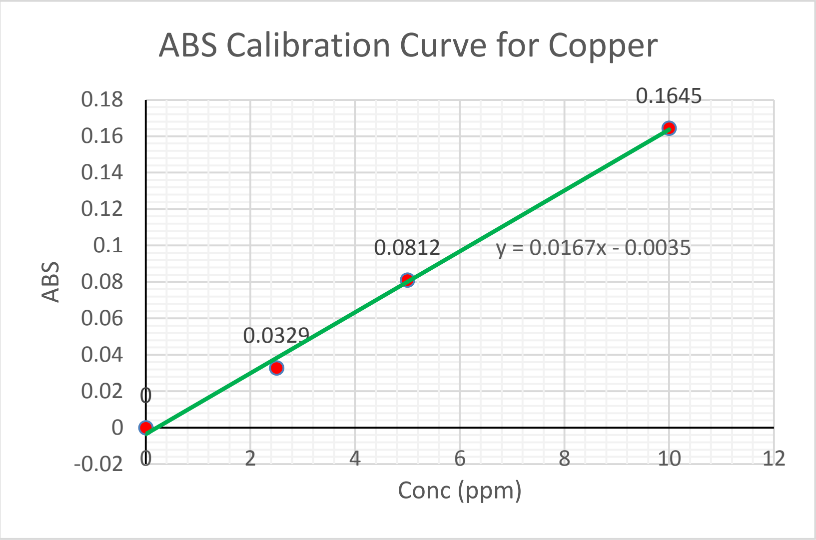
Correction Coefficient: 0.9999

Tabulated Data of ABS of Lead and the Concentration for Each Sample

Sample	ABS (Initial)	Initial Conc. (ppm)	ABS (Final)	Final Conc. (ppm)	Percentage removal (%)
A20	0.071	10.17	0.0108	1.58	84.46411
A32	0.071	10.17	0.0235	3.39	66.66667

(C) Copper

Conc. (ppm)	ABS
0	0
2.5	0.0329
5.0	0.0812
10.0	0.1645



Gradient = 0.0167
Y-intercept = -0.0035

Coefficient:
K3 = --
K2 = --
K1 = 1.672 x 10^{-2}
K0 = -3.500 x 10^{-3}

Correction Coefficient: 0.9986

Tabulated Data of ABS of Copper and the Concentration for Each Sample

Sample	ABS (Initial)	Initial Conc. (ppm)	ABS (Final)	Final Conc. (ppm)	Percentage removal (%)
A20	0.0879	5.47	0.0335	2.21	59.59781
A32	0.0879	5.47	0.0675	4.25	22.30347

(D) Crude Oil

Tabulated Data of Total Oil/Grease (TOG) Analysis

Sample	**Trial 1 (ppm)**	**Trial 2 (ppm)**	**Trial 3 (ppm)**	**Average (ppm)**
Pure (Before Adsorption)	145	165	152	154
A20	30	27	28	28.33
A32	33	35	78	48.67

Crude Oil Percentage Removal for Each Samples

Sample	**Initial Conc. (ppm)**	**Final Conc. (ppm)**	**Percentage removal (%)**
A20	154	28.33	81.60173
A32	154	48.67	68.39827