EFFECT OF CHEMICAL TREATMENT ON PRODUCTION OF ACTIVATED CARBON FROM *COCOS NUCIFERA L.* (COCONUT) SHELL USING MICROWAVE IRRADIATION

by

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DECLARATION

I declare that this thesis entitled " Effect of Chemical Treatment On Production of Activated Carbon from *Cocos Nucifera L.* (Coconut) Shell " is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

Signature   : _____

Name   : _____

Date   : _____

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Effect of Chemical Treatment On Production of Activated Carbon From Cocos Nucifera L. (Coconut) Shell

ABSTRACT

Activated carbon (AC) has attracted attention among researchers due to special properties such as high porosity, highly adsorption and low cost. In this research, activated carbon has been successfully produced from the coconut shell by using the chemical activation which are zinc chloride ($ZnCl_2$), phosphoric acid (H_3PO_4)and sodium hydroxide (NaOH) as the activating agent. The optimum parameter for the power of microwave radiation used was 380 W, impregnation ratio of activating agent to char was 3: 1 for H_3PO_4, 2:1 for NaOH, and for 1:1$ZnCl_2$ while concentration of each activating agents was 0.5M. The activation time that were implemented was 10 minutes using microwave radiation method. All samples then characterized using, FTIR, XRD and TGA in order to determine the functional groups, composition and element and weight loss of the activated carbon. The XRD results showed that the activated carbon that had been produced were amorphous. In the FTIR – ATR , the there were C = C bonds and phenyl ring existed in the activated carbons. In TGA results, it indicated that the activated carbon has very high resistant to weight loss compared to char, which range temperature were same. The result showed that phosphoric acid has the most significant effect on the synthesized AC properties since the moisture content was low and the highest yield percentage.

Kesan Rawatan Kimia Dalam Penghasilan Karbon Teraktif Daripada kulit
***Cocos Nucifera L.* (Kelapa)**

ABSTRAK

Karbon teraktif telah berjaya menarik perhatian dalam kalangan penyelidik disebabkan oleh tinggi saiz liang, tinggi penyerapan dan murah. Dalam penyelidikan ini, karbon teraktif berjaya dihasilkan dari tempurung kelapa dengan menggunakan pengaktifan kimia yang menggunakan zink klorida ($ZnCl_2$), asid fosforik (H_3PO_4) dan natrium hidroksida (NaOH) sebagai ejen mengaktifkan. Keadaan kuasa yang paling baik untuk kuasa ketuhar gelombang mikro digunakan adalah 380 watt, impregnasi nisbah pengaktifan kimia kepada arang adalah 3:1 H_3PO_4, 2:1 NaOH, and 1:1 $ZnCl_2$ manakala konsentrasi untuk pengaktifan kimia adalah 0.5M. Masa pengaktifan yang mana pelaksanaan adalah 10 minit dengan menggunakan radiasi ketuhar gelombang mikro. Semua sampel kemudian telah dicirikan dengan menggunakan, FTIR, XRD dan TGA untuk menentukan kumpulan berfungsi, komposisi dan unsur karbon dan kehilangan berat badan yang diaktifkan karbon yang diaktifkan. Keputusan XRD menunjukkan karbon teraktif yang telah dihasilkan adalah amorphous. Di dalam FTIR – ATR, terdapat kewujudan rantaian C=C dan gelung phenyl di dalam karbon teraktif. Di dalam keputusan TGA, diterangkan yang karbon teraktif mempunyai halangan yang sangat tinggi untuk kehilangan berat badan berbanding kepada arang, yang mana anggaran suhu yang sama. Hasilnya menunjukkan asid fosforik mempunyai satu kesan yang paling penting ke atas mengsintesiskan karbon teraktif sejak kandungan kelembapannya rendah dan peratusan hasilannya paling tinggi.

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LIST OF ABBREVIATIONS

AC	Activated Carbon
ACNM	Activated carbon Impregnated with NaOH Activate by Microwave
ACNWM	Activated carbon Impregnated with NaOH without Microwave
ACZM	Activated carbon Impregnated with $ZnCl_2$ Activate by Microwave
ACZWM	Activated carbon Impregnated with $ZnCl_2$ without Microwave
ACPM	Activated carbon Impregnated with H_3PO_4 Activate by Microwave
ACPWM	Activated carbon Impregnated with H_3PO_4 without Microwave
BbAC	Bamboos Activated Carbon
BET	Brunauer – Emmett - Teller
CS	Coconut Shell
FTIR	Fourier Transform Infrared Spectrophotometer
H_3PO_4	Phosphoric Acid
KOH	Potassium Hydroxide
NaOH	Sodium Hydroxide
NC	Native Carbon
SEM	Scanning Electron Microscope
TGA	Thermogravimetric Analysis
XRD	X-ray Diffraction
$ZnCl_2$	Zinc Chloride

LIST OF SYMBOL

%	percentage
˚C	degree Celsius
Ө	angle

CHAPTER 1

INTRODUCTION

1.1 Background of Study

The carbonaceous adsorbent is widely use as they have highly adsorption capacity. Many researches have been done to produce activated carbon which this activated carbon have the highly adsorption properties. Activated carbon (AC) is a form of carbon that have high porosity and high surface area so that the activated carbon become more versatile and commonly used as adsorbent. Activated carbon is produced from the variety carbonaceous source of materials. To be the best precursor, the application of product, cost and availability must be considered. For the production of activated carbon, the precursor used must be organic materials that rich in carbon.

Coal is the one of the great producer to produce activated carbon. However, the agriculture waste being the best choice in the certain condition besides agriculture waste is renewable sources since the it has successfully converted into AC (Prahas et al., 2008). The high cost of raw materials becomes the main factor that limits universal application of activated carbon, where the study has been extended on the production of activated carbon from the agriculture waste (Ke-qiang et al., 2009). Furthermore, by using the local waste of agriculture, the process to produce activated carbon is simple, inexpensive and effective process. The sources and quality are the important things to guarantee the quality and consistency of activated carbon.

Moreover, the local agriculture waste can reduce the ecological impact by converting into activated carbon (Cobb, 2012). The activated carbon can be produced

from many types of agriculture waste that will give different characterization such as palm kernel shells, coconut shell, and bamboo (Inegbenebor et al., 2012).

In order to obtain the high surface of activated carbon, the coconut shell has been used as raw material (Hu & Srinivasan, 2001). Furthermore, the conversion of coconut shell solid waste into activated carbon is the most desirable. Hence, coconut shell could be a potential candidate as precursor in this research due to its hardness and abrasion resistance. Moreover, the coconut shell is easily to find and inexpensive material.

In the last few decades, the usage and development of microwave equipment has grown rapidly. Nowadays, the microwave − induced is a new technique which finds other application in the area of material science, food processing, telecommunication, analytical science,wood drying, plastic and rubber treatment. In particular, microwave heating or induce can arise from direct interaction of matter with electromagnetic energy and it offers a number of of potential advantages over conventional heating. The main advantage of using microwave is that the reducing time and economical. In many cases, it represents a reduction in the energy consumption and green chemistry. In this study, the activation of activated carbon are using microwave (Yacob, 2013).

1.2 Problem Statement

Many fundamental studies have reported on the production of activated carbon from carbonization or pyrolysis of agriculture waste such as coconut shell, palm kernel shell, bamboo and nut shell. These agriculture waste will contribute to the enviroment pollution, if those waste are not properly disposed. *Cocos Nucifera L.* shell or coconut shell is the one of the agriculture waste that has been commercialized in the production of activated carbon which the uses of this waste can help to reduce the enviromental pollution (Pereira, 2016).

Research has been conducted on activated carbon in the water treatment process which was used as water filtration to treat the domestic waste water and to recycle the treated water. The activated carbon is being an important role in the science and technology in many industries and also has been proves to be a precursor for carbon production. The two principal mechanisms, adsorption and catalytic reduction are used by activated carbon to remove contaminant from water. Adsorption removes organic while catalytic remove residual disinfectants. Activated carbon is suitable for adsorption process since it contains high porosity and large surface area. For the preparation of micro porous activated carbon, coconut shell is suitable due to its excellent natural structure and low ash content. Activated carbon can be produced by chemical activation or physical activation. High density, high purity are the advantage of coconut shell carbons that make they suitable to be use in water treatment (Vol et al., 2015).

1.3 Objectives

The purposes of this research are :

    i.   To synthesis activated carbon from Cocos Nucifera L.

   ii.   To characterize and compare the prepared carbon using different chemical treatment.

1.4 Expected Outcomes/Significance of study

       The chemical treatment process would be crucial in the properties of activated carbon. Thus, this study could show the effect of the chemical treatment on activated carbon. Furthermore, the data of the best chemical for activation of activated carbon will be obtained. In addition, coconut shell (CS) that used as precursor in this research in order to obtain AC will reduce the environmental problem. On the other hands, the activated carbon that has the best properties can be used for further study such as dye removal in aqueous solution.

CHAPTER 2

LITERATURE REVIEW

2.1 Activated Carbon

Activation carbon (AC) is one of the best absorbents which using traditional steam carbon, the highly porous carbon can be produced. It has found a wide range of technology application since it forms the large and important class of porous solid. According to Al-Qodah & Shawabkah (2009), activated carbons are carbonaceous material that produced from the elemental carbon by the oxidation of the carbon atoms found on the outer and inner surfaces. The activated (AC) can be characterized by their specific surface area, tunable surface –containing functional group and also well-developed porosity (Chandra et al., 2009). Activated carbon can be produced whether in the form of powder, granular or pellet. Figure 2.1 shows the types of the activated carbon. Activated carbon can be produced from the low chemical impregnation which they will become predominantly meso porous by increasing impregnation ratio. However, coconut shell produces the activated carbon with low ash, high porosity and high surface area. Characterization of activated carbon is not only depends on the raw materials but also will be effected by chemical treatment by using different types of chemical activation agent (Gratuito et al., 2008).

To get the best activated carbon with high surface area, the optimum condition is needed (Chandra et al., 2009). Activated carbon can be used for the harmful impurities removal since it has high crystallinity a (Shankar, 2008). Generally, activated carbon can be prepared either by physical or chemical activation. For the physical the steam process is used for activation while in the chemical activation, the activating agent is used. In the previous research, the activating agent, $ZnCl_2$ is producing the AC with the higher specific area over the AC produced by H_3PO_4 (Al-Qodah & Shawabkah, 2009).
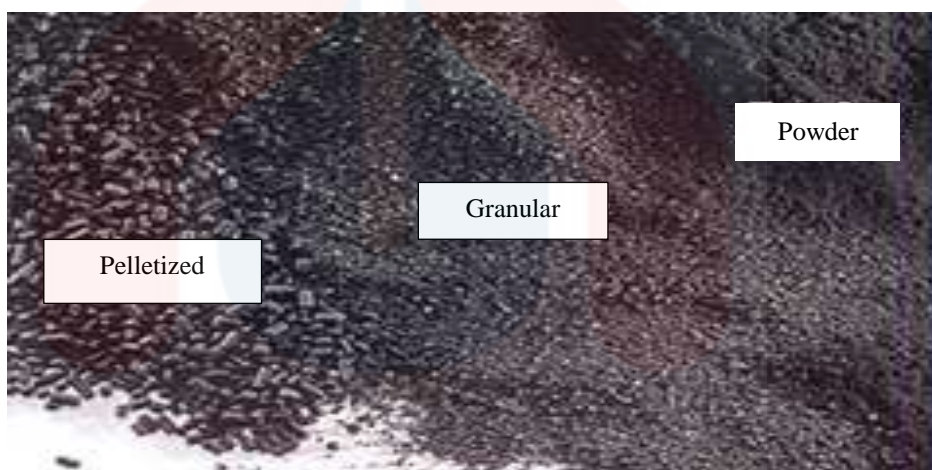
Figure 2.1 : Types of activated carbon (pellet, granular, powder)

(http://www.prominentinc.com/images/carbon.jpg)

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2.1.1 Characterization and Properties of Activated Carbon

Characterization of activated carbon is important in order to identify the specific uses of activated carbon in the variety of application. The different surface area and pore volume of carbon will be produced by the different chemical activating agent in chemical activation process (Liou, 2010). The characteristics of activated carbon can be classify as physical and chemical activated carbon. The pore characteristics and surface chemistry are worth to be identified by several methods (Prahas et al., 2008). Activated carbon also can be characterize by its adsorption capacity, surface area, internal pore structure, surface characteristic and the functional groups that present on the pore surface (Ke-qiang et al., 2009).

Due to the adsorptive properties that it has, AC is usually used to purify, detoxify, discolor or alter the concentration of many liquid and gaseous materials. The activated carbon is present of microcrystalline, during the carbonization process and during the activation process they have regular bonding that cause free valances which very reactive. The impurities and process condition influence formation of interior vacancies in microcrystalline structure.

The physical properties of AC such as ash content and moisture content can affect the use AC and render them whether they are suitable or not for specific application, while the chemical properties such as specific surface area and surface chemistry (Ain, 2007)

a) Morphology of The Activated Carbon

According to SEM micrograph, raw material before the chemical activation process does not have porous surface, while the external surface of the chemically activated carbon is rich with cavities (Aji *et al.*, 2015)The addition of the activating agent will be affected the pore development of the AC. Figure 2.2 below shows the image of activated carbon from coconut shell which is characterized by SEM. By the addition of the activating agent, pore size becomes wider from micro pores to meso pores.
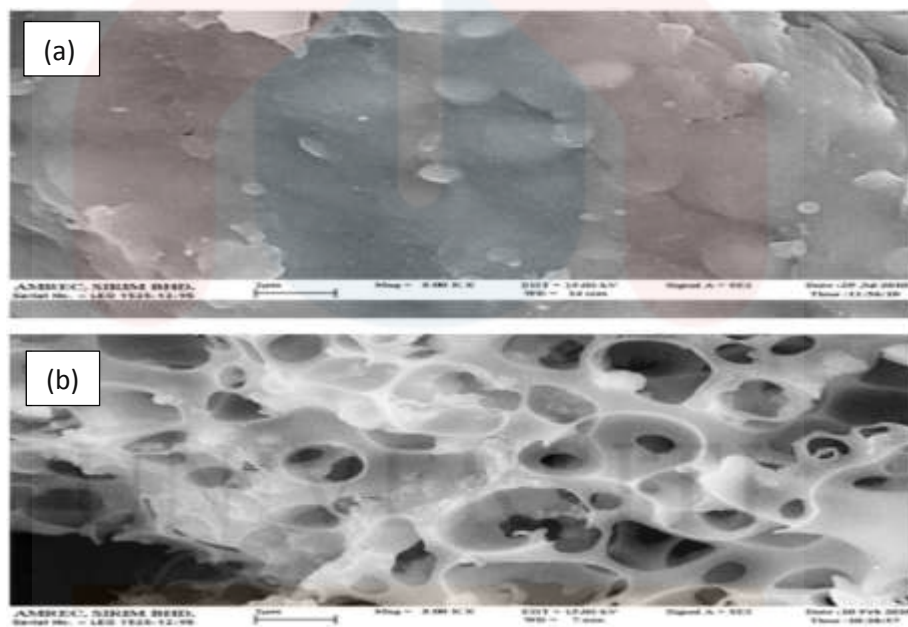
Figure 2.2: SEM micrographs of (a) coconut shell carbon and (b) coconut shell activated carbon

(Mohd Iqbaldin et al., 2013)

b) Ash Content

Ash is non-carbon or mineral additives, which is not chemically combined with the carbon surface. It consists of various useless mineral substances, which become more concentrate during the activation process. It comprises of 1-20 % and primarily depends on the type of raw material. High ash content is undesirable for activated carbon since it reduces the mechanical strength of carbon and affects adsorptive capacity (Abdullah et al., 2001). A good quality activated carbon should have low ash content as possible, and it can be obtain from the agriculture waste.

The inorganic material contained in activated carbon is measured as the ash content and this value should be in range of 2-10 %. The ash content generally gives a good idea about the inorganic constituents associated with carbon obtained by different carbonization methods. Low value of ash content indicates that the inherent carbon in the starting material is high. Activated carbon with high ash content is undesirable because it reduces the absorption capacity and mechanical strength of activated carbon (Ibrahim & Kwaghger, 2013).

c) Moisture Content

The moisture content is the amount of water physically bound to the activated carbon under normal condition. In the previous studies have shown that lower moisture content increases the rate of adsorption of contaminants. The practical limit for the level of moisture content allowed in activated carbon varies within 3% - 6% (Gumus & Okpeku,2015).

2.1.2 Porous Structure of Activated Carbon

One of the most important properties of activated carbon is highly micro porous and have large surface area. The adsorption capacity for molecule with the different shapes and sizes is affected by difference in pore size thus it is the important criterion that make carbon is suitable for specific application (Abdullah et al., 2001).Porosity is classified by IUPAC into three different groups of pore sizes. The porous structure of activated carbon can be classified into three porous structure, macro porous, meso porous and micro porous as shown in Figure 2.3. Macropore has the diameter range from 8180-50 nm, mesopore has the diameter range from 50-2 nm and the micropore has the diameter range less than 2 nm.
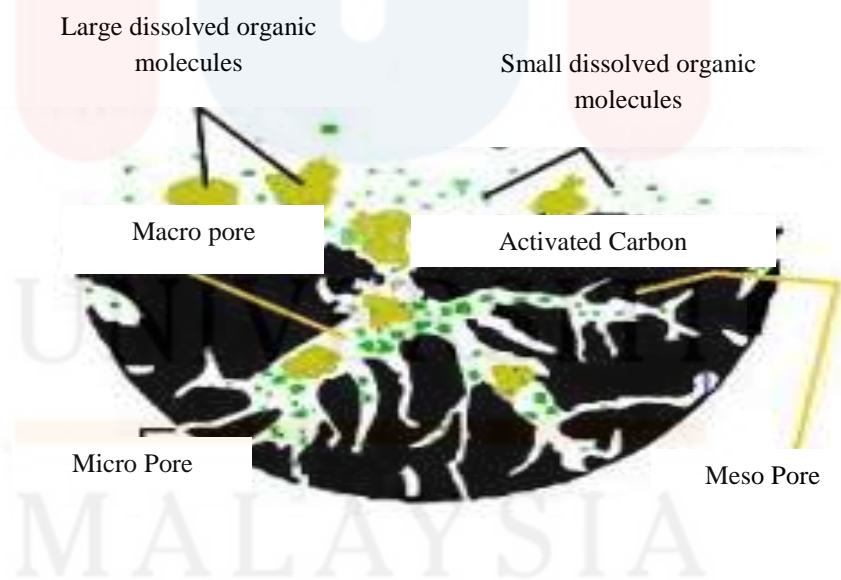

Figure 2.3 : The porous structure of activated carbon : macroporous, mesoporous and microporous

(http://www.sushrutchemicals.com/activatedCarbon.html)

The macropores are used as entrance of contaminated molecules onto AC, mesopores are used for transportation while the micropores are used to absorb molecules. The diffused molecules sticked to the internal surface after being removed onto AC. Smaller molecules will diffuse deeper onto AC and absorbed more surface area than molecules because of the size of the pores.

The pore structure of activated carbon in conventional application is micro porous. However, recently meso porous structure has been in the center of attention because it possesses a high pore volume and wide range of pore size (Liou, 2010). The porous structure will be affected by its adsorption capacity (Prahas et al., 2008). For the micro porous size, it always used in the gas phase, while, the meso porous size is always

used in the liquid phase which involved in the waste- water treatment process.The preparation of activated carbon with different pore sizes can be achieved by using either physical or chemical activation method. Both process involve in the development of porosity but in different process and mechanism. In the physical activation, the porosity took place via selective elimination of the more reactive carbon of the structure and further gasification led to the production of the AC with the sought pore structure. In the chemical activation agent, the precursor is mixed with the chemical activating agent such as $ZnCl_2$ or KOH, then is carbonized and washed to produce the AC. The activating agent will react with the product causing reduction in the evolution of volatile matter and inhibition of the particle shrinkage. Once, the chemical is removed, a large amount of porosity is formed (Abdullah et al., 2001).

2.2 Raw Materials

Most activated carbons are made from the agriculture waste or biomass as raw materials. However, to produce the most efficient activated carbon, the raw materials must have high carbon content, low ash where those characteristics can be found in coconut shell. Different applications can be found from these differences in properties of carbon (Inegbenebor et al., 2012). In order to provide the activated carbon, the raw material that used is in the process of carbonization process must be rich in carbon. However, in the process of manufacturing, the high volatile content is also needed. There are a lots of agriculture wastes that have contain high carbon contain that can be used as raw material for producing activated carbon such as palm fiber, rubber wood saw dust, date pits, bamboo, coconut shell etc. This agriculture watses are used in the prevention of the environmental pollution (Smrutirekha, 2014).

Based on the research from Thomas et al., (2015), bamboos were used as raw materials to prepare activated carbons (BbAC). Initially dried bamboo waste was crushed to the mesh size of 1-2 mm and was treated with H_3PO_4.

In this research, the coconut shell is used for activated carbon preparation because of their high density, hardness and volatile content making them an ideal option to manufacture the hard granular activated carbon. Furthermore, for the preparation micro porous activated carbon, the CS is suitable since it has excellent natural structure and low ash content. Coconut shell-based AC has the lowest ash content and is the purest type. The overwhelming majority of the ash present in an AC will be insoluble. ACs can be water and acid washed to reduce the ash content.

Coconut-based ACs have the lowest ash content after washing, with levels of 1% to 2%, whereas coal-based Acs have an ash content of 5% to 15% after washing (Portwara, 2012.). For a wide range of application coconut shells are used commercially for the production of micro porous activated carbons.

2.2.1 Coconut Shell (*Cocos Nucifera L.*)

The coconut palm, *Cocos Nucifera* also a member of the *plantea* order- *Arecales* of the *Family Arecaceae* (Palm Family). It is only accepted species in the genus cocos. The term coconut can be referred to the whole coconut palm, include seed and fruit which is not botanical nut but a drupe (Okafor et al., 2012). *Cocos Nucifera L.* is an agriculture crop that can be found at the tropics place especially at South-East Asian Peninsular and has cultivated for 400 years. Coconut tree usually grows along the tropical beaches. The fruits from coconut tree have many useful part which are husk, hard seed coat or coconut shell (ectosperm) and endosperm (Inegbenebor et al., 2012).

Coconut shell consists of cellulose and hemicelluloses and lignin. Coconut shell as shown in Figure 2.4 is also a renewable resource that can be used to produce new product through the selected process. Coconut shell also suit for chemical adsorption since it is micro porous which is least dusty and has the high hardness (Guo et al., 2009). Besides that, coconut shells also have high volatility, low ash content and it also can yield the increasing surface area. Coconut shell is one of the biomass waste that can be treated to produce the high surface area meso porous activated carbons (Jain et al., 2015).

Figure 2.4 : Coconut Shell

(http://coconutboard.nic.in/shell.htm)

2.3 Processing of Activated Carbon

There two types of process that will be used to produce the activated carbon which are carbonization and activation process. The activation process are divided by two which are physical activation and chemical activation.

2.3.1 Carbonization

Carbonization or pyrolysis is the process that carbonizes the raw material at the optimum temperature. This process can produce charcoal by drives off volatile matter at high temperature in the absence of oxygen. The producing charcoal usually not well develops (Phan et al., 2006)

2.3.2 Activation Process

To create or increase the porosity on the activated carbon surface, the process of activation is used. The activation process are divided into two methods either physical activation or chemical activation. The physical activation also called steam or carbon dioxide activation while chemical activation needs activating agent or dehydration (Ansari, 2009).

2.3.3 Chemical Activation

Chemical activation is mainly use for biomass precursor because it achieves the surface area and higher yield besides low operating and energy cost required (Gratuito et al., 2008). Chemical activation method uses materials that containing carbon for producing activated carbon. In the chemical activation method, chemical agent is impregnated with the starting materials which the impregnating materials needed for carbonization process. The chemical agent or dehydrating agent is used to help activating carbon to develop. The uses of chemical activation method gives more advantages such as it will lower the activation temperature, increase the activated carbon yields and give well-developed micro porosity (Yorgun & Yıldız, 2015).

a) Activating Agent

The activation agent influences the pyrolytic processes so that the formation of tar is restricted to a minimum and the amount of aqueous phase in the distillate is also less than in normal carbonization. In this research chemical activating agent is used as dehydrating agents and it may restrict formation of tar during carbonization. The chemical activating agent will be used Zinc Chloride ($ZnCl_2$), Potassium Hydroxide (KOH), Sodium Hydroxide (NaOH) and Phosphoric Acid (H_3PO_4).

The previous research had studied the effect of the preparation condition by using $ZnCl_2$, KOH and H_3PO_4 as activating agent. The result shown that, different activating agent will producing different size of pore. The results are depicted in Figure 2.5(a), 2.5(b) and 2.5(c) (Dinesh, 2011).

(a)

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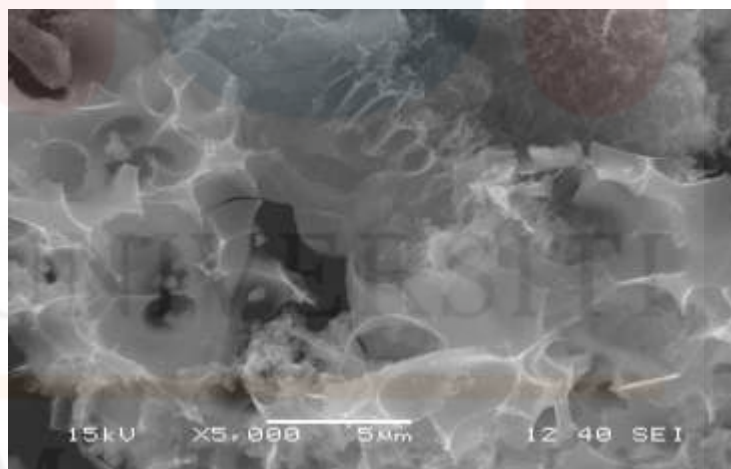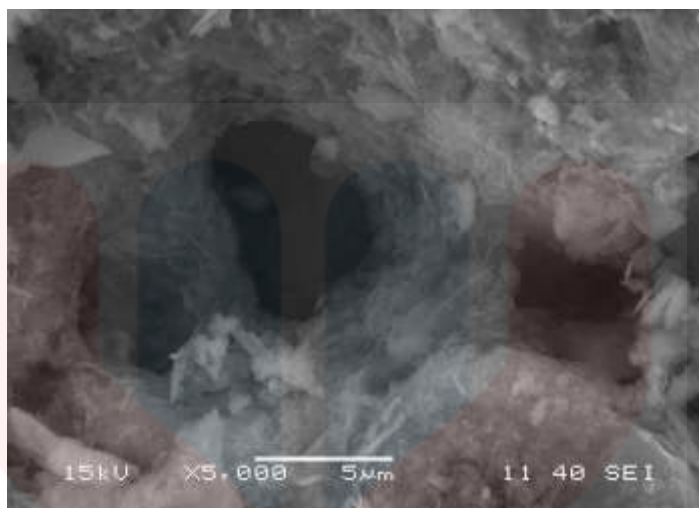
(b)
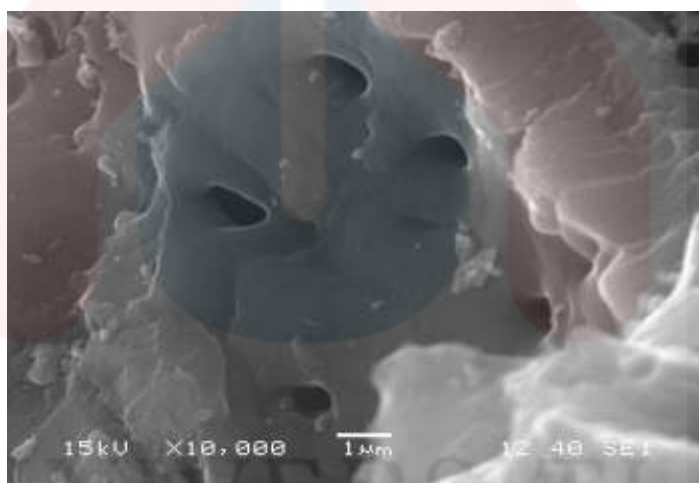
(c)

Figure 2.5 : SEM image of powder activated carbon using (a) KOH, (b) $ZnCl_2$, (c) H_3PO_4

(Dinesh, 2011).

2.4 Microwave

Microwave radiation method is the one of the method that can be replace after conventional heating method. Microwave radiation method is a possible method to solve the problems of thermal gradient and the high cost of activated carbon preparation. Promising results have been obtained by using this method for preparation of homogeneous inexpensive AC particles with high surface area and significant adsorption capacity. Higher sintering temperatures, shorter processing times and higher energy savings caused by using microwave radiation. Microwaves interact directly with the particles inside the pressed compact material and not conducted into sample from an external heat source which providing quick volumetric heating. The reaction from both internal and volumetric , where the huge thermal gradient from the interior of the sample to the cool surface allows the microwave – induced reaction proceed more quickly, shorter time and energy saving.

Thermal gradient in this method decreases gradually from the center to the surface of the sample due to higher temperatures in the interior that at the surface of the sample and it allows the light components are easily released to create more pores. Carbon materials are good microwave adsorbents, that allow carbonaceous materials to be transformed by microwave heating. For the microwave radiation method, the higher microwave power level, the higher rate of reaction between agent and precursor, which can promotes development of pore structure and active site. Increasing time activation also can intensified the formation of active site inside the AC (Hoseinzadeh et al., 2013).

CHAPTER 3

MATERIALS AND METHODS

3.1 Study area

This experiment was carried out at the laboratory of University Malaysia Kelantan (UMK). The raw materials, coconut shells were obtained from Pasar Jeli, while the chemicals were getting from the laboratory including the apparatus.

3.2 Chemicals and Apparatus

All of the chemicals that were used for this project were taken from stor (UPPKeM) or BaP lab. Chemical that has been used were, phosphoric acid (H_3PO_4), sodium hydroxide(NaOH), zinc chloride($ZnCl_2$), and hydrochloric acid (HCl).

For the apparatus that were used in this experiment are, furnace, pestle and mortar, test tube and electric beam balance.

3.2.1 Raw Material Preparation

This project were using coconut shells to form activated carbon. The coconut shells were obtain from market nearby. These coconut shells then were dried under the sunlight directly for two weeks. After dried these coconut shells were cleaned and washed to remove the impurities. After that it dried again for one week.

After dried directly under sunlight, the coconut shells then dried in the oven for 24 hours at 105 °C. Then, the coconut shells were grinded into small pieces. Next, there were a few steps in the process to identify the effect of chemical treatment on the production of activated carbon from the coconut shell. Figure 3.1 shows coconut shell dried in the oven and after grinding.

(a)

(b)

Figure 3.1 : (a) Coconut shell dried in oven (b) Grinded coconut shell

3.3 Production of Activated Carbon

The method that was used in this research are carbonization and chemical activation. The process of this experiment as shown in Figure 3.2.

```
┌─────────────────────────────────────────────┐
│        The coconut shell were cleaned        │
└─────────────────────────────────────────────┘
                       │
                       ▼
┌─────────────────────────────────────────────┐
│  Coconut shell were put in the furnace to  undergo │
│            carbonization process             │
└─────────────────────────────────────────────┘
                       │
                       ▼
┌─────────────────────────────────────────────┐
│  Coconut shell were crushed into powder and sieved │
└─────────────────────────────────────────────┘
                       │
                       ▼
┌──────────────────────────────────────────────────────────────┐
│ 3 samples were prepared to undergo activation process by impregnated with │
│ three different chemical activating agent with impregnation ratio, one of the │
│        sample will be used for variable constant test        │
└──────────────────────────────────────────────────────────────┘
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$ZnCl_2$ NaOH H_3PO_4

The samples were activated again using microwave irradiation. Then, sample were dried and then washed with distilled water

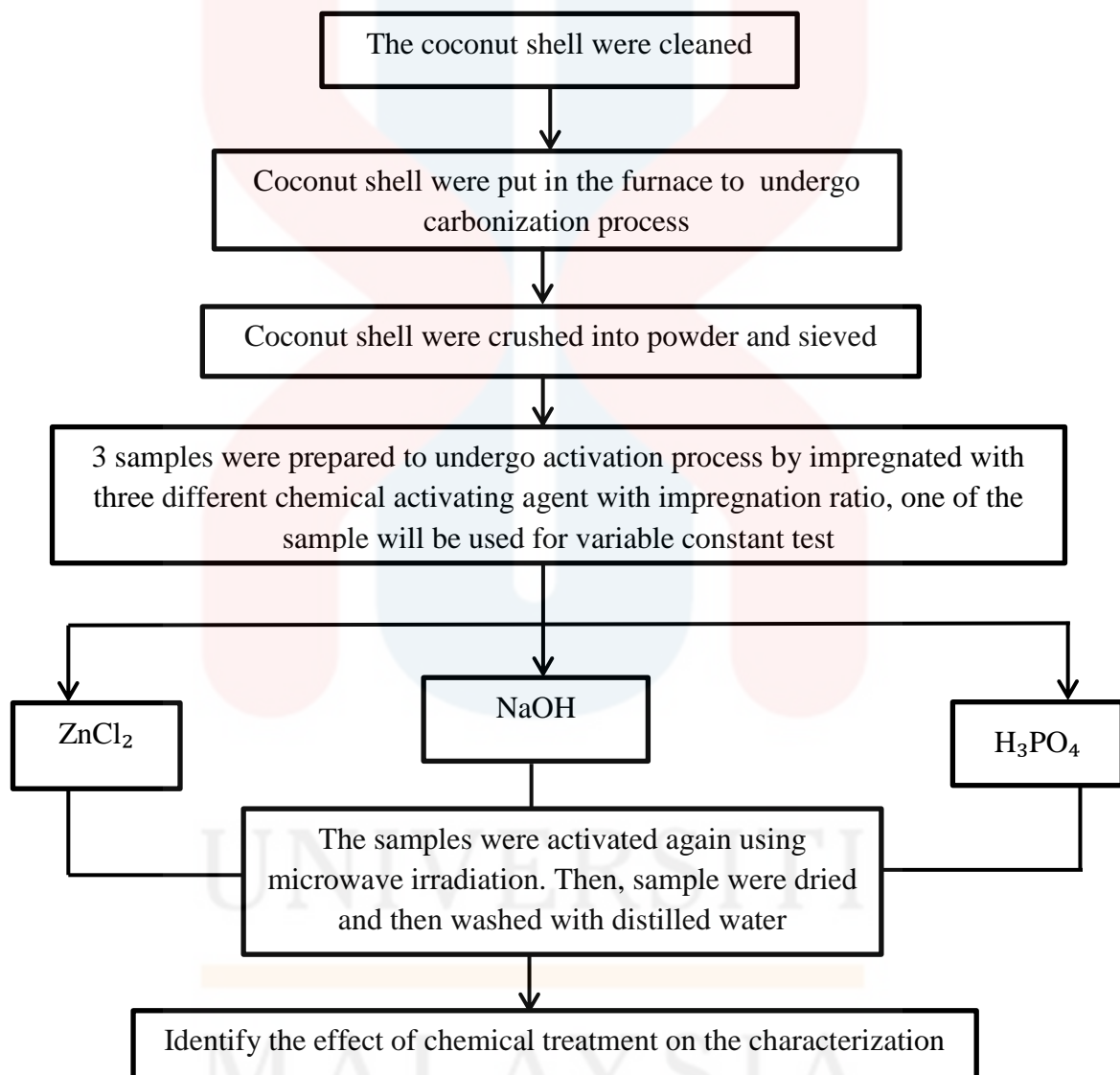Identify the effect of chemical treatment on the characterization

Figure 3.2 : Flow chart process to produce activated carbon

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3.3.1 Carbonization

The crushed coconut shells were put in the crucible before were put in the furnace to undergo the carbonization process. The furnace was set up to temperature at 500°C and then was held constant for one hour to allow the pyrolysis to take place with the absence of air until it becomes char (Asma et al., 2011). The purpose of this process is to enrich the carbon content and create char with an initial porosity (Ademiluyi, 2012). As is the case to avoid the dehydration, the charcoals obtained from pyrolysis were put in the airtight bags.

Then, the char were crushed into powder form by using mortar. When it became powder which give high surface area, the powder were sieved using 250 micron siever to get the same size of powder and to get rid of dust particles and others impurities (Inegbenebor et al., 2012). The powder then placed in airtight bags to prevent re-absorption of moisture from the atmospheric air. Figure 3.3 showed the char after sieved.

Figure 3.3: Char Powder after sieve

3.3.2 Chemical Activation Process

After pyrolysis process, the charcoal was underwent the chemical activation process (Yang et al., 2010). In this step, the char were separated into four parts which three of four parts were put in different activated agent Zinc Chloride ($ZnCl_2$), Sodium Hydroxide (NaOH) and Phosphoric Acid (H_3PO_4) while the other one stand as a control variable(Chandra et al., 2009).

First of all, the chemical activating agents NaOH and $ZnCl_2$ were prepared and H_3PO_4 were obtained from laboratory and put in to reagent bottle. For NaOH, the pallets were dissolved in distilled water to form 50% concentration base solution and the $ZnCl_2$ powders also dissolving with distilled water to get 50% concentration solution. These chemical activated agent which were act as dehydration used to develop activated carbon. After that, the char were impregnated with the activating agents with defined impregnation ratio. The impregnation ratio shown in the Table 3.1 was defined as the ratio of amount of chemical used for impregnation to the amount of precursor used. All the three chemicals used had a concentration of 50% w/w. The powdered coconut shell powder that was initially impregnated with activating agent were put in the beaker and dried in the room temperature for four hours as shown in Figure 3.4. After four hours, the impregnated samples were filtered. Next, the filtered impregnation samples then, put in the oven at 105 °C for 24 hours for drying.

Table 3.1 : Impregnation Ratio Activating Agent to Char

Sample	Impregnation Ratio Activating Agent to Char
NaOH	2:1
$ZnCl_2$	1:1
H_3PO_4	3:1

Figure 3.4 : Impregnation char with activating agent

The dry samples were then weighed and activate again by using microwave irradiation. The samples were put in the long glass test tube and then were put in the microwave as Figure 3.5 shown below. The microwave then set at 380 W and 10 minutes. Before start the microwave, the nitrogen were flowed through the wire for two minutes into the test tube. The parameter for the microwave radiation was shown in Table 3.2. The activation was performed under nitrogen flow rate of 150 cm³/min. The sample then put in the airtight bags to prevent moisture. After microwave process completed, the samples then had been washed to remove the impregnation agent using hot distilled water until get the neatural pH to ensure pore structure is available in activated carbon (Yorgun & Yıldız, 2015). After washed the sampled were put in the pastri dish and dried again in the oven at 80 °C for 16 hours. Then, all the sample were analyse with FTIR, XRD and TGA.

(a)

(b)

(c)

Figure 3.5 : Microwave irradiation method process
(a) Position of test tube
(b) The parameter was set up
(c) The full set up of microwave

Table 3.2 : The parameter of the experiment for four chemical activating agent

Activation Time	Weight Before (g)	Activating Agent		
		Sample 1	Sample 2	Sample 3
10 minutes	5	NaOH	ZnCl$_2$	H$_3$PO$_4$

3.4 Characterization

After that, the activated carbon were examined using, Fourier transform-infrared (FTIR), X-ray Diffraction (XRD) and thermogravimetric analysis (TGA).

3.4.1 Activation Carbon Yield

The percentage of the products were obtain by using the Equation 3.1.

$$\text{Percentage Yield} = \frac{\text{Weight final activated carbon}}{\text{Weight of initial native carbon}} \times 100\% \qquad (3.1)$$

3.4.2 Moisture Content

Moisture cotent was determined by using the moisture meter in Figure 3.6 below which is the measured the water bound to the activated carbon.

Figure 3.6 : Moisture measurement

3.4.3 Fourier transform-infrared (FTIR)

FTIR is most useful for identifying chemicals that are either organic or inorganic. It can be utilized to quantitate some components of an unknown mixture. It can be applied to the analysis of solids, liquids, and gasses. In this research, FTIR Analysis was used to study the surface organic structures and functional group presence at the surface of activated carbon. The wavelength that was used is from $4000 - 400$ cm $^{-1}$. The infrared spectrum is recorded by passing a beam of infarared light through the samples. The amount of energy that was absorbed at each wavelengths were reveal through the examination of transmitted light. This can be done by using a Fourier transform

instrument to measure all wavelengths at once or monochromatic beam. From this, a transmittance or absorbance spectrum can be produced.this technique work almost exclusively on samples with covalent bond. The technique has been used for characterization of various mixtures.

3.4.3 X- ray D iffraction (XRD)

X-ray scattering techniques are a family of non-destructive analytical techniques which reveal information about the crystallographic structure, chemical composition, and physical properties of materials and thin films. In this research, XRD will be conducted to identify the high degree of certainty the composition of the molecules, at atomic scale. XRD is the most reliable method to determine the composition of actiavated carbon.

3.4.4 Thermogravimetric Analysis (TGA)

This study also used thermogravimetric analyzer to conduct experiments on the activation carbon of coconut shells impregnated with activating agents. For each sample, weight of 5g was placed in the glass test tube. The samples were heated from 30 °C to 650°C at heating rate 10°C/min in nitrogen atmosphere with nitrogen flow 20mL/min. The study defines the remaining amount of sample decomposed in nitrogent as W/W_o. The percentage of weight loss and residue recorded. The TG and DTG curves also were recorded simultaneously as the temperature increased.

CHAPTER 4

RESULT AND DISCUSSION

4.1 Overview

This chapter discussed the results of the research from different testing such as XRD, FTIR and TGA. It also discussed the moisture content and yield percentage of the activated carbon which showed the differences of the activated carbon based on the chemical activating agent used. All results discussed about the activated carbon before and after the activation process.

4.2 Yield Percentage of Activated Carbon

The yield percentage of each activated carbon with different activating agents were calculated and showed in the Table 4.1 and Figure 4.1 below. The yield of products are higher for activated carbon with phosphoric acid activate with microwave ACPM , followed by activated carbon with sodium hydroxide (ACNM) and lastly the yield products was activated carbon with zinc chloride (ACZM). The lower yield product which was probably due to the formation of more micropores in the products as reported by Pradhan (2011).

Table 4.1 : Weight before and after microwave process and the yield percentage of the products.

Sample	Weight Before Microwave (g)	Weight After Microwave (g)	Yield Percentage (%)
ACNM	5.00	4.60	92.0
ACZM	5.00	4.43	88.6
ACPM	5.00	4.67	93.4

Yield Percentage (%)

ACNM - activated carbon with NaOH activated with microwave
ACZM - activated cabon with zinc chloride activated with microwave
ACPM - activated carbon with phosphoric acid activated with microwave
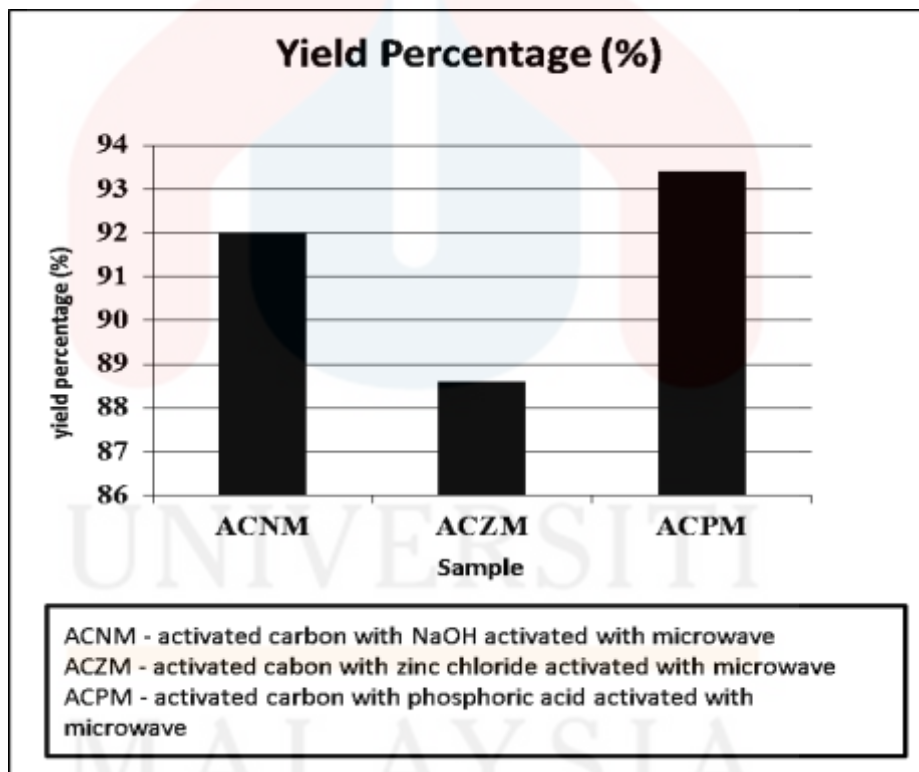
Figure 4.1 : The yield percentage of products graph

4.3 Moisture Adsorbance

The moisture adsorbance content of the native carbon (NC), activated carbon impregnated with NaOH activate with microwave (ACNM), activated carbon impregnated with $ZnCl_2$ activate with microwave (ACZM) and activated carbon impregnated with H_3PO_4 activate with microwave (ACPM) were examined and results were shown in Table 4.2. The temperature and time for test were fixed at 105^0C and 5 minutes. The result in Figure 4.2 show that the ACNM has higher moisture content than AZNM and APNM. Gumus and Okpeku (2015) reported that lower moisture content increases the rate of adsorption of contaminants.

Table 4.2 : Moisture Adsorbance (%)

Sample	Weight Before (g)	Moisture Adsorbance (%)
ACNM	0.532	14.66
ACZM	0.515	8.91
ACPM	0.527	9.89
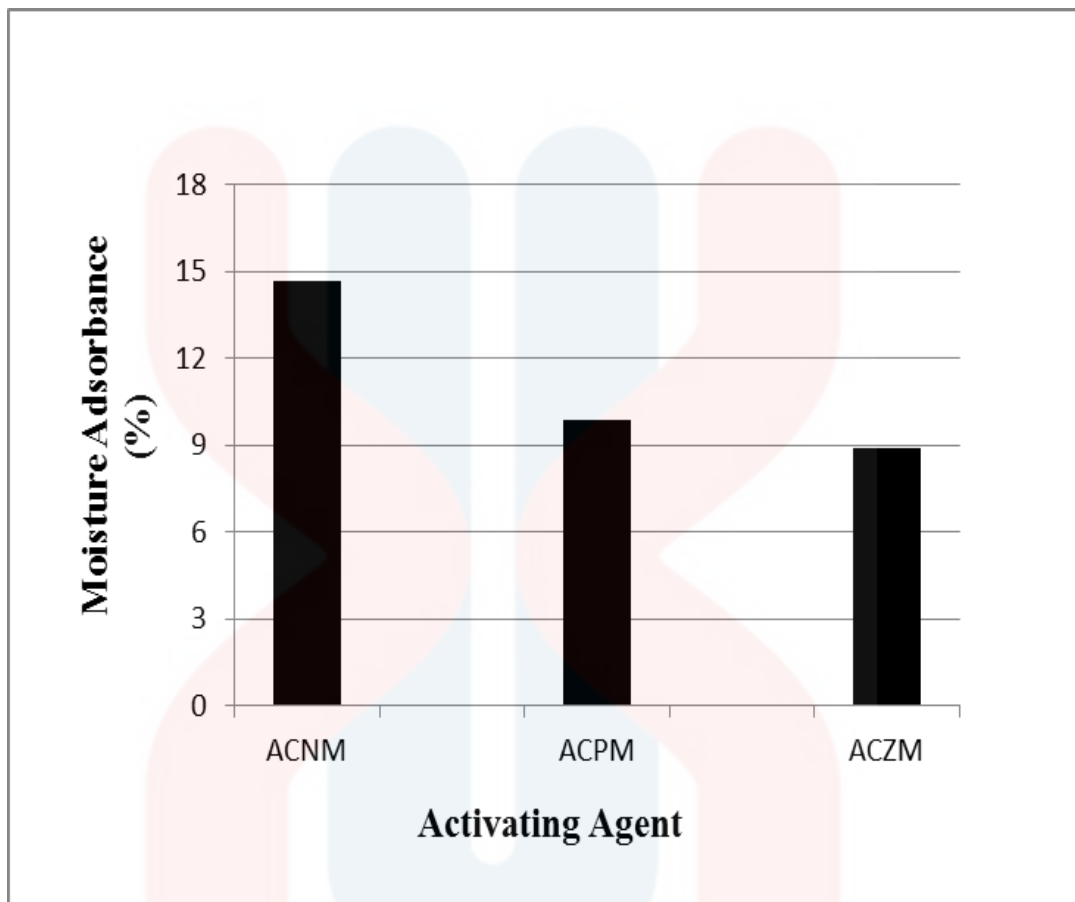
Figure 4.2 : The moisture adsorbance of the product graph
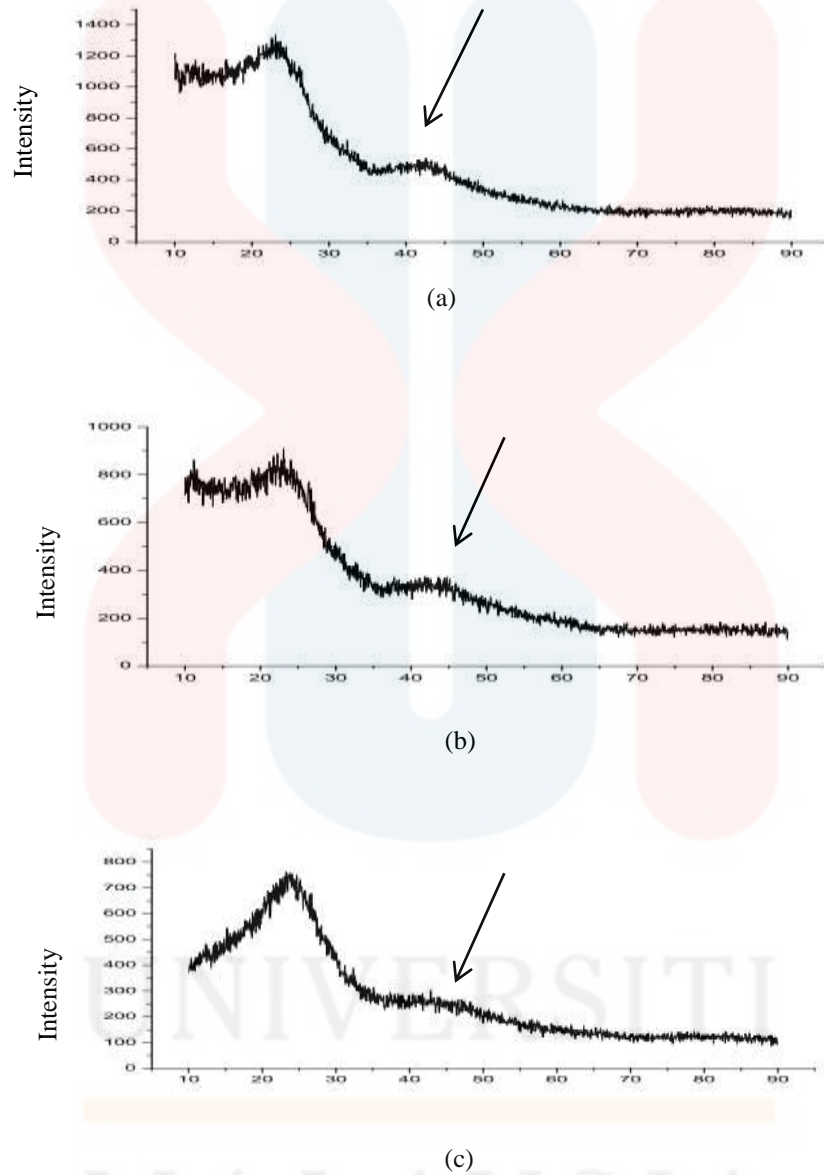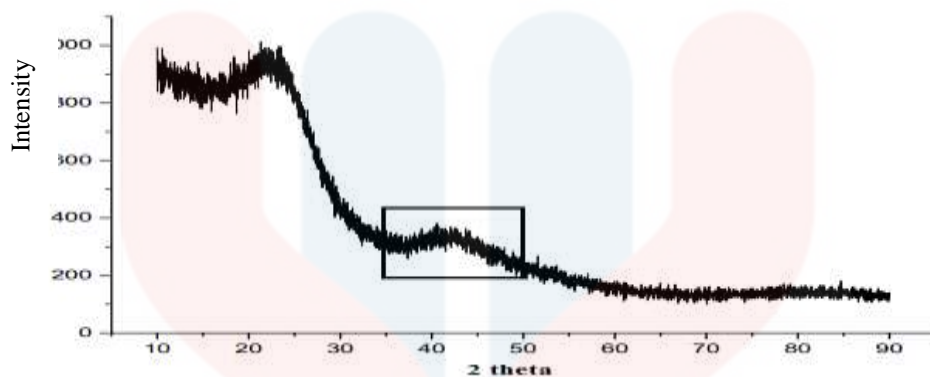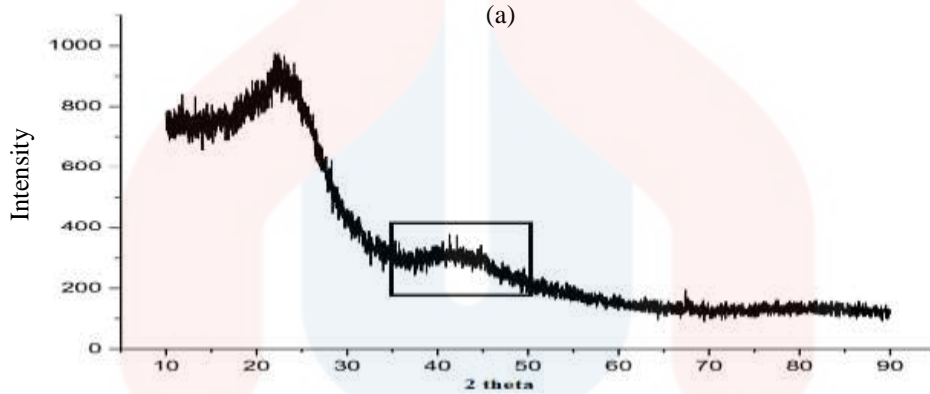
4.4 X-Ray Diffraction (XRD) Analysis
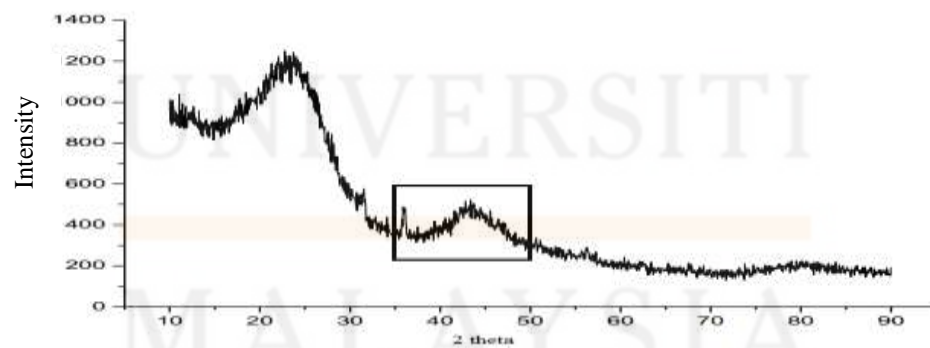

Figure 4.3 : Activated Carbon Impregnated with

(a) NaOH Without Microwave Process (ACNWM)

(b) ZmCl$_2$ Without Microwave Process (ACZWM)
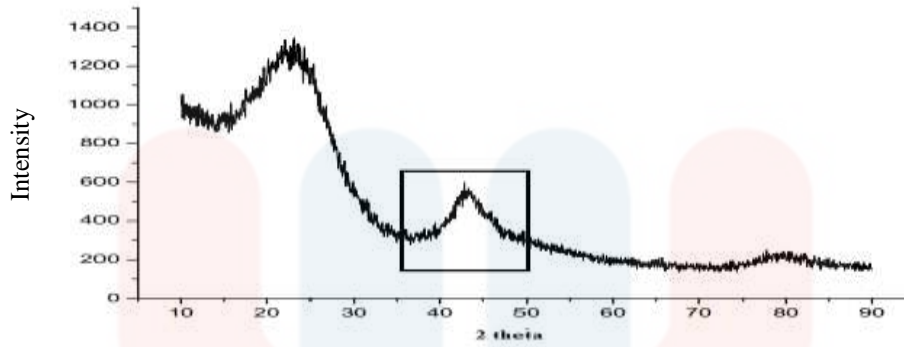
(c) H$_3$PO$_4$ Without Microwave Process (ACPWM)

(a)

(b)

(c)

(d)

Figure 4.4(a) Native Carbon (NC)
    (b) Activated Carbon Impregnated with NaOH Activate with Microwave (ACNM)
    (c) Activated Carbon Impregnated with $ZnCl_2$ Activate with Microwave (ACZM)
    (d) Activated Carbon Impregnated with H_3PO_4 Activate with Microwave (ACHM)

XRD analysis was carried out for each of the activated carbon samples for several times. Figure 4.3 and Figure 4.4 shows the X-ray diffraction (XRD) patterns of the activated carbon before and after the activation process that proved that all these char were amorphous. The broad peaks were identified at $2\Theta = 25°$ and $2\Theta = 45°$ for all the graphs. The broad peak at $2\Theta = 45°$ became stronger after activation with activating agent NaOH , $ZnCl_2$ and H_3PO_4 which indicated that carbon tends to crystallize at an elevated temperature.

As reported by Liou (2010) the peaks at $2\Theta = 45°$ are due to the creation of pores by the decomposition of carbon along the direction of the graphic structures. This produces relatively well - organized aromatic carbon that is more stable than amorphous – like carbon. The sharp peak was produced due to better layer alignment which was characteristic of a crytalline structure. Das (2015) claimed that, absence of sharp peaks in the activated carbon was predominantly amorphous structure which is advantageous property for well – defined adsorbents.

4.4 Functional group analysis of the activated carbons
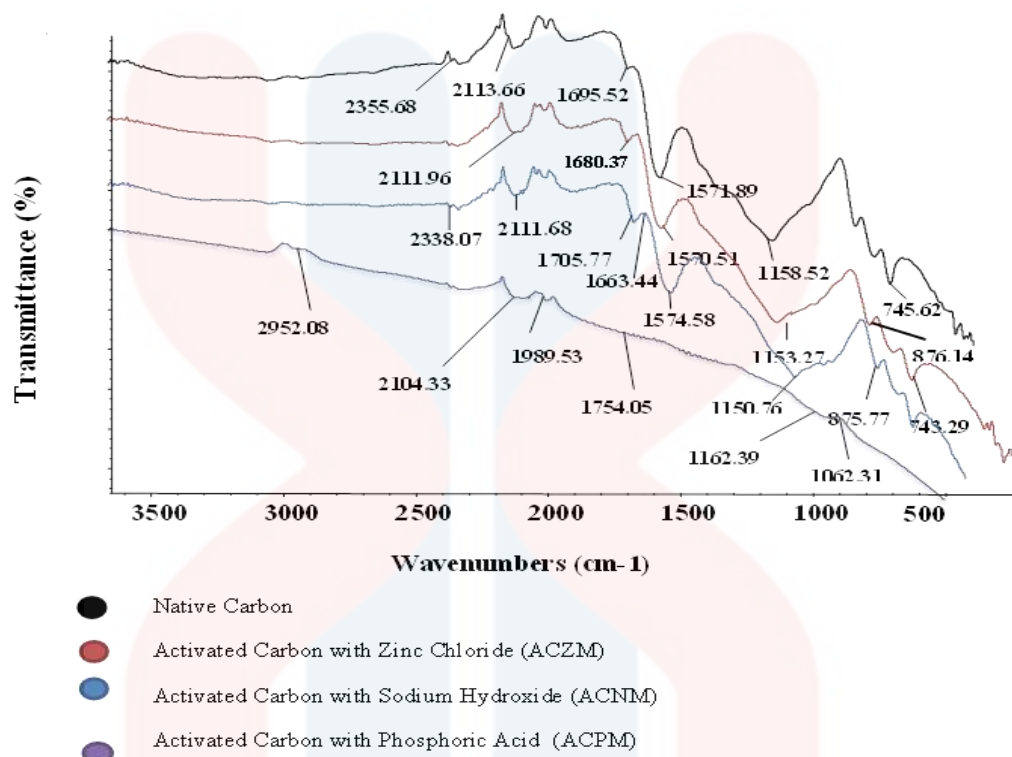

Figure 4.5 : FTIR- ATR Spectra For Activated Carbon

It is well known that activated carbons have a wide variety of surface functional groups. These groups depend on the precursor and method of activation. These groups are very important characteristics of the activated carbon, because they determine the surface propertiesof the activated carbon. Figure 4.5 above shows the Fourier transformed infra-red spectra of the activated carbons prepared using microwave heating with different activation agent. The FTIR spectroscopy provides information on the chemical structure of the materials. It can be observed from the figure that irrespective of the activation agent utilized the overall shapes of the spectra are very similar.

The sample of native carbon (NC), activated carbon impregnated with NaOH and activated by microwave radiation (ACNM), activated carbon impregnated with $ZnCl_2$ and activated by microwave radiation (ACZM), showed that three major adsorption bands at $1900\text{-}2500$ cm^{-1}, $1500\text{-}1600$cm^{-1} and $500\text{-}1200$cm^{-1}. The bands at $1100\text{-}1200$ cm^{-1} and $2100\text{-}2150$ cm^{-1} shows the wide band with two maximum peaks. The band around $1500\text{-}1700$ cm^{-1} were assigned to C = C streching vibration mode of olefinic C = C bonds as claimed by Das, (2015). The bands near 1700 cm^{-1} may indicate the C-H bonds of the phenyl ring substitution overtones (Dinesh, 2010) . The peaks near 1570 cm^{-1} for AC and others were assigned to a conjugated hydrogen bonded carboxcyl groups. At the peak around 1200 cm^{-1}, it was assigned as C – O vibration. In ACZM, at 1570.51 cm^{-1} , C=C vibration was formed and at 1153.27 cm^{-1} and 875.77 cm^{-1} the C – O and C – H vibration assigned.

For activated carbon impragnated with phosphoric acid and activated with microwave (ACPM) the peaks near 1160 cm^{-1} (P=O) was characteristic of PO2 stretching. The region between 700 and 1000 cm^{-1} contain bands related to aromatic. For ACPM the presence of phosphoric species are detected in the band aroun 900 cm^{-1} – 1200 cm^{-1}. At 1175cm^{-1} can be assigned to C – O stretching vibration in chain of C – O – P linkage. Unlike the FTIR spectrum showed by NC, ACNM, and ACZM, HM illustrates less absorption peaks. From the HM sample spectra, clearly, most of the absorption peaks of functional group were diminished. The adsorption patterns have almost same among each samples although the samples were prepared via various activating agents.
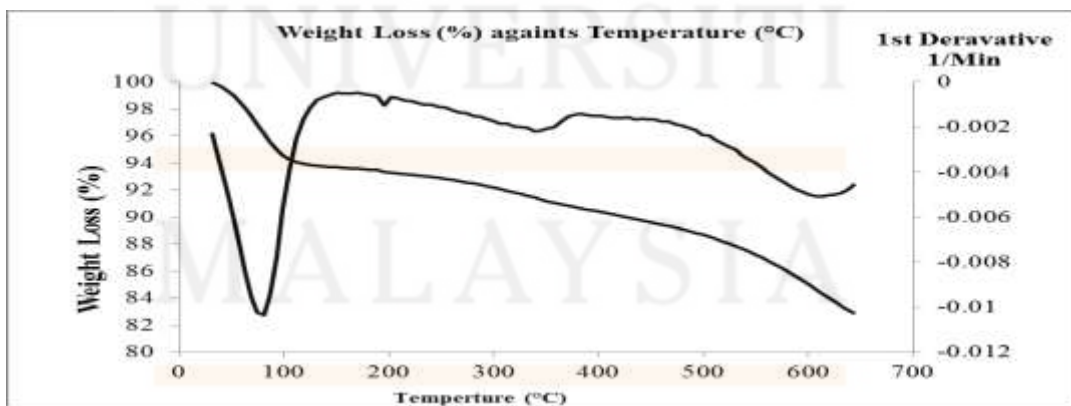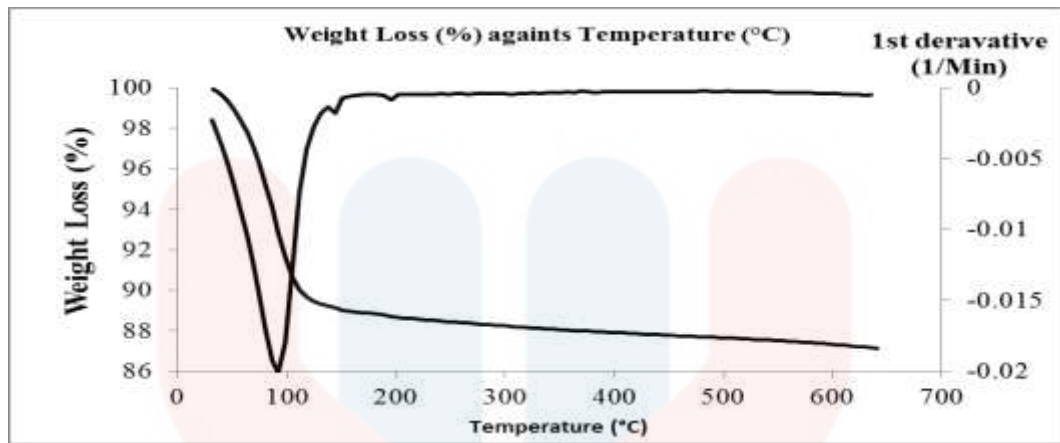
4.5 Thermogravimetric Analysis
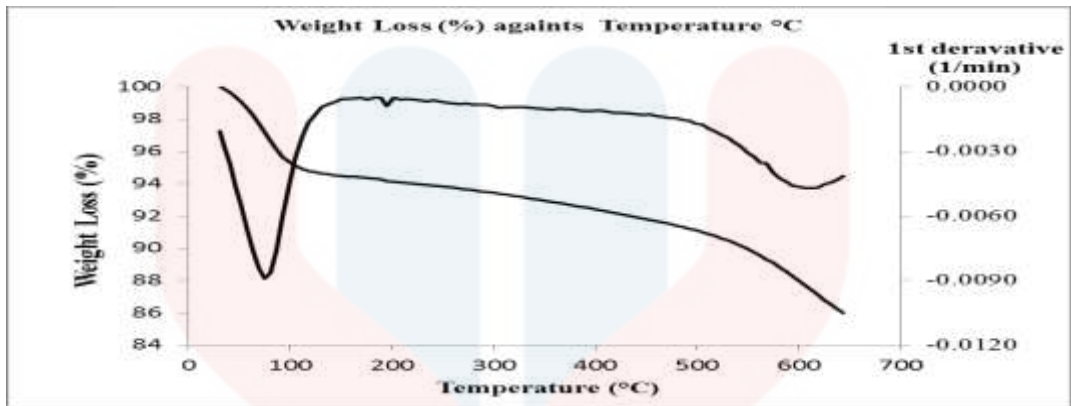
(a)
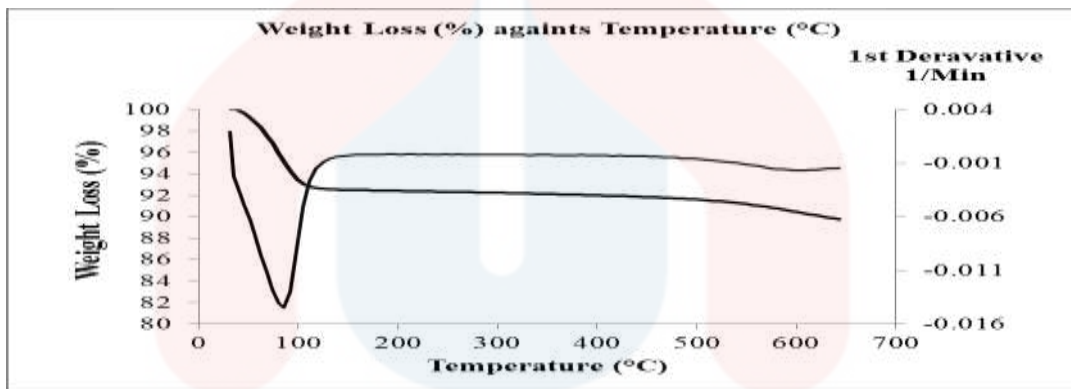
(b)

(c)

(d)

Figure 4.6 : TGA/DTG results of
(a) native carbon,
(b) activated carbon with phosphoric acid,
(c) activated carbon with sodium hydroxide, and
(d) activated carbon with zinc chloride

Figure 4.6 above shows the TG and DTG curves for weight loss versus temperature of sample of native carbon (NC), activated carbon with phosphoric acid (ACPM), activated carbon with sodium hydroxide (ACNM) and activated carbon with zinc chloride (ACZM) at the impregnation ratios prepared. The TG curves shows the samples clearly indicates that the initial weight loss were began at a temperature around 30 °C. It could be noted that the maximum loss of weight at the temperature around 100 °C. The constant line shows from 100 °C until 600 °C implies the constant ash that is left over before it start to loss weight for the last time at 600 °C.

It was observed that weight loss for activated carbons were around 11.41 % - 12.0 % compared to 14.25 % for the native carbon when the temperature was raised from 30 °C to very high temperature 650 °C . So, activated carbon is suitable

adsorbent as it has high thermal stability and more preferred over the native carbon. Das, (2015) , claimed that the weight loss of raw precursor is more than activated carbon.

Native carbon and ACHM have two stage which are the first stage decreasing slope was maximum as the organic matter decomposes releases the gaseous volatiles. For native carbon and ACHM, the temperature range from 30 °C – 110 °C and 30 °C – 130 °C while for the stage two, with further rise in temperature the downward slope again increase rapidly for both cases. In the stage two the temperature range from native carbon is 191.17 °C – 649.13 °C and ACHM is from 142.57 °C – 649.45 °C. The ACNM and ACZM divided into three stage which the first stage, the decreasing slope was maximum and for ACNM the temperature range was from 30.90 °C – 138.58 °C and 31.07 °C – 151.05 °C was the temperature range for ACZM. At stage two, the decreasing was a bit slowly from the range 137.61 °C – 384.38 °C for ACNM and 151.55 °C – 347.27 °C for ACZM and at this stage the chemical activating agents start to melt or decompose. At the last stage, the downward slope again increases rapidly for ACNM which range from 384.38 °C – 649.63 °C while downward slowly for ACZM as range from 374.75 °C - 649.84 °C as the temperature rise. At this stage, for all cases that account to severe erosion of material and the char reacts with activating agents, causing the pores to open.

By analyzing both graphs , it was observed the activated carbon has very high resistant to weight loss compared to char, which range temperature rise was same from 30 °C – 650 °C. Thus the activated carbon can be subjected till 650 °C without much significant weight loss of adsorbent.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

In this study coconut shell was used as raw material for activated carbon. Activation carbon was produced from activation charcoal by using chemical activating agent such as zinc chloride, sodium hydroxide and phosphoric acid. This study gave a very such helpful in choosing the appropriate precursor and activating agents in the process to produce better activated carbon by it proximate results. In this study also show that the activated carbon activate by phosphoric acid as activating agent was the best among the three chemical.

The higher yield product which was probably due to the formation of more micropores in the products. The lower moisture content showed that the increasing of rate of adsorption of contaminant. The X–ray Diffraction (XRD) was give the result that allow us to know the composition and the crystallinity of the activated cabon. It shows the peak where we will know whether it is crsytalline or amorphous and in this study it prove that the activated carbon is amorphous.

Fourier transformed infra-red spectra (FTIR-ATR) shows that the adsorption patterns have almost same among each samples although the samples were prepared via various activating agents.The Thermogravimetric Analysis (TGA) was provide the result that make the study easier since it acted as the guidline for the determination of the exact temperature range in which the activation was to be carried out. It was very helpful since the results gave the exact optimum temperature for the activation of coconut shells.

5.2 Recommendation

For the future research of this study it is recommended to add the characterization technique such as Brunauer-Emmett-Teller (BET), and Scanning Electron Microscopy (SEM) to obtain the significant data and morphology The SEM will show the micro structure of the sample while the BET will examine surface area, pore size and pore volume of the sample. In addition other agriculture waste can be considered such palm kernel, coconut husk and orange peel.

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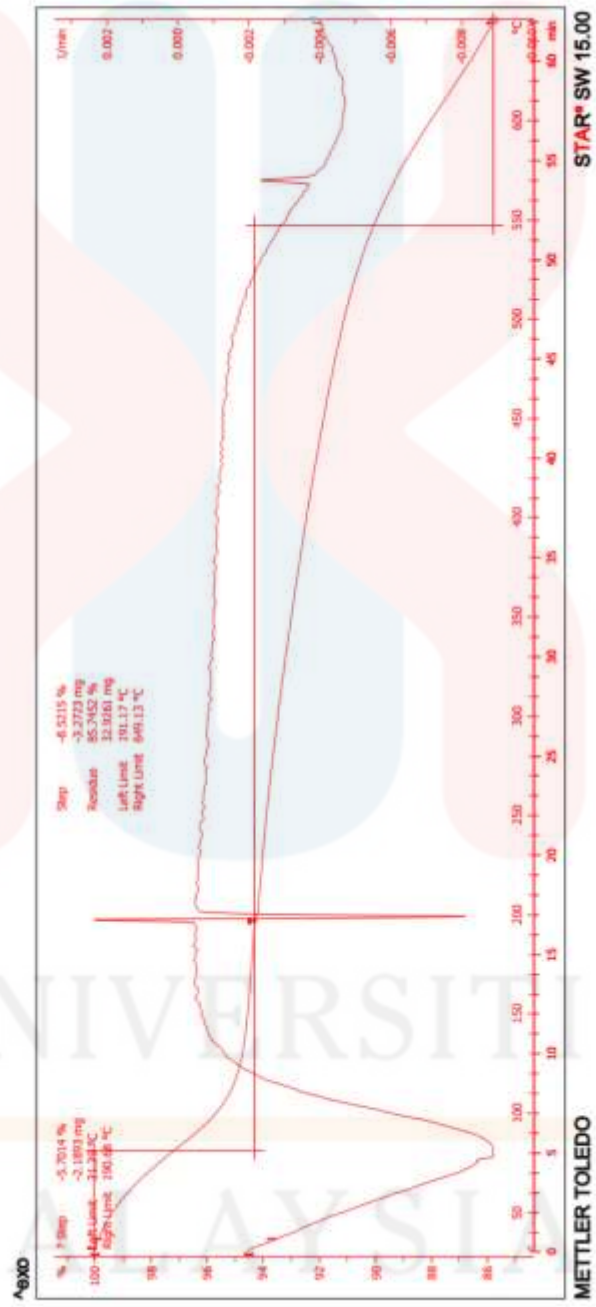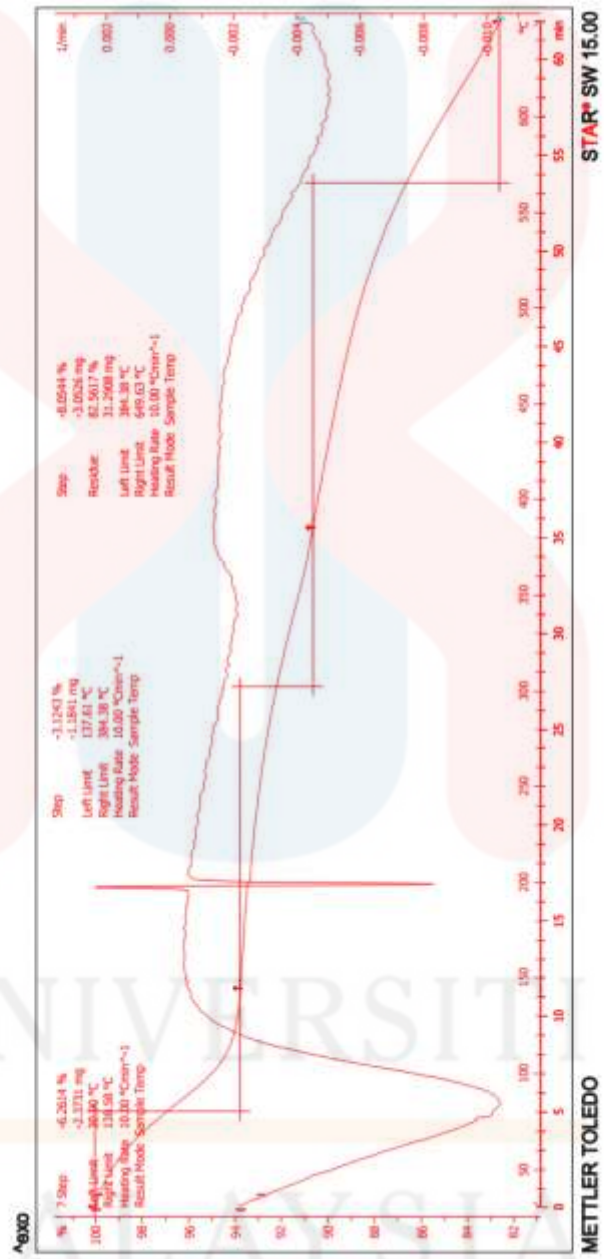
Fig: TGA graph of Native Carbon

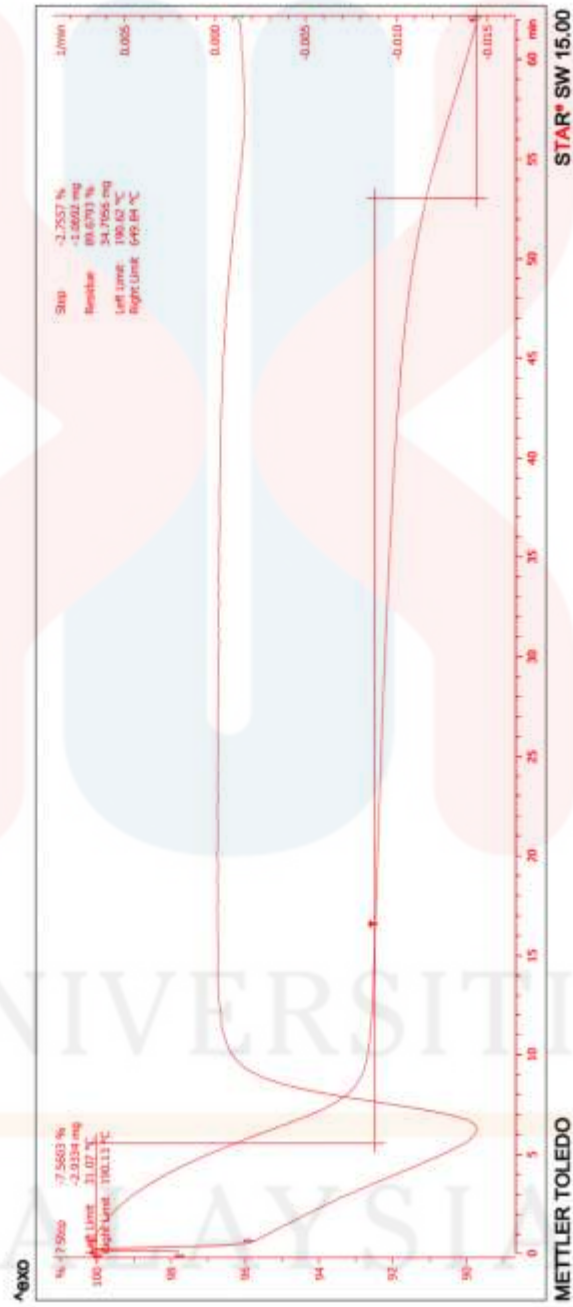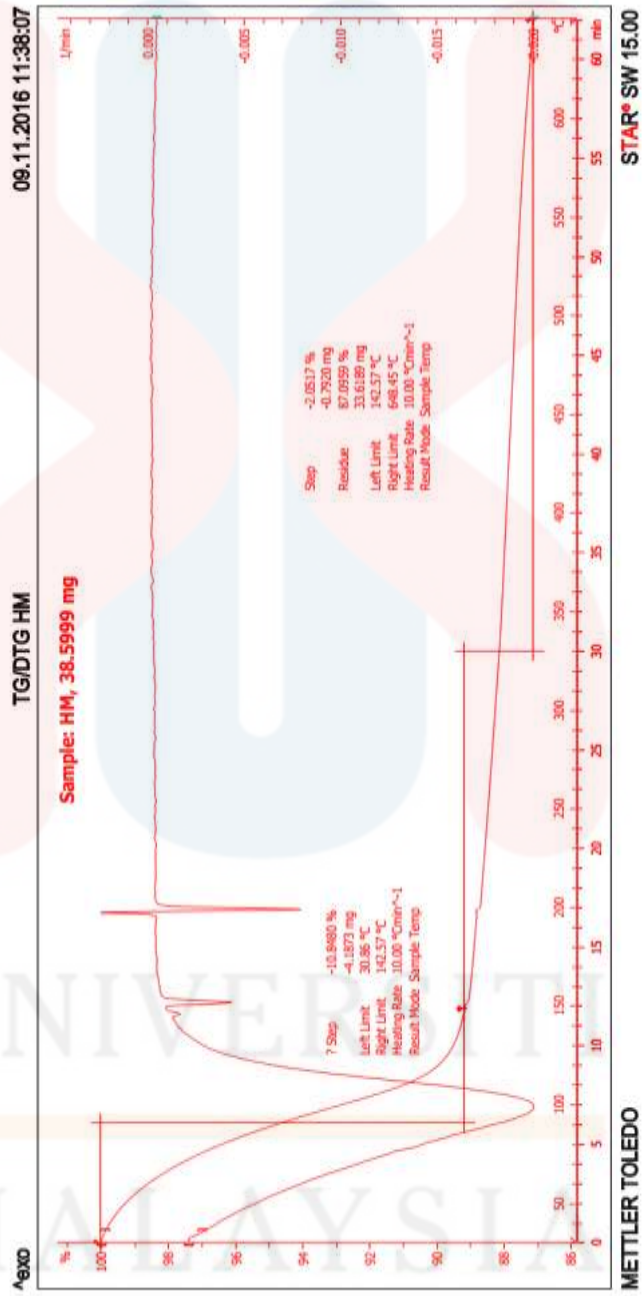**Fig:** TGA graph of activated carbon with NaOH

APPENDIX C

Fig: TGA graph of activated carbon with ZnCl$_2$

APPENDIX D

Fig: TGA graph of activated carbon with H_3PO_4

50