MEA WASTEWATER TREATMENT VIA BANANA PEEL BASED ACTIVATED CARBON

by

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14835

Dissertation submitted in partial fulfilment of

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Universiti Teknologi PETRONAS

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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the

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BACHELOR OF CHEMICAL ENGINEERING (HONS)

Approved by,

____
(Mr.Azry Borhan)

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

Jan 2015

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.

VIKNESWARAN A/L ANALAGAN

ABSTRACT

The main purpose of this project is to study the potential of using banana peel (BP) as bio-sorbent in removal of mono-ethanolamine (MEA) from industrial waste water. The study emphasizes on the parameters involved in the preparation phase of the BP adsorbent, such as particle sizes, impregnation ratio, carbonization temperature and duration. The dried BP is first grinded into two different particle sizes (0.25mm and 5.00mm), then chemically activated using potassium hydroxide (KOH) and carbonized at different sets of temperature (400^{o}C – 600^{o}C) and duration (1 – 2 hours) 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 analyser (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 characterisation result, sample A11 which is of particle size of 0.25mm, activated using potassium hydroxide (KOH) at 1:1 impregnation ratio, carbonized at 400^{o}C for 2 hours, is found to have the largest S_{BET} (259.5643 m^2/g). The total pore volume (V_T) of sample A11 is 0.01464cm^3/g while its average pore diameter (D) is 0.2498nm. The produced BP based activated carbon samples are tested for their adsorption capacity of MEA by testing for the Chemical Oxygen Demand to determine the highest percentage removal of MEA in wastewater. The BP based activated carbon also tested for adsorption capacity of heavy metal ion. The heavy metal ion studied in this project is Nickel (Ni^{2+}), where the adsorption capacity of sample A11 is specifically studied. Sample A11 yields higher percentage removal of MEA in wastewater and also adsorption of Nickel (Ni^{2+}).

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CHAPTER 1: INTRODUCTION

In petrochemical industry, especially in natural gas processing plant, raw natural gas which contains carbon dioxide needs to be treated to remove the CO_2 prior to further processing activities. In other industries, CO_2 also has been removed from the flue gases before releasing the flue gases to atmosphere through stack. This is done to minimize the greenhouse effects and circuitously generate revenue to the company by selling the recovered CO2. The most commercially used technology is amine based CO_2 absorption systems. Currently, aqueous mono-ethanolamine (MEA) is widely used for removing carbon dioxide and hydrogen sulphide from flue gas streams.

1.1 Background of Study

This project is related to removal of Monoethanolamine (MEA) in wastewater using banana peel based activated carbon. There are few ways to remove MEA in wastewater, for instance, by adsorption, photo-fenton oxidation, photocatalytic degradation and also by membrane technology. Adsorption is substantially preferred for the removal of MEA in wastewater due to its high efficiency, high readiness of raw materials and its cost effectiveness. Besides that, 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).

Activated carbon is one of the preferable types of adsorbent used in wastewater treatment because of its highly porous characteristic. The huge surface area of the activated carbon will contribute to the adsorption process itself, since there are many reactive sites for the adsorbates to bind on the surface of the activated carbon. Activated carbon 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). Recently, many researchers conducted the study on the practicability of converting agricultural wastes like banana peel, coffee grounds, melon seeds and orange peels into activated carbon [1]. Activated carbon can be formed from an extensive range of raw materials. As long as the waste material contains sufficient carbon content, it can be capable as the precursor for the production of activated carbon. These adsorbents produced from agriculture wastes or biomass are known as 'bio-sorbent' (Ahalya, Ramachandra, & Kanamadi, 2003), (Nilanjana, Vimala, & Karthika, 2008).

The agricultural waste that will be experimented in this project is banana peel. Based on a study conducted by the Department of Agriculture, Malaysia produces 535,000 metric tons of bananas per year and the numbers have been increasing annually. Banana peel is an agriculture waste that is enormously reusable in many areas, such as being used as shoe polish, wart removal and itch relief from bug bites (R.W. Thompson, 2009).

Banana peel has the prospective to be used as bio-sorbent to remove harmful particles such as MEA and heavy metal ions from industrial effluents. This is because banana peel is easily accessible in Malaysia due to banana being one of the common fruits planted commercially in the country. Banana peel is low cost precursor as it is normally thrown away as wastes, hence making the production of activated carbon from banana peel very cost effective. In addition, banana peel is organic in nature, therefore 100% biodegradable and eco-friendly, where it being parallel with the concept of sustainability.

The main focus of this project is to study the prospective of using banana peel as bio-sorbent in removal of MEA in wastewater. The adsorption capacity is correlated with the porous structure where the activation of raw materials increases its efficiency. Study shows that, there are two methods used in carbon activation, which includes physical activation and chemical activation [1]. This project will highlights on particular parameters which involved in the preparation of banana peel bio-sorbent, such as particle sizes, impregnation ratio, carbonization temperature and period.

1.2 Problem Statement

Latterly, water pollution has become a threat to humans and environment due to unrestricted release of lethal substances [2]. MEA in wastewater has become one of the major environmental problems in oil and gas industries. MEA is an organic chemical compound which has both primary amine and a primary alcohol. MEA is produced by reacting ethylene oxide with ammonia [3]. Raw natural gas has to be treated to remove carbon dioxide (CO_2) in natural gas processing plant. However, during the process and maintenance time, a small portion of MEA is carried out and discharged into wastewater. As the Chemical Oxygen

Demand (COD) is high, treatment of MEA contaminated wastewater is essential in natural gas processing plant in order to protect natural environment. As there are no specific ways to measure MEA content in wastewater, COD, BOD and TOC were measured to study the amine concentration level in wastewater [4].

Pointing at carbon dioxide absorption process, the reaction between MEA and carbon dioxide will contribute to foaming problem. On the other hand, this foaming issue will eventually create few other problems such as increased amine loss, reduced absorption efficiency and diminished product gas quality which minimize the overall performance.

Figure 1 : Foaming problem in wastewater (Interleith, 2004)

Furthermore, MEA contaminated wastewater also be partly responsible to the minimization of wastewater treatment plant profit margin. As the amine concentration in wastewater causes COD level to overshoot 200,000 ppm and makes it not viable to be sent to the wastewater treatment plant, the MEA wastewater has to be kept for disposal. Therefore, this is conducive to waste disposal handling, which costs money and eventually minimizes the profit margin of the plant [5].

In addition, large release of MEA to wastewater treatment facilities can result in poor treatment and toxic shock to biologically active species. MEA is expected to partition (preferentially locate) in water when released to the environment. MEA biodegrades rapidly and it will bio accumulate in the aquatic food chain due to its water solubility and reactivity with other compounds. Large release of MEA can also affect the pH of nearby water, resulting in possible toxic shock to biologically active species. MEA also may react with acidic compounds in sewer stream and produce undesirable odours.

Figure 2 : Effect of MEA to aquatic life (fewresources.org)

On the other hand, heavy metal pollution has also become one of the serious environmental problems. Presence of heavy metals, even in small traces, is extremely toxic and harmful to environment to the point of upsetting the whole ecosystem in the polluted location. When effluent waste consist of heavy metals, for instance Nickel (Ni^{2+}) are directly or indirectly being discharged into the environment, it will cause serious environmental contamination and even threatening human life (Volesky, 1990a). When living organisms are exposed to extreme amount of heavy metal, the organisms' body system will be prominently affected, effects ranging from damage of central nervous system to corrosion of living tissue.

Removal of MEA and heavy metals has always been a challenge to scientists and engineers in this field. Bio-sorption has good prospective to develop a noble alternative for the removal of MEA and heavy metal ions in industrial wastewater. It is economically feasible and the precursor materials are easily available. However, extensive characterization study has to be carried out on banana peel, in order to determine the best preparation condition of converting the precursor to activated carbon. Activated carbon plays an important role of adsorbent due to its large surface area and porosity which aids in the removal of MEA and heavy metal ions.

1.3 Objective

The focal objective of this project is to study the possibility of using banana peel as a potential adsorbent in removing MEA and heavy metal ions from the industrial effluent. Besides that, the best preparation condition of converting banana peel to activated carbon is studied to determine the relationship between different preparation condition of the banana peel and the adsorption capabilities of the adsorbent. The efficiency of using banana peel as adsorbent in the removal of MEA and heavy metal ions is also determined from this project.

In summary, the objectives of this project are:-

a) To study the feasibility of using agricultural wastes (banana peel) as bio-sorbent in wastewater treatment.

b) To determine the best preparation condition (particle sizes, activating agent, impregnation ratio, carbonization temperature and period) to convert banana peel to activated carbon.

c) To study the removal efficiency of MEA and heavy metal ions in wastewater using banana peel based activated carbon

1.4 Scope of Study

This project focuses on discovering the best preparation condition (particle sizes, impregnation ratio, carbonization temperature and period) to convert banana peel to activated carbon so that it can be used as bio-sorbent to remove MEA and heavy metal ions in wastewater. Chemical activation method is used in this project instead of physical activation where the justification is included in next part of this report. Potassium hydroxide (KOH) is used in this project as the activating agent, which will activate the carbon content in banana peel. The carbonization temperature is limited to 400^{o}C – 600^{o}C, whereas the carbonization time is within 1 – 2 hour. This is because it has been proved from previous study that these ranges of temperature and time facilitate the formation of pores better. Besides that, the particle size that will be experimented in this project is 0.25mm and 5.0mm, meanwhile the impregnation ratio will be 1:1, 1:2 and 1:3. However, this project also discovers the effectiveness of the banana peel based activated carbon in terms of removing MEA and heavy metal ions (Ni^{2+}) from waste water.

1.5 Relevancy of Project

This project stresses on defining the best preparation condition to convert banana peel into activated carbon which will be used as adsorbent in removing MEA and heavy metal ions in wastewater. Bio-sorbent adsorption is believed to carry a substantial value in removing harmful substances such as MEA and heavy metal ions from wastewater. Thus, activated carbon derived from agricultural waste, banana peel is believed will be an efficient adsorbent in removal of MEA and heavy metal ions. Hence, this project is relevant as development of activated carbon derived from banana peel for MEA and heavy metal ions removal has not been widely studied yet.

1.5 Feasibility of Project

This project is feasible as the scope of experiment is narrowed whereby only four parameters (particle sizes, impregnation ratio, carbonization temperature and carbonization time) are tested. It is within ability to be executed with aids and guidance from the supervisor and the coordinator. The time frame for this project is about 28 weeks. According to the Gantt Chart, the project should be completed by week 26 (FYP II Week 12). It is promising that this project can be completed within the time allocated with the acquiring of equipment and materials needed.

CHAPTER 2 : LITERATURE REVIEW

Literature reviews provide a handy guide and a solid background to a particular topic. This chapter explores the subtopic of mono-ethanolamine (MEA), adsorption theory, activated carbon, and banana peel. This discussion concerns the works of the previous researches that related to this research.

2.1 Mono-ethanolamine (MEA)

According to Wikipedia, Mono-ethanolamine (MEA) is an organic chemical compound that is both a primary amine and a primary alcohol (due to the presence of hydroxyl group). This makes MEA useful in many industrial applications which include production of agricultural chemicals [6]. In addition, MEA is present in the formulation of detergents for laundry and dishwashing liquid. MEA acts as a weak base like other amines. Besides that, MEA is also flammable, colourless, and viscous liquid which has an odour of ammonia at room temperature. MEA is a corrosive and toxic upon exposure to human skin. In few countries such as Malaysia, Japan and Spain, the exposure limit of MEA should not exceed 2 – 3 ppm. MEA is one of the absorbent that has been used extensively in carbon dioxide removal [7]. MEA provides enough alkalinity to absorb carbon dioxide, which makes it to be used in many acid gas recovery systems. Scrubbing of carbon dioxide from flue gas using MEA is widely studied and it’s able to effect high volume of acid removal at a fast rate [8].

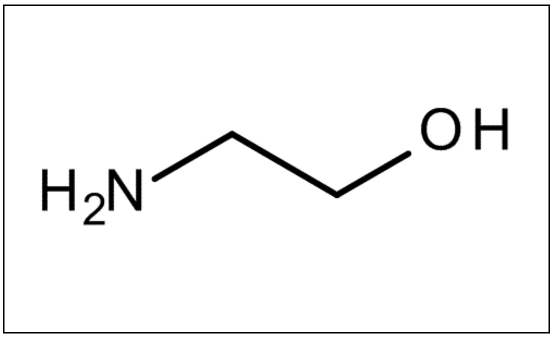


Figure 3 : Chemical structure of monoethanolamine

2.1.1 Mono-ethanolamine (MEA) in CO_2 Scrubbing

In aqueous solution, MEA can be used for scrubbing acidic molecules such as carbon dioxide and hydrogen sulphide. This characteristic makes MEA useful in gas stream scrubbing for the removal of CO_2 in flue gas emitted from oil and gas industries. Aqueous solution of MEA which acts as a weak base can dissolve CO_2 in the flue gas and neutralize the acidic compounds of CO_2.

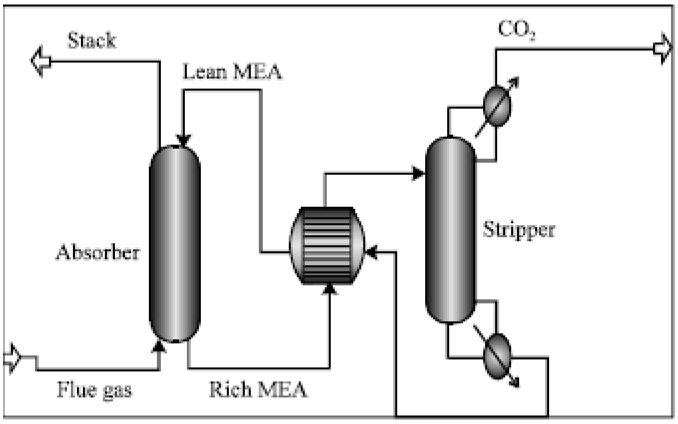


Figure 4 : Conventional MEA CO_2 capture flow sheet

Figure above shows the conventional MEA CO_2 capture flow sheet (Alie et al., 2004). The flue gas containing carbon dioxide enters the absorber counter-currently with the aqueous MEA. MEA as weak base will reacts exothermally with carbon dioxide which is a weak acid to form a water soluble salt. The salt solution rich with MEA will then be pre-heated and then sent to a stripper. In the stripper, the solution is separated back into CO_2 gas and MEA. CO_2 will leave through the top of the stripper while MEA will be recycled back to the absorber.

Scrubbing of CO_2 from flue gas using alkanolamines solution especially MEA is widely studied and used as it is very reactive and able to effect high volume of acid removal at a fast rate (Supap et al., 2008). Problem arises when small amount of MEA is carried out during the process and being discharged in the wastewater. This causes the increase in the chemical oxygen demand (COD) value of the wastewater. Another issue arises from this technology is the high energy requirement for it to be operated; hence various studies were conducted especially in process simulation to maximize the performance of the process.

2.2 Adsorption

Adsorption is defined as the adhesion of atoms, ions or molecules from a gas, liquid, or a dissolved solid to a 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 [9]. Absorption involves the whole volume of the material, meanwhile adsorption is a surface based process only. In a bulk material, all the bonding requirements of the constituent atoms of the material are filled by other atoms in the material. However, atoms on the surface of the adsorbent are not wholly surrounded by other adsorbent atoms and therefore can attract adsorbates. Adsorption falls under 2 types of category, which are physisorption (physical adsorption) and chemisorption (chemical adsorption). Physisorption is a process where the electronic structure of the molecule hardly unsettled upon adsorption. The exertion of attractive forces by all molecules, especially molecules at the surface of a solid is the reason for physical adsorption to occur. Physisorption comprises weaker bonding force (Van der Waals force) between the molecules. It generally occurs among the adsorbed molecules and the adsorbent internal pore surface. In contrast, chemisorption generally involves strong chemical bonding (covalent bond). The process is also highly specific on the adsorbate molecules and more selective [9].

Adsorption methods can be studied using several methods. The parameters that are regularly studied in adsorption are the adsorption temperature, contact time, effects of solution pH, adsorbent dosage and adsorbate concentration present in the solution (Philomina & Enoch, 2012). Studies show that the adsorption is most favourable in higher temperature, pH around 4 to 5, and contact time in range of 30 to 40 minutes. Shorter time for adsorption to reach equilibrium is affected by higher amount of adsorbate concentration and adsorbent dosage.

Adsorption process can be described precisely using 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 numerous existing adsorption isotherm, such as the Linear, Freundlich, Langmuir and the Brunauer, Emmett and Teller (BET) isotherm. (Geankoplis, 2003). BET theory is normally used to describe and approximate the adsorption of gas molecules on a solid surface by assuming multilayer adsorption.

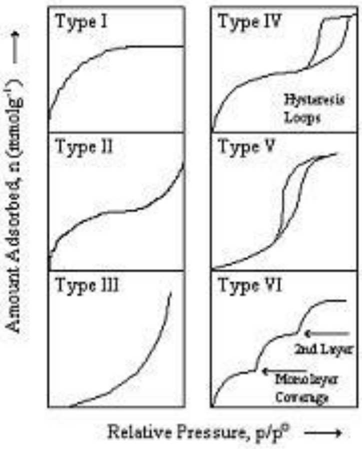


Figure 5 : IUPAC classification of adsorption isotherm

Figure above shows the IUPAC classification of adsorption isotherm according to the shape of the curves. The Type I isotherm are known by microporous solids having comparatively small external surfaces, for instance molecular sieve zeolites and activated carbon whereby the limiting uptake is being governed by the available micropore volume rather than by the internal surface area. Type II isotherm is the common form of isotherm where it has characteristics of non-porous or macroporous adsorbent which represents unlimited monolayer-multilayer adsorption. Type III isotherm is frequently related with water vapour adsorption on pure non-porous carbons or when the adsorbent-adsorbate interaction is weak compared to the adsorbate-adsorbate interaction. Type IV isotherm commonly have hysteresis loop, which is connected with capillary condensation taking place in mesopore, and limiting the uptake over a range of high p/p°. Type V isotherm is associated to Type III isotherm where the adsorbate-adsorbate interaction is known to be weak. Finally, type VI isotherm signifies stepwise multilayer adsorption on an even non-porous surface (Sing, 1982).

2.3 Activated Carbon

Activated carbon is charcoal that has been treated with oxygen to open up millions of tiny pores between the carbon atoms [10]. One gram of activated carbon has a surface area in excess of 500m^2, due to its high degree of micro porosity. The surface area of activated carbon is very large, where one pound of carbon provides a surface area equivalent to six football fields [11]. Since there are more reactive sides for the adsorbates to bind on the surface of the activated carbon, the large surface area of the activated carbon will contribute to the adsorption process itself. Using a controlled atmosphere and heat, the carbon-based material can be transformed to activated carbon by thermal decomposition in a furnace. Due to this, a grid of sub-microscopic pores will be produced, where the adsorption process occur. There are several shapes and sizes of pores in activated carbon, where the pores size can be classified to six types.

Table 1 : IUPAC Classification of Pore Sizes [12]

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

Activated carbon can be derived from a variety of precursors via physical or chemical activation. Physical activation is regularly 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 existence of steam, carbon dioxide, or air at temperatures in the range of 800 - 1000°C. Chemical activation is usually carried out in one step, which comprises of impregnation of the raw material with activating agent, such as phosphoric acid (H_3PO_4), zinc chloride ($ZnCl_2$), potassium bicarbonate (K_2CO_3), sodium hydroxide (NaOH) or potassium hydroxide (KOH) and then heating the mixture to temperatures of 400 - 800°C to instantaneously form and activate the carbon (Marsh & Rodriguez-Reinoso, 2006).

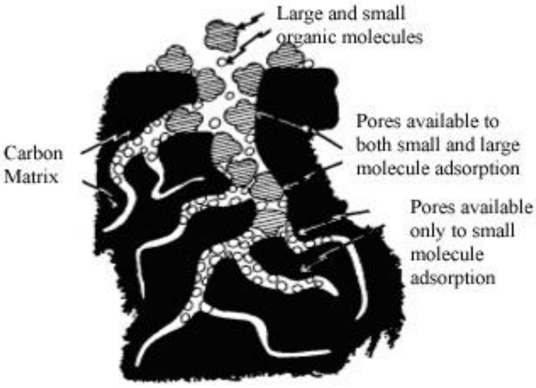


Figure 6 : Activated carbon particle

Chemical activation offers several 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 regularly 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).

In general, the yield of activated carbon decreases with increase in activation temperature, activation time and impregnation ratio, while the pore characteristic develops with increase in the above stated parameters, mostly to an optimum value and decreases beyond (Adinata, Daud, & Aroua, 2007). It has been proved that the impregnation ratio, which is the weight ratio of impregnator to precursor and the activation temperature, affects the properties of the resultant activated carbons (Diao, Walawender, & Fan, 2002).

However, there is a boundary to the positive effects of temperature and the impregnation ratio to the activated carbon. Extreme heat energy given at high temperature or long time interval to the carbon is recognized to diminish the overall surface area of the activated carbon because of the knocking and breaking of some porous wall (Borhan & Kamil, 2012). Excessive high impregnation ratio can also cause extreme reaction between the activating chemical and the activated carbon, hence hinders the formation of pores (Cao, Xie, Liv, & Bao, 2006). According to Wu, Tseng and Hu, 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 sensible range after the carbonization phase. On top of that, the pore size of the banana peel bio-sorbent must be at least of mesopore level (20Å < D < 500Å) according to the IUPAC classification (Borhan & Kamil, 2012).

2.4 Banana Peel

Banana peel is the outer skin which covers the banana fruit. Bananas are the world's utmost popular fruit and one of the world's vital main foods, together with wheat, rice and maize. Bananas are produced in 135 countries and regions across the tropics and subtropics [13]. The huge majority of producers are smallholders farmers who grow the crop for either home consumption or for local markets. According to Food and Agriculture Organization of the United Nations, imports and exports of banana in world keep on increasing every year, from 2011 to 2013.

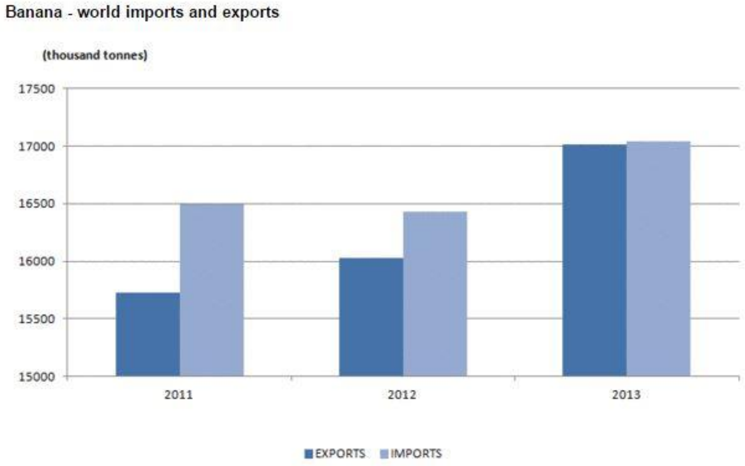


Figure 7 : World imports and exports of banana (FAO, 2014)

The second most popular fruits grown in Malaysia are banana. According to Malaysia Agriculture Stats 2014, Malaysia produces 535,000 metric tonnes of bananas per year [14]. Moreover, Cavendish type is the most common type of banana cultivated in Malaysia. As Malaysia being ranked 9th in Banana Production amongst Emerging Markets list, the large production of banana gave the perfect justification for choosing banana peel as precursor in this project.

As per the Survey Report on the Distribution and Waste Disposal of Bananas by the Association of Australian Banana Wholesalers 2006, 68.6 tons of bananas gathered as raw material waste every year. India has the largest banana waste as it was the largest producer of banana in the world with an annual production of 29.8 million metric ton [15]. Banana peel is composed mainly of lignin and cellulose (Deithorn & Mazzoni, 2014). Cellulose has the characteristics to be used as an adsorbent for the carboxyl and hydroxyl functional group which becomes the active binding site of the metal (Deithorn & Mazzoni, 2014). In addition, elements such as extractives, lipids, proteins, simple sugars, starches, water, hydrocarbons, ash, and other components with plentiful functional groups are also comprised. Futhermore, these components which contained in banana peel assist the metal complexations which directly help the isolating heavy metals as well as exhibit metal bio-sorption capacity (Deithorn & Mazzoni, 2014).

Figure 8 : Banana peel waste

Several studies on the subject of bio-sorption has been carried out using numerous 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), and pecan shells (Shawabkeh, Rockstraw, & Bhada, 2002). It was proved in previous studies that banana peel has high potential in removal of arsenic, copper, cadmium, chromium and iron contaminants (Philomina & Enoch, 2012).

Nevertheless, most of these studies are more associated to the factors that affect the adsorption process such as effect of dosage, temperature, pH, concentration and agitation (Philomina & Enoch, 2012), while others are studying on the kinetics and the thermodynamics of the adsorption isotherm using banana peel as adsorbent (Memon, et al., 2008). Energy Dispersive X-ray (EDX) Spectroscopy analysis on banana peel shows that the carbon content in it is about 49.60% (Suantak, Chandrajit, & Shri, 2012) which is sufficient to be commercially converted into activated carbon (Wu, Tseng, & Hu, 2005) . Therefore, all these studies on the application of banana peel based bio-sorbent verify the potential of using banana peel in waste water treatment.

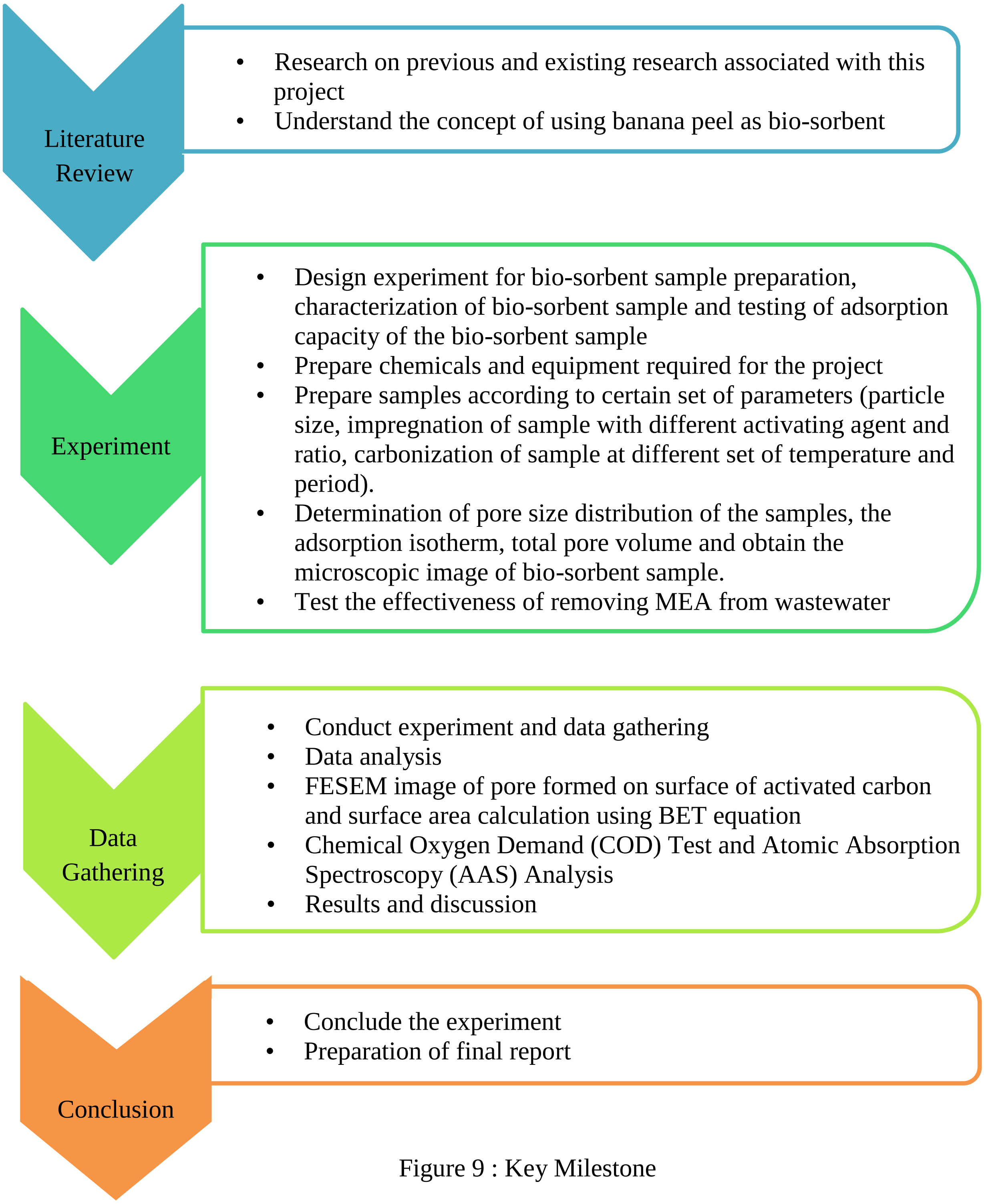
2.5 Previous Studies on Agricultural Waste Based Activated Carbon

Project	Authors	Objective	Method	Outcome
Bio-sorption of Heavy Metal Ions from Industrial Waste Water by Banana Peel Based Bio-sorbent	Phoon Kok Hoong, Mohd Faisal Taha, Azry Borhan	To study the potential of using banana peel as a bio-sorbent in removing heavy metal ions and oil/grease particles from industrial waste water	Chemical Activation (Zinc Chloride & Phosphoric Acid) and carbonized at different sets of temperature and duration into activated carbon.	-Phosphoric Acid is a better activating agent. -Pore Classification : Mesopores or smaller Best Preparation Condition (400^{o}C, 2 hours, 1:1)
Novel Low-Cost Activated Carbon Shell and Its Adsorptive Characteristics for Carbon Dioxide	N.A.Rashidi, S.Yusup, A.Borhan	To produce the microporous activated carbon resulting from coconut shell and study its applicability for carbon dioxide adsorption.	New activation method – One-step CO_2 activation involves single activation technique under CO_2 flow, without undergoing carbonization process under inert atmosphere.	The micro-porosity in the activated carbon is very useful for gas adsorption process, provided that the gases molecular diameter is between the ranges of 0.4 mm – 0.9 mm.
Development of Activated Carbon Derived from Banana Peel for Carbon Dioxide Removal	Subhashini Thangamuthu	To study the prospective of using banana peel as adsorbent for eliminating carbon dioxide from polluted air in atmosphere.	Chemical Activation (Potassium Hydroxide) and carbonized at different sets of temperature and duration into activated carbon.	Best Preparation Condition (400^{o}C, 2 hours, 1:1) -Pore Classification : Mesopores or smaller
Removal of Zinc, Chromium and Nickel from Industrial Waste-Water Using Banana Peels	M.N.A. Al-Azzawi, S.M.Shartooh, S.A.K. Al-Hiyaly	To study the potential of using banana peels (fresh, small pieces and powder) to remove zinc, chromium and nickel from industrial waste water	Banana peels (fresh, small pieces and powder) tested under environmental factors, pH, temperature and contact time	Powder form has the highest capability in removing all zinc, chromium nickel ions.
Bio-sorption of Cu (II) from Water by Banana Peel Based Bio-sorbent : Experiments and Models of Adsorption and Desorption	M.A. Hossain, H.H. Ngo, W.S. Guo, T.V. Nguyen	Banana peel based bio-sorbent was evaluated for adsorptive removal of copper from water and it's desorption capability.	The effects of experiment conditions such as pH, particle sizes, doses, contact time and temperature were investigated for copper adsorption onto banana peel.	The optimal conditions for bio-sorption were found at pH 6.5, bio-sorbent size of less than 75µ, dose of 0.5g/100ml and 1-hour contact time.

CHAPTER 3 : METHODOLOGY

In this chapter, detailed explanation of the steps in the process of designing the research and procedures to conduct the experiment have been presented. This explanation will be helpful in supporting this research work.

3.1 Key Milestone



- Research on previous and existing research associated with this project
- Understand the concept of using banana peel as bio-sorbent

- Design experiment for bio-sorbent sample preparation, characterization of bio-sorbent sample and testing of adsorption capacity of the bio-sorbent sample
- Prepare chemicals and equipment required for the project
- Prepare samples according to certain set of parameters (particle size, impregnation of sample with different activating agent and ratio, carbonization of sample at different set of temperature and period).
- Determination of pore size distribution of the samples, the adsorption isotherm, total pore volume and obtain the microscopic image of bio-sorbent sample.
- Test the effectiveness of removing MEA from wastewater

- Conduct experiment and data gathering
- Data analysis
- FESEM image of pore formed on surface of activated carbon and surface area calculation using BET equation
- Chemical Oxygen Demand (COD) Test and Atomic Absorption Spectroscopy (AAS) Analysis
- Results and discussion

- Conclude the experiment
- Preparation of final report

Figure 9 : Key Milestone

3.2 Research Methodology

3.2.1 Bio-sorbent sample preparation

Banana peel wastes will be collected from various places to be used in this project. They will be thoroughly washed in order to remove dirt and cut into smaller pieces. The washed banana peels will be kept in air to remove water from its surface and dried in microwave oven at 100°C overnight to remove excess moisture. Once the banana peels are completely dry, they will be grinded into smaller pieces until become powder form. After grinding, the banana peels will be sieved to separate particles of different size (0.25mm and 5.0mm) and keep in air tight container for activation [16].

Figure 10 : Powdered banana peel 0.25mm

Figure 11 : Grinded banana peel 5.0mm

3.2.2 Activation of carbon in banana peel

The activation agents that will be used in this project is potassium hydroxide (KOH). From the literature, the most common activating agents used are potassium hydroxide, phosphoric acid and zinc chloride. From the studies conducted for chemical activation with zinc chloride, many problems were identified such as incompetent chemical recovery, corrosion and environmental disadvantages. On the other hand, potassium hydroxide (KOH) is identified as one of the effective activating agent as it causes more localized reaction and effective for higher ordered materials. Therefore, potassium hydroxide (KOH) has been finalized to be used as activating agent since there are significant advantages of it. The impregnation ratios that will be studied in this project are 1:1, 1:2, and 1:3. The impregnation ratio studied in this project is 1:1, 1:2, and 1:3. Impregnation ratio is the dry weight of powdered banana peel, W_{BP} divided by the dry weight of activation agent used, W_{KOH}.

$$Impregnation\ ratio = \frac{W_{BP}}{W_{KOH}}$$

About 10g of banana peel bio-sorbent will be soaked in 100mL of activating chemical agent overnight. This procedure is to ensure that the reagents are completely soaked and adsorbed into banana peel powder.

Figure 12 : Banana peel powder soaked in KOH

The banana peel is then will be filtered from the chemical agents [16]. The residue, impregnated banana peel powder, is then will be carbonized in tubular furnace under steady flow of nitrogen gas (N_2) that act as carrier gas which promotes the pore formation in the sample. The ranges of temperature set for the carbonization process are 400°C, 500°C and 600°C for one hour and two hours durations. This is the point, where the banana peel powder turned into activated carbon [16].

Figure 13 : Banana peel before carbonization

Figure 14 : Banana peel after carbonization

When the samples burned in furnace have cooled down to room temperature, they are washed sequentially several times with hot distilled water (70°C) and 0.1M Hydrochloric Acid (HCl) until the pH of the washing solution reached 6-7. This step is taken so that there are no traces of chemicals or impurities which might trap in the pores of activated carbon and eventually, interrupt the adsorption activity of MEA and heavy metal ions later.

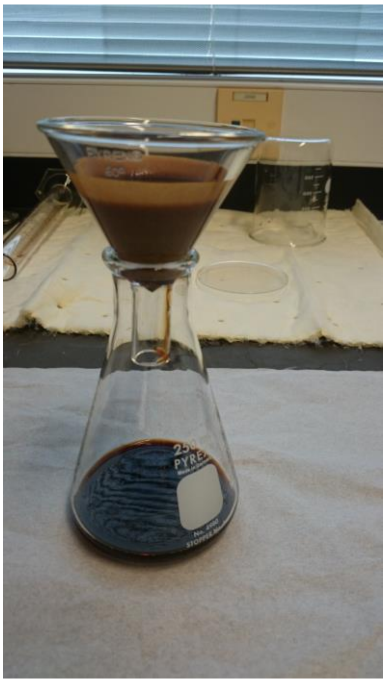


Figure 15 : Before washing

Figure 16 : After washing

Finally, the samples are placed in air tight container with correct labelling and stored in desiccator to prevent humidity contaminating the samples. Each set of parameters (impregnation ratio, carbonization temperature and duration) is used for two particle sizes of banana peel powder, which are 0.25mm and 5.00mm. In total, there are 36 samples to be prepared for all the combination of parameters under study. The preparation condition and the status of each sample is attached in APPENDIX, meanwhile the breakdown of sample preparation is shown in the figure below:

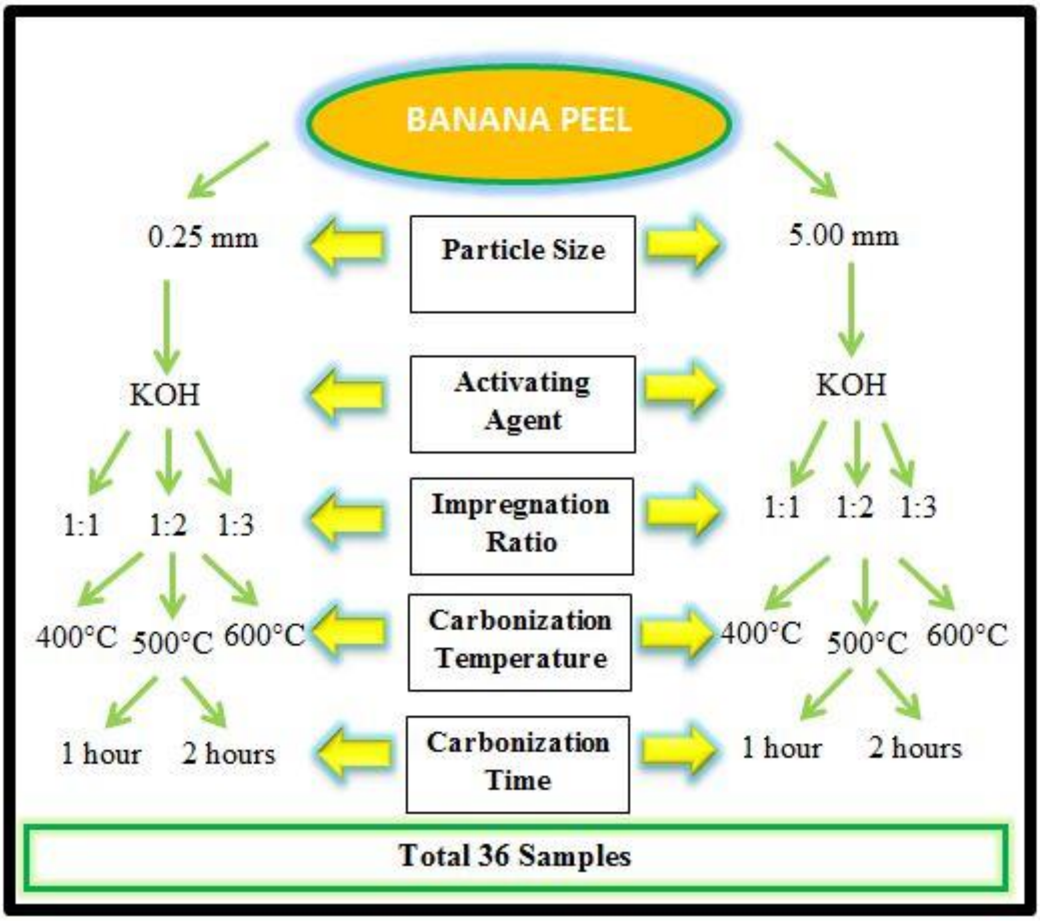


Figure 17 : Activated carbon sample preparation

3.3 Characterisation of Sample

There are few equipment used to analyse and characterize the sample. First and foremost, FESEM was used to provide magnification (10 – 100,000 times) of the surface of banana peel based activated carbon in order to confirm the formation of adsorption pores (macropores, mesopores and micropores) by comparing with the FESEM images of the raw banana peel (without activation). The elemental composition of the samples was determined using the Energy Dispersive X-ray Spectroscopy (EDX) in the FESEM equipment. Comparison of the elemental composition of the samples before and after activation was done in order to study the sufficiency of carbon content in raw banana peel and banana peel based activated carbon.

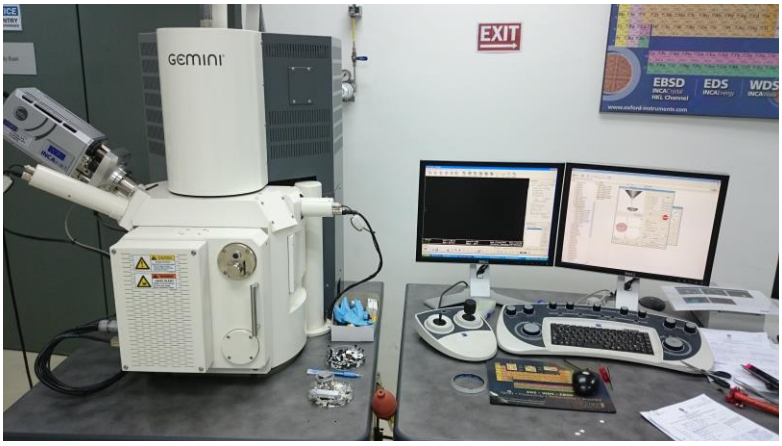


Figure 18 : Field Emission Scanning Electron Microscope (FESEM)

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

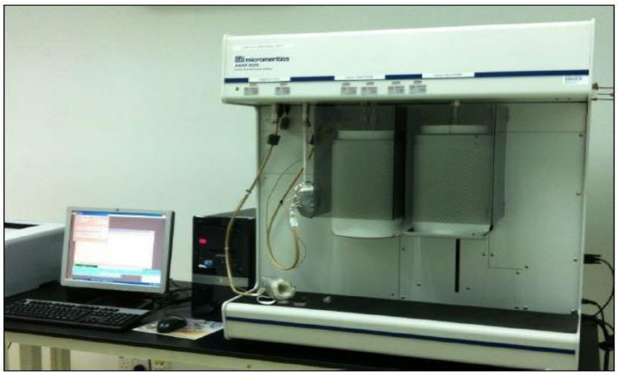


Figure 19 : Micromeritics ASAP 2020

3.4 Adsorption Capacity Test

3.4.1 Chemical Oxygen Demand (COD) Test

Spectrophotometer HACH DR 5000 was used to study the MEA adsorption capacity on banana peel based activated carbon. Since there are no specific equipment to measure MEA concentration, Chemical Oxygen Demand (COD) will be measured to determine the MEA concentration in the sample. COD is the amount of oxygen consumed by the organic compounds and in-organic matter which were oxidized in water. COD reflect the pollution degree of the water, and are the comprehensive index of the relative content of organics.

Figure 20 : Spectrophotometer HACH DR 5000

250ppm MEA stock solution is prepared by dissolving 0.062ml Mono-ethanolamine (C_2H_7NO) in 250ml distilled water. Adsorption capacity test is carried out by batch adsorption, where 1.0g banana peel based activated carbon is stirred at 100rpm in 10mL of MEA stock solution (250ppm) for 1 hour at room temperature. 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 and raw banana peel were used to act as an experiment control and to provide comparison of performance between the three samples. The experiment is repeated at different amine concentration (500ppm & 750ppm), different stirring speed (no stirring, 300rpm), different temperature (50^{o}C & 75^{o}C) and different pH (acid & alkali). The mixture is then filtered and the filtrate which is the test solution after adsorption is collected and tested for Chemical Oxygen Demand (COD). The sample will be reacted with an acidic solution of potassium dichromate in the presence of a catalyst (silver) and digested for 2 hours at a temperature of 150°C. Oxidizable organic compounds reduce the dichromate ion ($Cr2O7^{2-}$) to the chromic ion (Cr^{3+}). The test results are expressed as the number of milligrams of oxygen consumed per liter of sample (mg/Liter COD).

3.4.2 Nickel (Ni^{2+}) Removal Test

The potential of using banana peel based activated carbon to remove heavy metal ions is also explored in this study. Nickel Nitrate ($Ni(NO_3)_2$) solution was prepared by dissolving the salt crystal in distilled water. Molecular weight of $Ni(NO_3)_2$ is 290.81 g/mol, meanwhile molecular weight of Nickel is 58.6394 g/mol. Thus, dividing the molecular weight of $Ni(NO_3)_2$ with the molecular weight of Ni gives 4.959g of $Ni(N03)_{2.}$ Hence, using this weight of $Ni(N0_3)_2$ and dissolving it in 1L volume of distilled water will give a1000 ppm concentration of nickel solution. Using $M_1V_1 = M_2V_2$ formula, 50ppm concentration of $Ni(NO_3)_2$ solution was prepared. Adsorption capacity test is carried out by batch adsorption, where 3.0g banana peel based activated carbon is stirred at 100rpm in 200mL of Nickel solution (50ppm) for 1 hour at room temperature. The activated carbon sample that has the largest specific surface area (SBET) was used for this test. Residual adsorbate analysis was carried out at 15, 30, 45, 60, 75, 90, 105, and 120 minutes respectively. The samples were then filtered and final adsorbate concentration was measured using Atomic Absorption

Spectrometer. The experiment was repeated using another sample of activated carbon with almost similar parameters and raw banana peel for comparison purpose.

Figure 21 : Atomic Absorption Spectrometer

3.5 Tools and Equipment

No	Tools/Equipment	Uses
1	Beaker	Diluting KOH pellets
2	Conical flask	Preparing aqueous solutions of KOH, and H_3PO_4
3	Measuring cylinder	Measure volume of chemical activation agents
4	Sieves (0.25mm & 5.0mm)	To separate the particles of different sizes
5	Filter funnel and filter paper	Filtration of soaked banana peel
6	Tubular Furnace	Carbonization of banana peel
7	Grinder	Grind banana peel to powder form
8	Oven	Drying banana peel

9	Field Emission Scanning Electron Microscope (FESEM)	To provide magnified view (10 – 10,000 times) of the structure of activated carbon produced from the banana peel.
10	Micromeritics ASAP 2020	To determine the pore size distribution, specific surface area and porosity of the banana peel bio-sorbent by nitrogen adsorption-desorption isotherms.
11	Spectrophotometer (HACH DR 2800)	To test for Chemical Oxygen Demand (COD) in wastewater
12	Atomic Absorption Spectrometer (AAS)	To check Ni^{2+} concentration

3.6 Substance and Chemicals

No	Material	Uses
1	Banana Peel	To be used as raw material to develop activated carbon
2	Potassium Hydroxide (KOH)	To impregnate powdered banana peel by means of chemical activation to increase pore volume for adsorption
3	Hydrochloric Acid (HCl)	To wash the activated carbon so that there are no traces of chemicals or impurities which might trap in the pores of activated carbon
4	Nickel (II) Nitrate [$Ni(NO_3)_2$]	To prepare Nickel solution for Adsorption Capacity Test

3.7 Project Activities

3.7.1 Proposed Experiment Procedures for MEA Adsorption

Referring to the previous research done by Rengaraj, Arabindoo and Murugesan in their project, Preparation and Characterization of Activated Carbon from Agricultural Wastes, the procedures for the experiment are as follows [17].

1. Waste banana peels are collected from various sources and samples are prepared accordingly.
2. The washed banana peels are kept in air to remove water from its surface and dried in microwave oven at 100°C overnight.
3. The completely dried banana peels are grinded into smaller pieces until become powder form.
4. After grinding, the banana peels are sieved to separate particles of different size (0.25mm and 5.0mm) and kept in air tight container for activation.
5. About 10g of banana peel bio-sorbent is soaked in 100mL of activating chemical agent (potassium hydroxide) overnight. Make sure that the reagents are completely soaked and adsorbed into banana peel powder.
6. The banana peel is then filtered from the chemical agents and then the residue, is carbonized in tubular furnace under steady flow of nitrogen gas (N_2).
7. The ranges of temperature set for the carbonization process are 400°C, 500°C and 600°C for one hour and two hours durations.
8. FESEM is used to provide magnification (10 – 10,000 times) to the view for the surface morphology of banana peel bio-sorbent in ultra-high resolution images in order to confirm the formation of adsorption pores.
9. Micromeritics ASAP 2020 is used to analyse the pore size distribution, specific surface area and the porosity of the samples with N_2 adsorption-desorption, using nitrogen gas as adsorbate while being degassed at 350°C for 4 hours
10. Adsorption capacity test is carried out by batch adsorption, where 1.0g banana peel based activated carbon is stirred at 100rpm in 10mL of MEA stock solution (250ppm) for 1 hour at room temperature.
11. The experiment is repeated at different amine concentration (500ppm & 750ppm), different stirring speed (no stirring & 300rpm), different temperature (50°C & 75°C) and different pH (acid & alkali).

11. The mixture is then filtered and the filtrate which is the test solution after adsorption is collected and tested for Chemical Oxygen Demand (COD).
12. 2mL of filtrate was put into test tube containing COD Reagent and shake.
13. Thermo reactor is set at 150^{o}C and the samples are placed in the reactor for 2 hours.
14. The samples tested for COD using spectrophotometer (HACH DR 5000).

3.7.2 Proposed Experiment Procedures for Nickel (Ni^{2+}) Adsorption

1. 50ppm of $Ni(NO_3)_2$ stock solution is prepared by dissolving 0.496g of $Ni(NO_3)_2$ pellets using distilled water.
2. Adsorption capacity test is carried out by batch adsorption, where 3.0g banana peel based activated carbon is stirred at 100rpm in 200mL of Nickel solution (50ppm) for 1 hour at room temperature. The flask was covered with aluminium foil to seal the flask.
3. Residual adsorbate analysis was carried out at every 15 minutes for duration of 2 hours
4. The mixture is then filtered and the final adsorbate concentration was measured using Atomic Absorption Spectroscopy.

3.8 Gantt Chart

Table 2 : FYP I Gantt Chart

No	Detail	Week													
		1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Title Selection and Allocation	🟦													
2	Title and Supervisor Distribution		🟦												
3	Preliminary Research Work		🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦
4	Preparation of Extended Proposal				🟦	🟦	🟦								
5	Submission of Extended Proposal							🟦							
6	Proposal Defence								🟦						
7	Gathering Resources and Materials						🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦
8	Submission of Interim Draft Report													🟦	
9	Submission of Final Interim Report														🟦

Table 3 : FYP II Gantt Chart

No	Detail	Week													
		15	16	17	18	19	20	21	22	23	24	25	26	27	28
1	Literature Review	■	■	■	■	■	■	■							
2	Collection of banana peel	■	■					■							
3	Bio-sorbent sample preparation & chemical activation			■	■				■						
4	FESEM Analysis					■									
5	Micromeritics ASAP 2020 Analysis						■								
6	Chemical Oxygen Demand Test						■	■	■						
7	Submission of Progress Report								■						
8	Atomic Absorption Spectroscopy Analysis									■	■	■			
9	Pre - SEDEX											■			
10	Submission of Dissertation & Technical Paper													■	
11	Oral Presentation														■
12	Submission of Hardbound														■

CHAPTER 4 : RESULTS & DISCUSSION

In order to analyse and characterize the samples accordingly, several analysing equipment have been utilized. First and foremost, Field Emission Scanning Electron Microscope (FESEM) was used to give magnified images of the surface of activated carbon derived from banana peel. In addition, the pore size distribution, specific surface area as well as the porosity of the samples is determined by the nitrogen adsorption-desorption isotherms characterized by the Micromeritics ASAP 2020. This equipment operates using nitrogen gas as adsorbate while being degassed at 350°C for 4 hours. Atomic Absorption Spectrophotometer (AAS) was also used to measure the Ni^{2+} concentration.

4.1 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:

$$\text{Yield} = \frac{MAC}{MBP} \times 100\%$$

Where:

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 will be calculated. It is expected that although the weight of banana peel powder used for all samples is fixed at 10g, there will be some loss in banana peel powder mass during the transfer from the filter paper to the crucible for carbonization after the banana peel powder is impregnated by the chemical agent, potassium hydroxide (KOH).

4.2 FESEM Imaging & Elemental Composition Analysis

Table 4 : Elemental Composition of RAW material and Sample

Element	**Before Carbonization (RAW)**		**After Carbonization (A11)**	
	Weight %	**Atomic %**	**Weight %**	**Atomic %**
Carbon, C	60.99	70.88	59.74	71.32
Oxygen, O	29.32	25.58	26.17	23.46
Silicon, Si	0.32	0.16	0.57	0.29
Potassium, K	8.41	3.00	10.27	3.77
Chlorine	0.96	0.38	3.25	1.16
Total	**100**	**100**	**100**	**100**

It is determined from the analysis of Energy Dispersive X-ray (EDX) Spectroscopy that the carbon content (weight) of raw banana peel sample is **60.99%** , which indicates that banana peel is appropriate 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 [18]. On top of that, sample A11 has been impregnated with potassium hydroxide (KOH) solution and carbonized. This is shown in the EDX analysis for the sample, as potassium, K content is found among other elements. The oxygen, O content is also higher in sample A11. Both of these observations can be recognized as insufficient washing of the samples after the overnight impregnation with chemical reagent. Silicon and chlorine can be considered as impurities in the sample which probably originated from the crucible that holds the sample in the furnace during the carbonization process.

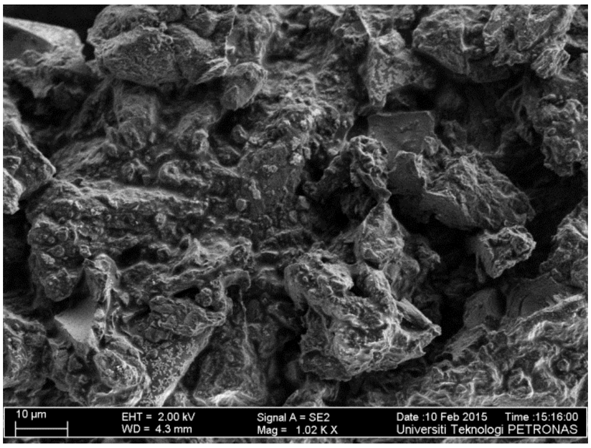


Figure 22 : RAW Sample FESEM Image

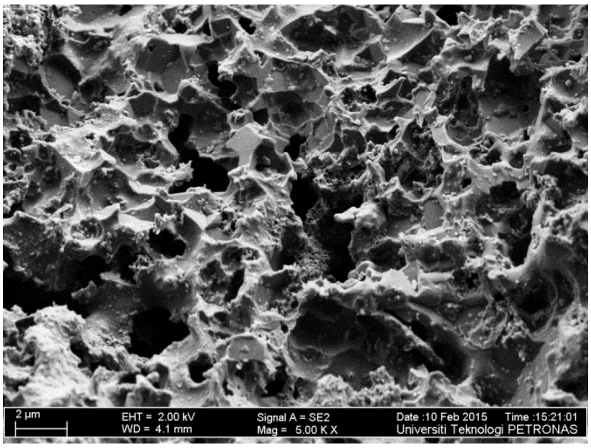


Figure 23 : A11 Sample FESEM Image

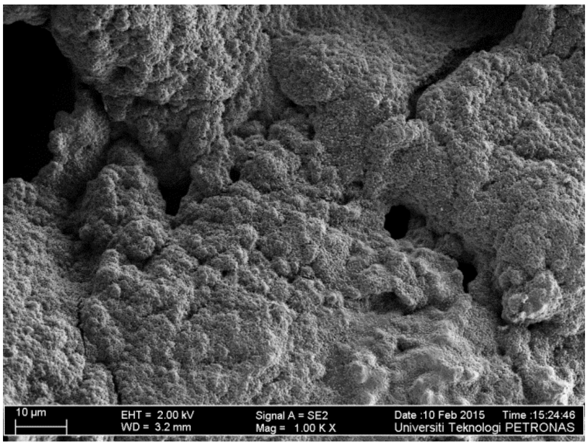


Figure 24 : B22 Sample FESEM Image

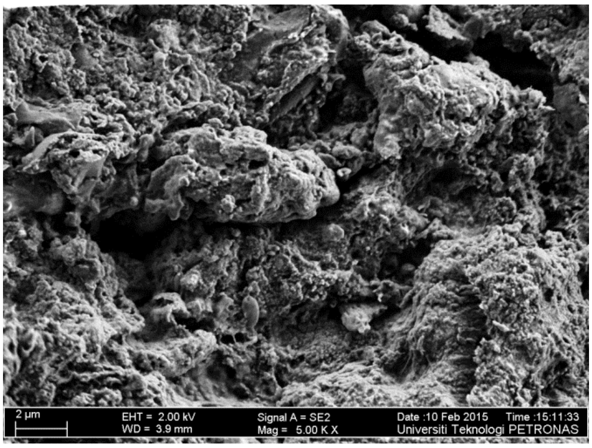


Figure 25 : B10 Sample FESEM Image

Based on the FESEM imaging, Figure 21 displays the passage construction in raw banana peel sample (0.25mm), which is vital in production of activated carbon. The canal allows the banana peel powder to absorb the chemical activation agent to activate pore development. In contrast, Figure 22 is the 5000 times magnification on sample A11. The image clearly shows that pores have already been formed on the sample at 400°C and two hours of carbonization. More well-structured pores are observed on the surface morphology of sample B22 as shown in Figure 23, but at 500°C of carbonization temperature for one hour, the porous wall are slightly broken. Furthermore, the effect of implying excessive heat during carbonization may results in the knocking and breaking of the porous formation in the sample (Borhan & Kamil, 2012). 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 decreases the reactive sites for the adsorption process. Figure 24 shows the magnified pore formation of raw material with particle size of 5.0mm, where it shows the complete collapse of the pore formation and the passage construction is not clearly seen as in raw material of 0.25mm.

4.3 Surface Area and Porosity Analysis

Table 5 : Surface area and porosity results for selected samples

Sample	Particle Size	IR	Car. Temp (°C)	Car. Time (min)	S_{BET} (m^2/g)	V_T (cm^3/g)	D (nm)
A1	0.25 mm	1:1	400	60	31.4678	0.1593	4.5137
A8	0.25 mm	1:2	600	60	12.5643	0.00294	0.7908
A11	**0.25 mm**	**1:1**	**400**	**120**	**259.5643**	**0.01464**	**0.2498**
A17	0.25 mm	1:1	500	120	255.3283	0.1185	0.1986
A20	0.25 mm	1:3	500	60	13.7594	0.00472	1.9763
B7	5.0 mm	1:2	400	120	8.4762	0.00614	2.6494
B12	5.0 mm	1:3	600	120	1.2975	0.00198	0.2839
B15	5.0 mm	1:2	400	60	7.8026	0.01273	6.0024
B18	5.0 mm	1:3	600	180	9.6327	0.00318	0.8653
B22	5.0 mm	1:1	500	60	2.8214	0.01587	4.2739

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

Table 5 shows the resulting surface area of the pore formed, total pore volume and average pore diameter on banana peel based activated carbon at different preparation conditions. Based on the results, it can be seen that 400°C is the maximum carbonization temperature for banana peel based activated carbon and any higher activation temperature than 400°C produces poor results.

Samples A8, A17, A20, B12, B18 and B22 are all carbonized at 500°C and 600°C, where it yield low S_{BET} with the exception of sample A11, which is carbonized at 400°C for 2 hours, but yields comparatively higher S_{BET}. Moreover, group B samples which are of bigger particle size (5.00mm) during grinding, yields smaller surface area, S_{BET} compared to group A samples with smaller particle size (0.25mm). This phenomenon occurs because larger particle size exposes less surface area for activation during impregnation phase, thus resulting in smaller S_{BET}.

Generally, pore widening will happen due to the increase in activation temperature and the impregnation ratio of KOH. Pore development occurs in the precursor due to the intercalation of the activating chemical, which is often a dehydrating 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 this dehydrating agent that can be uptake which beyond would reduce the pore formation. If there is too much of KOH, it could lead to excessive reaction between the activating chemicals and the carbon, which may hinder the pore formation (Cao, Xie, Liv, & Bao, 2006).

Apart from that, due to carbon gasification enhancement with elevated KOH ratio, the pore size in activated carbon is enlarged together with the porosity. Raising the activation temperature directly increases the reaction rate of C-KOH reaction, causing increased carbon burn-off. Since KOH reagent is a strong base, it facilitates the boundary with carbon atoms to increase the rate of dehydrogenation and oxidation, inviting the growth in tar formation and development of porosity (Mopoung, 2008). Samples containing large compositions of potassium element explain that high impregnation ratio yields potassium carbonate, K_2CO_3 and potassium oxide, K_2O during pyrolysis. Therefore, we can conclude that higher impregnation ratio forms insulating layer which covers the particles and reduces the interaction of pores and surrounding environment, thus resulting in lower activation rate (Mopoung, 2008).

Besides that, by comparing between samples A11 and B18, results show that high impregnation ratio is not desired for KOH activation as it reduces the efficiency of pore formation with smaller surface area compared to those which are impregnated at smaller ratio. The highly microporous activated carbon shifts to a different form, where the mesopores become governing in whole pore size distribution, especially exceeding the certain limit of activating agent (Örkün, Karatepe, and Yavuz, 2011). It is also noticeable that as the concentration of activating agent crosses its limit, there will be a significant change in pore size developments due to high composition of phosphorous which will react with lignocellulosic contents during activation as well as impregnation phases (Örkün, Karatepe, and Yavuz, 2011). On top of that, the higher the impregnation ratio, the higher the amount of dehydrating agent which further promotes pore formation. Unfortunately, when the limit is exceeded, again it reduces the pore formation (Cao, .Xie, Liv, & Bao, 2006). Hence, the excessive activating chemical decomposes into water resulting in gasification under high temperature (Hoong & Borhan, 2013).

Lastly, it is also been proved that all the samples analysed are at most to contain pores of class mesoporosity. The result also shows that sample A11 yields the biggest surface area, S_{BET} with area **259.5643m^2/g** with pore diameter **0.2498nm** of sub-microporous group. As sample A11 exhibits the best result among others, hence, this sample was used to study the adsorption capacity of MEA and Ni^{2+}.

4.4 Nitrogen Adsorption-Desorption Isotherm

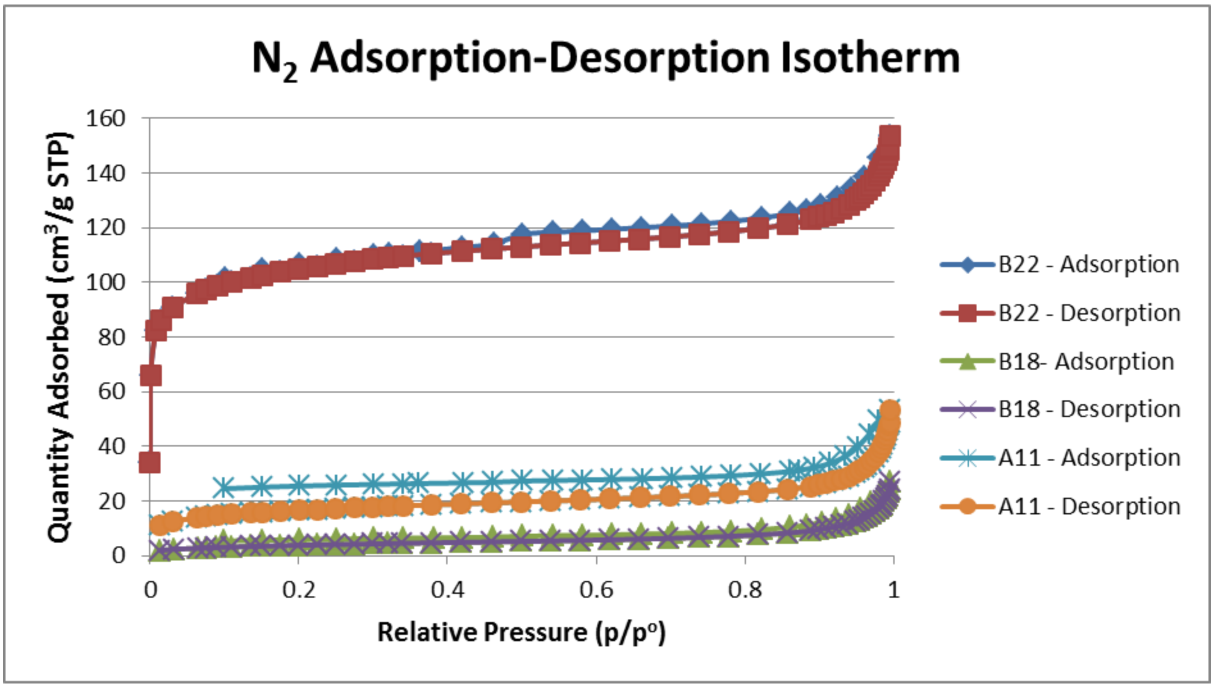


Figure 26 : Nitrogen Adsorption-Desorption Isotherm for Selected Samples

In the adsorption isotherm analysis, isotherm graphs of selected samples are compared. This analysis is done to recognize the correct adsorption isotherm type based on the IUPAC classifications as shown in Figure 5. 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 25 shows that samples A11, B18 and B22 resemble closely the combination of Type II and Type III isotherms. These two types 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. Even though the average pore diameter results of these samples are of the micro porosity 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 25 also illustrates the isotherm for sample A11, which has the largest S_{BET} among all the other sample analysed. 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 analysis of the sample, which shows that the pores formed in it is of micro porosity (pore diameter - 0.2498nm).

4.5 Chemical Oxygen Demand (COD) Test

Adsorption capacity test is carried out by batch adsorption, where 1.0g banana peel based activated carbon is stirred at 100rpm in 10mL of MEA stock solution (750ppm) for 1 hour at room temperature. The experiment was repeated at different amine concentration (500ppm & 750ppm), different stirring speed (no stirring & 300rpm), different temperature (50^{o}C & 75^{o}C) and different pH (acid & alkali) for comparison purpose. The samples were tested for COD using spectrophotometer (HACH DR 5000). Following shows the result of COD.

Table 6 : Chemical Oxygen Demand results for RAW material

RAW		**Amine Concentration**		
		250ppm	**500ppm**	**750ppm**
Stock Solution		308	399	497
Stirring Speed	**No Stirring**	348	457	576
	100rpm	315	434	552
	300rpm	246	385	509
Temp	**25^{o}C**	246	385	509
	50^{o}C	369	576	868
	75^{o}C	452	764	902

pH	**Acid**	246	385	509
	Neutral	427	539	758
	Alkali	414	609	818

Table 7 : Chemical Oxygen Demand results for sample A11

A11		**Amine Concentration**		
		250ppm	**500ppm**	**750ppm**
Stock Solution		308	399	497
Stirring Speed	**No Stirring**	303	387	489
	100rpm	278	325	475
	300rpm	203	251	338
Temp	**25^{o}C**	203	251	338
	50^{o}C	323	543	771
	75^{o}C	415	628	881
pH	**Acid**	203	251	338
	Neutral	386	598	1023
	Alkali	347	572	838

Table 8 : Chemical Oxygen Demand results for sample B18

B18		**Amine Concentration**		
		250ppm	**500ppm**	**750ppm**
Stock Solution		308	399	497
Stirring Speed	**No Stirring**	384	475	592
	100rpm	359	452	569
	300rpm	279	339	465

Temp	**25ºC**	279	339	465
	50ºC	413	478	607
	75ºC	497	562	693
pH	**Acid**	279	339	465
	Neutral	454	537	667
	Alkali	417	499	634

Chemical Oxygen Demand (COD) is the amount of oxygen consumed by the organic compounds and inorganic matter which were oxidized in water. This reflects the pollution degree of water and is the comprehensive index of the relative content of organics. This measurement is commonly used to determine the degree of organic contamination in water. Since the only organic compound in the synthetic wastewater is MEA, it can be said that decrease of COD value can represent the decrease in concentration of MEA in the sample, although the exact concentration might be slightly varied. Graph of the effect of stirring speed, effect of temperature and effect of pH against COD has been plotted for 250ppm MEA concentration.

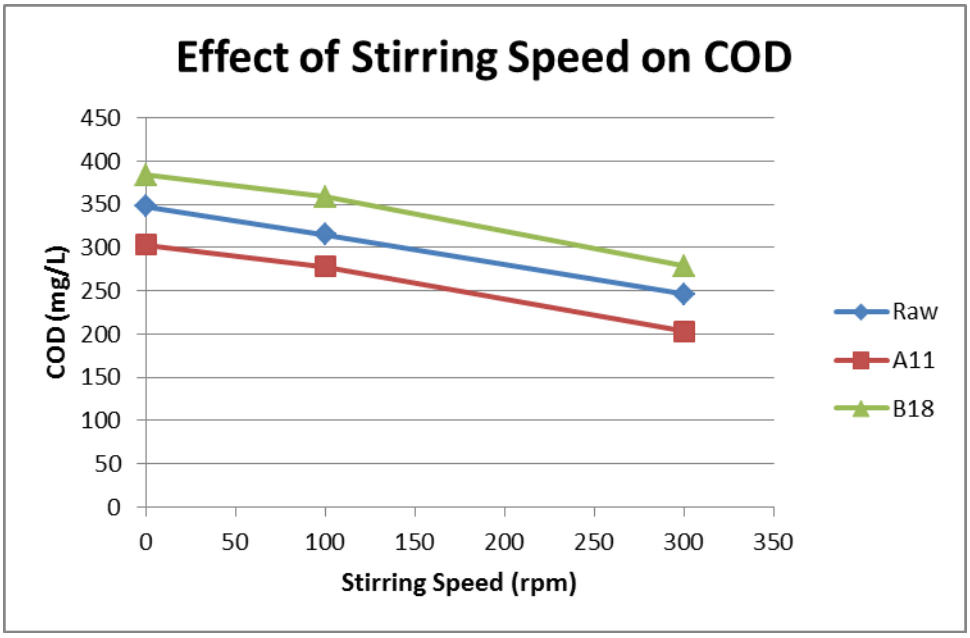


Figure 27: Graph of Stirring Speed vs COD for 250ppm MEA concentration

Figure 26 show that the stirring speed has a significant effect on COD level where the higher the stirring speed, the lower the COD level in the sample. This is because the agitation in mixture of MEA stock solution with banana peel based activated carbon will cause a rapid mass transfer of MEA molecules to the adsorption sites. This will eventually increases the efficiency of MEA removal from the mixture. The main function of stirring speed is to transfer efficiently the MEA molecules into the adsorption sites. If MEA molecules do not disperse efficiently, content of the mixture cannot be homogenous and regional differences can be seen. From Figure 26, it can be seen that bio-sorbent sample A11 (best preparation condition) shows the lowest highest removal of MEA compared to raw material and sample B18.

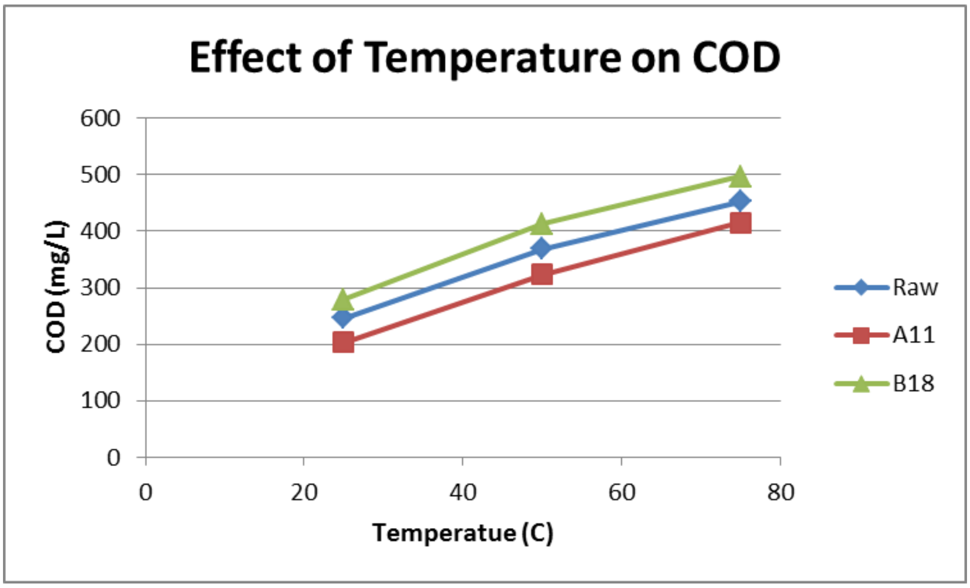


Figure 28 : Graph of Temperature vs COD for 250ppm MEA concentration

Figure 27 show the influence of temperature on COD values. It was found that at temperature 25°C, all 3 bio-sorbent (raw, sample A11 and sample B18) shows the lowest COD values, 246 mg/L, 203mg/L and 279 mg/L respectively. It could be observed that as the temperature increases, the COD level also increases proportionally. It is clearly shown that at temperature higher than 25°C, the removal efficiency of MEA decreases rapidly. This can be explained in term of wastewater whereby the activity of microorganism becomes lower after 25°C, which means the ability to remove pollutants decreases. The bio-sorbent sample A11 (best preparation condition) shows the lowest highest removal of MEA compared to raw material and sample B18.

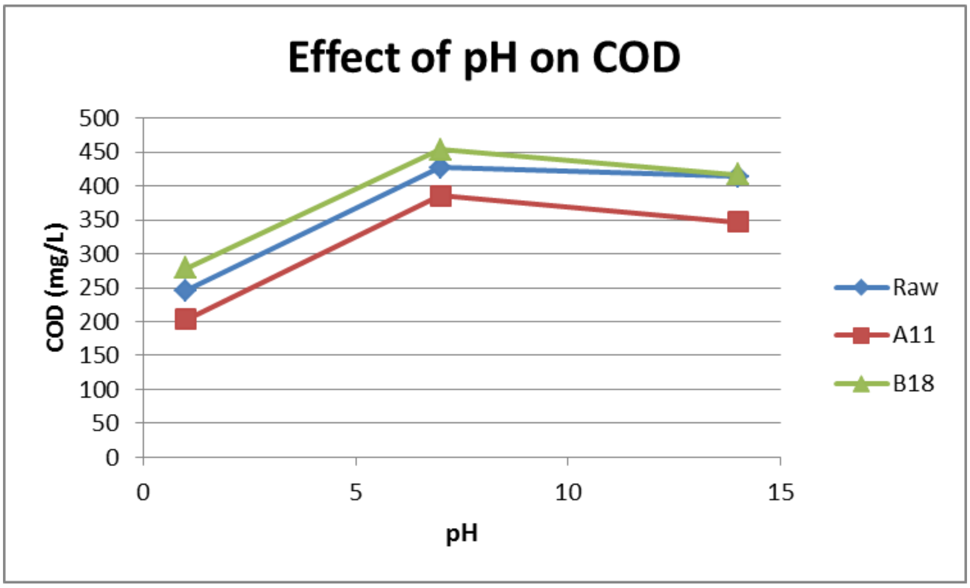


Figure 29 : Graph of pH vs COD for 250ppm MEA concentration

The influence of pH on MEA removal from wastewater is illustrated in Figure 28. It was found that the MEA removal is more sensitive to pH of wastewater. It was observed that the increase in the pH decreases the COD removal rate. Sample A11 shows the lowest COD level of 203mg/L at acidic phase followed by 347 mg/L and 386 mg/L at alkali and neutral phase respectively. At high pH value, probably the reaction mechanism changes and the formation of OH• radicals may interfere with the oxidation of organic matter of wastewater.

In summary, when the amine concentration and temperature increases, the COD level increases as well. Meanwhile, when the stirring speed increases, the COD level decreases. For the sample in alkali and neutral condition, the COD level is high, which gives an overview that removal of MEA is efficient in acidic pH.

4.6 Nickel (Ni^{2+}) Removal Test

In the Nickel (Ni^{2+}) removal test, raw, sample A11 and B18 are selected to be used in the batch adsorption Nickel. Sample A11 (activated with KOH 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, raw and sample B18 are selected. Table 9 shows the atomic absorption spectroscopy results and nickel removal percentage.

Table 9 : Atomic Absorption Spectroscopy results

Contact Time (min)	Concentration (mg/L)			Nickel Removal (%)		
	Raw	A11	B18	Raw	A11	B18
0	49.89	49.89	49.89	-	-	-
15	34.75	4.26	25.84	30.35	91.46	48.21
30	34.04	3.54	23.72	31.77	92.90	52.46
45	33.98	2.97	22.14	31.89	94.05	55.62
60	33.26	2.85	21.06	33.33	94.29	57.79
75	33.34	2.92	21.32	33.17	94.15	57.27
90	32.87	2.57	20.74	34.12	94.85	58.43
105	32.19	2.35	19.87	35.48	95.29	60.17
120	31.78	1.94	19.03	36.30	96.11	61.86

Nickel removal percentage is calculated using following equation:

$$Nickel\ Removal\ \% = \frac{Initial\ Concentration - Final\ Concentration}{Initial\ Concentration} \times 100\%$$

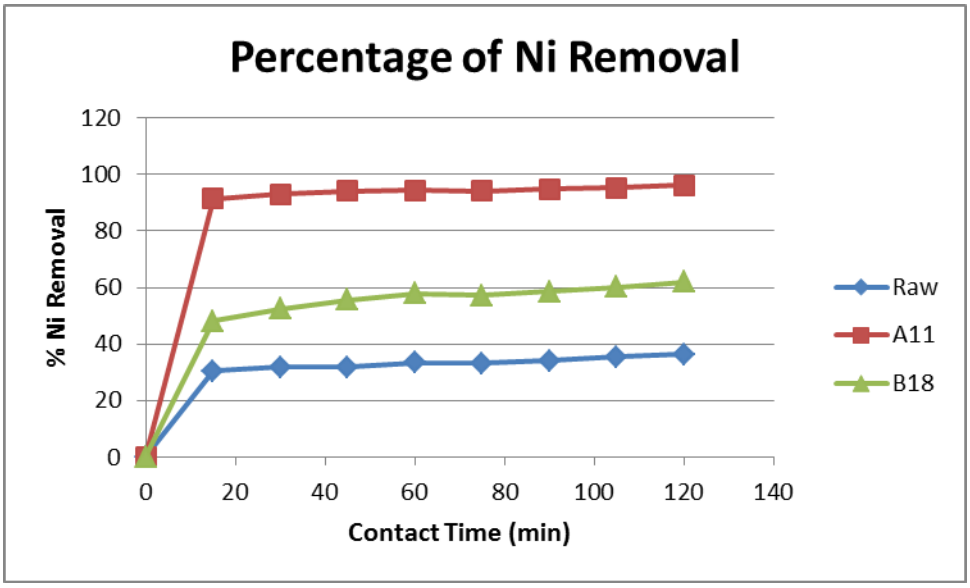


Figure 30 : Graph of Nickel Removal Percentage vs Contact Time

Figure 29 demonstrates the percentage of Nickel removal versus contact time. The samples were taken at every 15 minutes interval throughout 120 minutes of time. From the graph, RAW starts with a 30.35% Nickel removal and showed a steady increase until the 60th minute. At the 75th minute the graph shows a slight decrease and after that a sharp increase is visible until the 120th minute with a 36.30% of removal. Next, sample B18 shows a slightly higher removal percentage than RAW, which is 48.21%. However, starting at the 60th minute, the removal percentage has slightly decreases. Sample B18 shows a 61.86% removal of Nickel at 120th minute. For sample A11, it shows a promising increase at the beginning with 91.46% Nickel removal, which is higher than both RAW and sample B18. At the 75th minute the graph shows a slight decrease and after the Nickel percentage removal of A11 increases steadily until 120th minute with 96.11% of removal. It can be concluded that for this experiment, sample A11 is the most suitable bio-sorbent followed by sample B18 and RAW, which could be attributed to the high value of S_{BET} in sample A11.

In general, rate of metal ion (Ni^{2+}) removal for all metal ions is fast at the initial stages. Once the system reached equilibrium, only slight variations on metal ion removal is be observed. Metal ions occupy a large number of pores in bio-sorbent at the beginning of adsorption process and number of pores available for metal ions to occupy reduced as the contact number increased. This caused the adsorption rate of metal ions became slower until the system reached equilibrium. The behaviour of this adsorption process reflects that metal ion adsorption is a surface phenomenon where the adsorbent surfaces are readily accessible to metal ions [19]. The trend of adsorption rate is also due to the occurrence of a rapid external mass transfer follow by a slow internal diffusion process of metal ions. This slow internal diffusion process might attribute to the slow diffusion adsorbed metal ions (Ni^{2+}) from the surface film into the least accessible sites for adsorption, for instance into micropores.

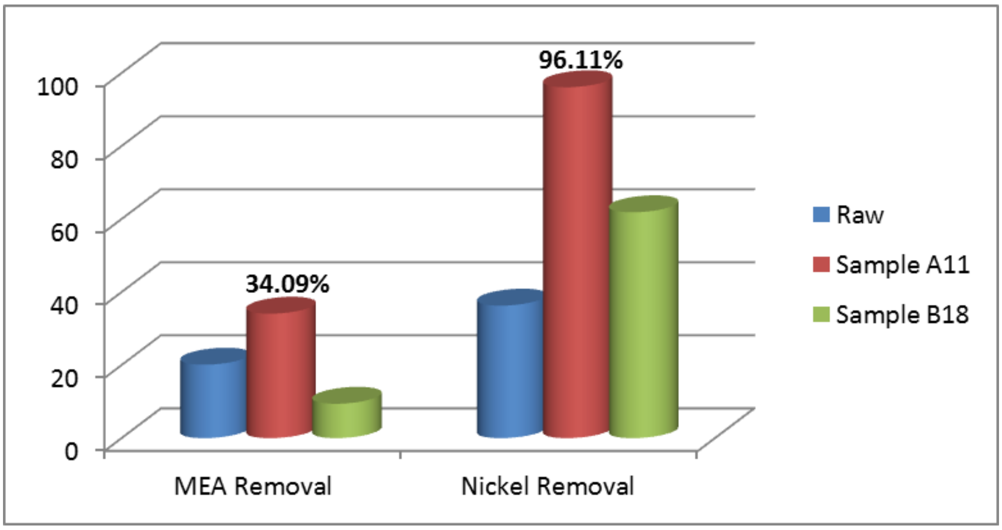


Figure 31 : Comparison between MEA removal & Nickel Removal

CHAPTER 5 : CONCLUSION & RECOMMENDATION

5.1 Conclusion

In a nutshell, alternative ways to remove MEA and heavy metal ion in wastewater has been discovered through this project. Thus, it will be very helpful to the oil and gas industry which encounters contamination of MEA and heavy metal ion in wastewater. One of the effective ways to encounter this problem is through activated carbon adsorption, where agricultural waste (banana peel) has been converted to activated carbon due to its high carbon content. Chemical activation method has been used in this project instead of physical activation because it requires low activation temperature, short activation time, and single step activation, besides provide higher yields and better porous structure. The activating agent used in this project is potassium hydroxide.

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 potassium hydroxide (KOH) 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.

The preparation condition for sample A11 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 proved to be efficient in removal of MEA and heavy metal ion (Ni^{2+}) in wastewater through adsorption.

5.2 Recommendation

The project can be improved to the next level of research, that is, to study on the feasibility of different types of agriculture wastes as precursor to be converted into activated carbon for the removal of MEA in wastewater. Examples of recommended agricultural wastes are coconut shell, coffee grounds, melon seeds and orange peels. Activated carbon made from different precursor will have different preference or adsorption capacity, depending on its respective preparation conditions. Additional information can be obtained through similar research with different raw materials in order to identify better bio-sorbent to remove pollutants. Hence, the study of developing adsorbent derived from agricultural waste would be a great exploration to deal with as it gives a better alternative economically as well as environmentally to preserve pollution-free environment.

Apart from the parameters discussed in this project, there are also other parameters which may influence the feasibility of converting banana peels into activated carbon, for instance, the amount of adsorbent present, the pH of solution, and the contact period of the adsorption process. These factors can be investigated in future to enhance the findings of this research. The study on the adsorption process itself is vital as it governs 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.

Besides that, for heavy metal ion adsorption capacity test, other heavy metal ions which can be commonly found in wastewater can also be tested. Some of the example of such heavy metal ion is Copper (Cu), Zinc (Zn), Cadmium (Cd) and Arsenic (As). These ions which cause harmful effects when come into contact with human should be eliminated for the benefit of environment and also human.

REFERENCES

[1] C.Djilani, R.Zaghdoudi, A.Modarressi, M.Rogalski, F.Djazi, and A.Lallam. (2012, February). Elimination of organic micropollutants by adsorption on activated carbon prepared from agricultural waste. Chemical Engineering Journal. [Online].Available: http://www.sciencedirect.com/science/article/pii/S1385894712002732

[2] A. Namane, A. Mekarzia, K. Benrachedi, N. Belhaneche-Bensemra, A. Hellal Determination of the adsorption capacity of activated carbon made from coffee grounds by chemical activation with ZnCl2 and H3PO4

[3] Harold, A., B. Wittcoff, G. Bryan, J. Reuben and S. Plotkin, 2004. Industrial Organics Chemicals. 2nd Edn., John Wiley Sons Ltd., New York, pp: 151.

[4] S. Harimurti, A.U. Rahmah , A.A. Omar and T. Murugesan , 2012. Application of Response Surface Method in the Degradation of Wastewater Containing MDEA using UV/H2O2 Advanced Oxidation Process. Journal of Applied Sciences, 12: 1093-1099.

[5] M.N. Razali, R.M. Yunus, Z. Jemaat and S. Alias, 2010. Monoethanolamine Wastewater Treatment via Adsorption Method: A Study on Comparison of Chitosan, Activated Carbon, Alum and Zeolite. Journal of Applied Sciences, 10: 2544-2550.

[6] What is ethanolamine?. (2003). wisegeek.com.[Online]. Available: http://www.wisegeek.com/what-is-ethanolamine.htm

[7] Al-Baghli, N. A., S. A. Preuss, V. F. Yesavage and M. S. Selim. 2001. A Rate-Based Model for the Design of Gas Absorbers for the Removal of CO2 and H2S Using Aqueous Solutions of MEA and DEA. Fluid Phase Equilibria. 185 (1–2): 31–43.

[8] Supap, T., Idem, R., Tontiwachwuthikul, P., & Saiwan, C. (2008). Kinetcs of sulphur dioxide- and oxygen-induced degradaton of aqueous monoethanolamine solution during CO? absorption form power plant flue gas system. Elsevier.

[9] Geankoplis, C. J. (2003). Liquid-Liquid and Fluid-Solid Separation Processes. In *Transport Processes and Separation Process Principles 4th Edition* (p. 760). New Jersey: Pearson Prentice Hall.

[10] What is activated charcoal and why is it used in filters?. (2000, April). HowStuffWorks.com.[Online]. Available: http://science.howstuffworks.com/environmental/energy/question209.htm

[11] D.Jang and S.J.Park, “ACS clean coal,” in Fuel, vol., 102, Ed. Eric Suuberg, Amsterdam: Elsevier, 2014, pp. 439-444. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S001623611200261X

[12] Gad.H.M.H. and El-Sayed.A.A., 2009, “Activated carbon from agricultural by-products for the removal of rhodamine-B from aqueous solution”, *Journal of Hazardous Material,* **168:** 1070-1081.

[13] Anne Vezina (July 2014). Where bananas are grown. [ONLINE] Available at: http://www.promusa.org/Banana-producing+countries+portal. [Last Accessed 31 October 2014].

[14] "Malaysia Agriculture Stats", NationMaster. Retrieved from http://www.nationmaster.com/country-info/profiles/Malaysia/Agriculture

[15] FAOSTAT: ProdSTAT: Crops, Food and Agriculture Organization, 2005.

[16] N.A.Rashidi, S.Yusup, and A.Borhan. (2014). Novel low-cost activated carbon from coconut shell and its adsorptive characteristics for carbon dioxide. UTP Institutional Repository. [Online]. 594-595, pp. 240-244.
Available: http://eprints.utp.edu.my/10637/

[17] Rengaraj, S., Arabindoo, B., & Murugesan, V. (1998). Preparation and Characterization of Activated Carbon from Agricultural Wastes. J.Sci. Ind. Res.(57), 129-132.

[18] Hoong.P.K., Borhan.A., and Taha.M.F., 2013, “Biosorption of heavy metal ions, oil and grease from industrial waste water by banana peel”, Available: http://utpedia.utp.edu.my/8484/

[19] K.K. Wong, C.K. Lee, K.S. Low, and M.J. Haron, Chemosphere 278, 23-28 (2003).

[20] Abbasi.Z., Alikarami.M., Nezhad.E.R., Moradi.F., and Moradi.V., 2013, “Adsorptive removal of Co2+ and Ni2+ by peels of banana from aqueous solution”, University Journal of Chemistry, 3: 90-95.

[21] Sud.D., Mahajan.G., and Kaur.M.P., 2008, “Agricultural waste material as potential adsorbent for sequestering heavy metal ions from aqueous solutions – a review”, Bio resource Technology, 99: 6017-6027.

[22] Tock.J.Y., Lai.C.L., Lee.K.T., Tan.K.T., and Bhatia.S., 2009, “Banana biomass as potential renewable energy resource: a Malaysian case study”, Renewable and Sustainable Energy Reviews, 14: 798-805.

[23] Cobb.A., Warms.M., Maurer.E.P., and Chiesa.S., 2012, “Low-tech coconut shell activated charcoal production”, International Journal for Service Learning in Engineering, 7: 93-104.

[24] Achak.M., Hafidi.A., Ouazzani.N., Sayadi.S., and Mandi.L., 2008, “Low cost biosorbent ‘banana peel’ for the removal of phenolic compounds from olive mill wastewater: kinetic and equilibrium studies”, Journal of Hazardous Materials, 166: 117-125.

[25] Viswanathan.B., Neel.P.I., and Varadarajan.T.K., 2009, “Methods of activation and specific applications of carbon materials”. Available: http://nccr.iitm.ac.in/e%20book-Carbon%20Materials%20final.pdf

[26] Kim.M.J., and Chea.G.H., 2012, “Study on the PV driven dehumidifying system with oyster shell and thermoelectric device”, Thesis, Kunsan National University, Korea.

[27] Marsh, H., & Rodriguez-Reinoso, F. (2006). Activated Carbon. Oxford, UK: Elsevier.

[28] Mokhtarud-din, H., & William, R. (2010). STATUS OF BANANA CULTIVATION AND DISEASE INCIDENCES IN MALAYSIA. Crop Protection & Plant Quarantine Division, Department of Agriculture, Malaysia.

[29] Memon, J. R., Memon, S. Q., Bhangar, M. I., Memon, G. Z., El-Turki, A., & Allen, G. C., 2008, “Characterization of Banana Peel by Scanning Electron Microscopy and FT-IR and its use for cadmium removal”, Colloids Surfaces B: Biointerfaces, 66: 260-265.

[30] Ademiluyi, F. T., & David-West, E. O., 2012, “Effect of Chemical Activation on the Adsorption of Heavy Metals Using Activated Carbons from Waste Materials”, International Scholarly Research Network, 2012: 1-5.

[31] Diao, Y., Walawender, W. P., & Fan, L. T., 2002, “Activated Carbon Prepared From Phosphoric Acid Activation of Grain Sorghum”, Bioresource Technology, 81: 45-52.

[32] Lim, W., Srinivasakannan, C., & Balasubramanian, N., 2010, “Activation of palm shells by phosphoric acid impregnation for high yielding activated carbon”, Journal of Analytical and Applied Pyrolysis, 88: 181-186.

[33] Molina-Sabio, M., Rodriguez-Reinoso, F., Caturla, F., & Selles, M. J., 1996, “Development of porosity in combined phosphoric acid- carbon dioxide activation”, Carbon, 34: 457-462.

[34] Laine, J., Calafat, A., & Labady, M., 1994, “Pore size distribution analysis and networking: studies of microporous sorbents”, Characterization of Porous Solid III, Proceedings of the IUPAC Symposium (COPS III), Elsevier, Amsterdam.

[35] Borhan, A., & Kamil, A. F., 2012, “Preparation and Characterization of Activated Carbon from Rubber Seed Shell by Chemical Activation”, Journal of Applied Science, 1-6.

[36] Cao, Q., Xie, K. C., Liv, Y. K., & Bao, W. R., 2006, “Process effects of activated carbon with large specific surface area from Corncob”, Bioresource. Technol., 97: 110-115.

[37] Wu, F. C., Tseng, C. C., & Hu, C. C., 2005, “Comparisons of pore properties and adsorption performance of KOH-activated and steam-activated carbons”, Micropore. Mesopore. Mater 80: 95-106.

[38] Sudaryanto, Y., Hartono, S. B., Irawaty, W., Hindarso, H., & Ismadji, S., 2006, “High surface area activated carbon prepared from Cassava Peel by chemical activation”, Bioresource. Technol. 97: 734-739.

[39] Ozdemir.I., Sahir.M., Orhan.R., and Erdem.M., 2014, “Preparation and characterization of activated carbon from grape stalk by zinc chloride activation”, Fuel Processing Technology, 125: 200 – 206.

[40] Liou.T.H., 2009, “Development of mesoporous structure and high adsorption capacity of biomass-based activated carbon by phosphoric acid and zinc chloride activation”, Chemical Engineering Journal, 158: 129 - 142.

[41] Esteves.I.A.A.C., Lopes.M.S.S., Nunes.P.M.C., and Mota.J.P.B., 2008, “Adsorption of natural gas and biogas components on activated carbon”, Separation and Purification Technology, 62: 281 – 296.

[42] Fenrong.L.I., Honghong.Y.I., Xiaolong.T., Ping.N., Qiongfen.Y.U., and Dongjuan.K., 2010, “Adsorption of carbon dioxide by coconut activated carbon modified with Cu/Ce”, Journal of Rare Earths, 28: 334-337.

[43] Guo.B., Chang.L., and Xie.K., 2006, “Adsorption of carbon dioxide on activated carbon”, Journal on Natural Gas Chemistry, 15: 223 – 229.

[44] Dantas.T.L.P., Luna.F.M.T., Silva Jr.I.J., Torres.A.E.B., de Azevedo.D.C.S., Rodrigues.A.E., and Moreira.R.F.P.M., 2011, “Carbon dioxide-nitrogen separation through pressure swing adsorption”, Chemical Engineering Journal, 172: 698 – 704.

[45] Heidari.A., Younesi.H., Rashidi.A., Ghoreyshi.A., 2013, “Adsorptive removal of CO2 on highly microporous activated carbons prepared from Eucalyptus camaldulensis wood: Effect of chemical activation”, Journal of the Taiwan Institute of Chemical Engineers, 45: 579 – 588.

APPENDICES

No	Activating Agent	IR	Activating Temperature (°C)	Activation Time (hour)	Impregnation	Carbonization	Weight before carbonization (g)	Weight after carbonization (g)	Yield (%)
1	KOH	1:1	400	1	Yes	Yes	8.72	3.81	43.7
2	KOH	1:2	400	1	Yes	Yes	9.46	2.98	31.5
3	KOH	1:3	400	1	Yes	No	7.74	-	-
4	KOH	1:1	500	1	Yes	No	9.05	-	-
5	KOH	1:2	500	1	Yes	No	7.34	-	-
6	KOH	1:3	500	1	Yes	Yes	7.80	2.25	28.8
7	KOH	1:1	600	1	Yes	No	7.45	-	-
8	KOH	1:2	600	1	Yes	Yes	6.32	4.87	77.1
9	KOH	1:3	600	1	Yes	Yes	9.50	2.73	28.7
10	KOH	1:1	400	2	Yes	Yes	9.00	4.65	51.7
11	KOH	1:2	400	2	Yes	No	7.58	-	-
12	KOH	1:3	400	2	Yes	Yes	9.70	5.90	60.8
13	KOH	1:1	500	2	Yes	Yes	7.56	2.25	29.8
14	KOH	1:2	500	2	Yes	Yes	6.92	1.14	16.5
15	KOH	1:3	500	2	Yes	No	8.76	-	-
16	KOH	1:1	600	2	Yes	No	8.90	-	-
17	KOH	1:2	600	2	Yes	Yes	8.50	2.95	34.7
18	KOH	1:3	600	2	Yes	Yes	7.21	2.25	31.2

List of samples Group A (particle size = 0.25mm) with respective preparation conditions

No	**Activating Agent**	**IR**	**Activating Temperature (°C)**	**Activation Time (hour)**	**Impregnation**	**Carbonization**	**Weight before carbonization (g)**	**Weight after carbonization (g)**	**Yield (%)**
1	KOH	1:1	400	1	Yes	No	8.52	-	-
2	KOH	1:2	400	1	Yes	Yes	9.82	3.95	40.2
3	KOH	1:3	400	1	Yes	No	7.54	-	-
4	KOH	1:1	500	1	Yes	No	7.98	-	-
5	KOH	1:2	500	1	Yes	No	9.46	-	-
6	KOH	1:3	500	1	Yes	No	8.78	-	-
7	KOH	1:1	600	1	Yes	No	6.78	-	-
8	KOH	1:2	600	1	Yes	No	9.45	-	-
9	KOH	1:3	600	1	Yes	Yes	7.42	1.56	21.0
10	KOH	1:1	400	2	Yes	No	7.89	-	-
11	KOH	1:2	400	2	Yes	Yes	9.90	7.89	79.7
12	KOH	1:3	400	2	Yes	No	9.89	-	-
13	KOH	1:1	500	2	Yes	No	6.89	-	-
14	KOH	1:2	500	2	Yes	No	8.75	-	-
15	KOH	1:3	500	2	Yes	Yes	6.55	2.46	37.6
16	KOH	1:1	600	2	Yes	Yes	9.67	4.23	43.7
17	KOH	1:2	600	2	Yes	No	7.56	-	-
18	KOH	1:3	600	2	Yes	Yes	7.89	2.88	36.5

List of samples Group B (particle size = 3.00mm) with respective preparation conditions

B18

10/02/2015 15:37:54

Spectrum processing :

No peaks omitted

Processing option : All elements analyzed (Normalised)

Number of iterations = 5

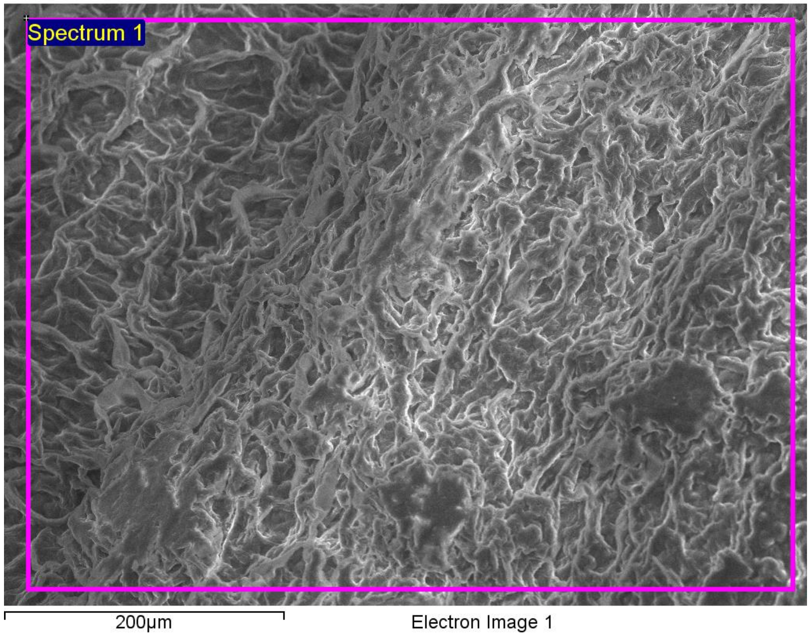
Standard :

C CaCO3 1-Jun-1999 12:00 AM

O SiO2 1-Jun-1999 12:00 AM

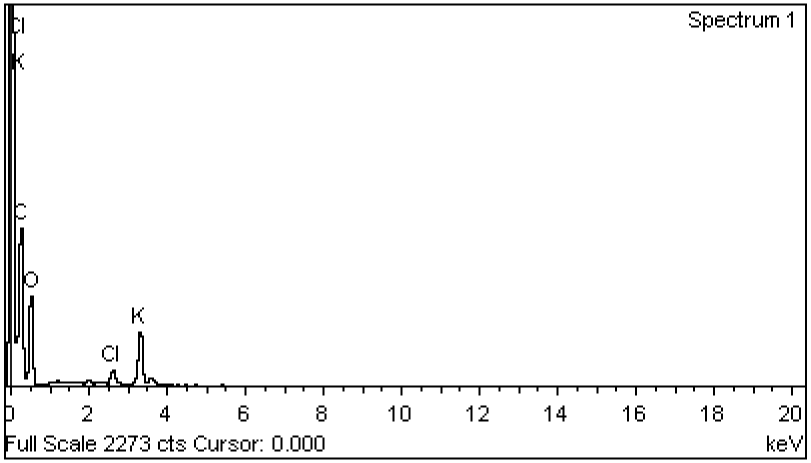
Cl KCl 1-Jun-1999 12:00 AM

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



Electron Image 1

Element	Weight%	Atomic%
C K	31.31	40.08
O K	57.81	55.56
Cl K	1.95	0.85
K K	8.94	3.51
Totals	100.00	



Spectrum processing :

No peaks omitted

Processing option : All elements analyzed (Normalised)

Number of iterations = 5

Standard :

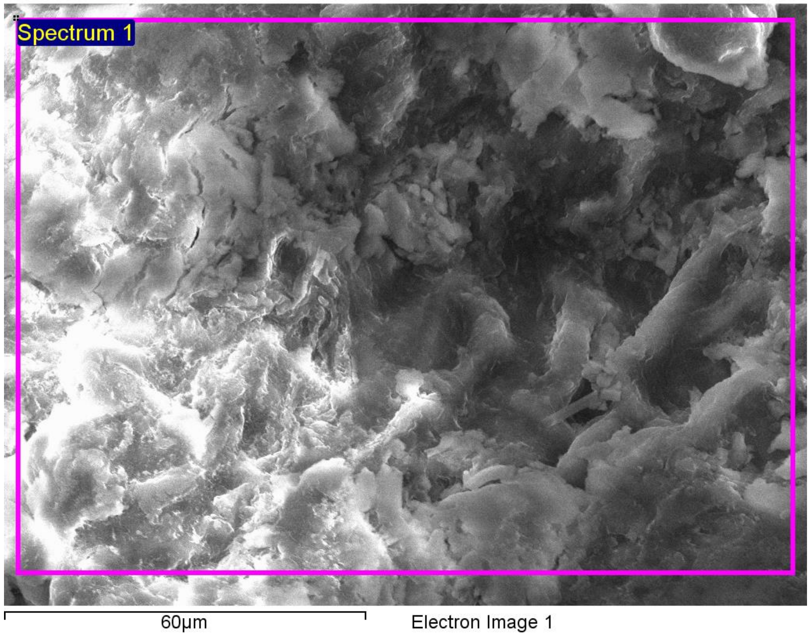
C CaCO3 1-Jun-1999 12:00 AM

O SiO2 1-Jun-1999 12:00 AM

Si SiO2 1-Jun-1999 12:00 AM

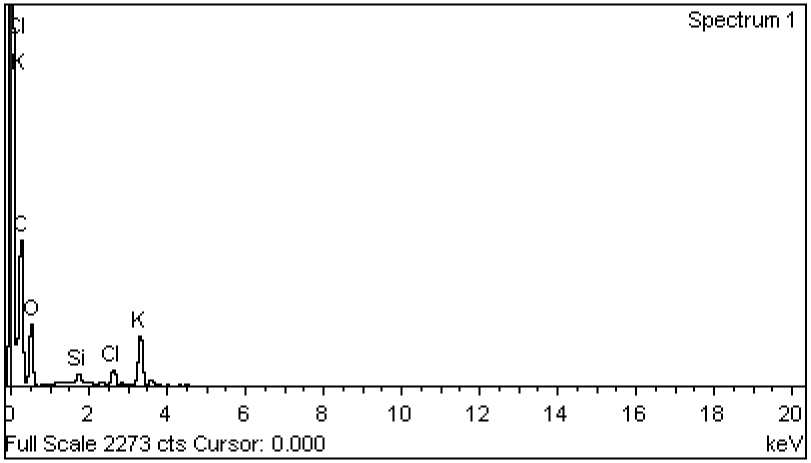
Cl KCl 1-Jun-1999 12:00 AM

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



Electron Image 1

Element	Weight%	Atomic%
C K	60.99	70.88
O K	29.32	25.58
Si K	0.32	0.16
Cl K	0.96	0.38
K K	8.41	3.00
Totals	100.00	



A11

10/02/2015 15:42:56

Spectrum processing :

No peaks omitted

Processing option : All elements analyzed (Normalised)

Number of iterations = 4

Standard :

C CaCO3 1-Jun-1999 12:00 AM

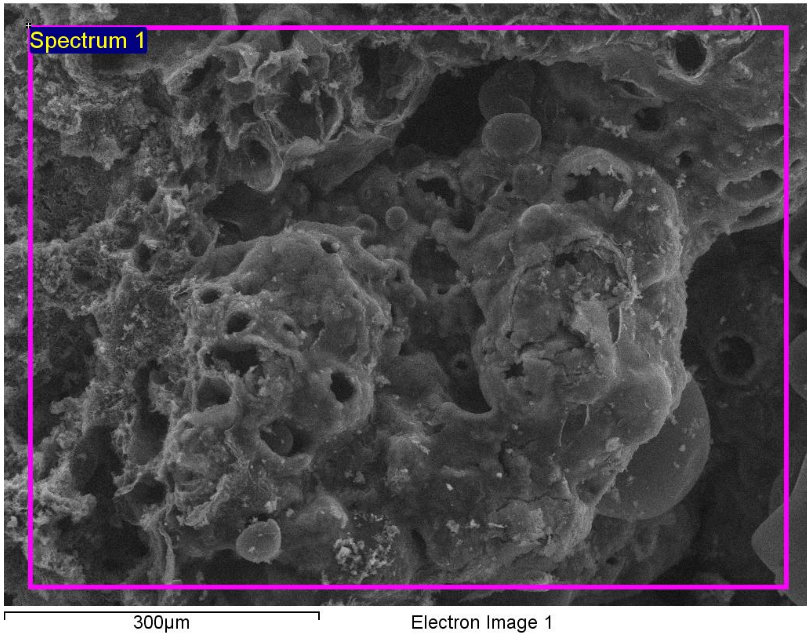
O SiO2 1-Jun-1999 12:00 AM

Si SiO2 1-Jun-1999 12:00 AM

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

Ca Wollastonite 1-Jun-1999 12:00 AM

Element	Weight%	Atomic%
C K	59.74	71.32
O K	26.17	23.46
Si K	0.57	0.29
K K	10.27	3.77
Ca K	3.25	1.16
Totals	100.00	



Electron Image 1