# การเตรียมถ่านกัมมันต์จากกากตะกอนของเสียปิโตรเคมี โดยการกระตุ้นเชิงเคมีและกายภาพ

นาง ชนกพร แซ่อึ้ง

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
สาขาวิชาปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์
คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2552

# PREPARATION OF ACTIVATED CARON FROM PETROCHEMICAL WASTE SLUDGE BY CHEMICAL AND PHYSICAL ACTIVATION.

Mrs. Chanokporn Saeung

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science Program in Petrochemistry and Polymer Science
Faculty of Science
Chulalongkorn University
Academic Year 2009

| | |
|---|---|
| Thesis Title | PREPARATION OF ACTIVATED CARON FROM PETROCHEMICAL WASTE SLUDGE BY CHEMICAL AND PHYSICAL ACTIVATION. |
| By | Miss Charnokporn Saeung |
| Field of Study | Petrochemistry and Polymer Science |
| Thesis Advisor | Associate Professor Tharapong Vitidsant, Ph.D. |

---

Accepted by the Faculty of Science, Chulalongkorn University in Partial Fulfillment of the Requirements for the Master's Degree

……………………………… Dean of the Faculty of Science
(Professor Supot Hannongbua, Dr.rer.nat.)

THESIS COMMITTEE

……………………………………………….. Chairman
(Professor Pattarapan Prasassarakich, Ph.D.)

……………………………………….…….Thesis Advisor
(Associate Professor Tharapong Vitidsant, Ph.D.)

……………………………………………….. Examiner
(Associate Professor Wimonrat Trakarnpruk, Ph.D.)

……………………………………………….. External Examiner
( Suneerat  Pipatmanomai, Ph.D.)

ชนกพร แซ่อึ้ง : การเตรียมถ่านกัมมันต์จากกากตะกอนของเสียปิโตรเคมี
โดยการกระตุ้นเชิงเคมีและกายภาพ (PREPARATION OF ACTIVATED CARON FROM PETROCHEMICAL WASTE SLUDGE BY CHEMICAL AND PHYSICAL ACTIVATION.) อ. ที่ปรึกษาวิทยานิพนธ์หลัก : รศ.ดร. ธราพงษ์ วิทิตศานต์, 93หน้า.

งานวิจัยนี้เป็นการศึกษากระบวนการเตรียมถ่านกัมมันต์จากกกากตะกอนของเสียปิโตรเคมีโดยกระบวนการคาร์บอไนซ์และการกระตุ้นทางกายภาพด้วยคาร์บอนไดออกไซด์และไอน้ำร้อนยวดยิ่งและกระตุ้นทางเคมีโดยการเปรียบเทียบสารเคมีที่เหมาะสมในการกระตุ้นโดยใช้ฟอสฟอริก แอซิด โปตัสเซียมไฮดรอกไซด์ และซิงค์คลอไรด์.ในการวิจัยนี้มีสองขั้นตอน เริ่มต้นด้วยการหาอุณหภูมิที่เหมาะสมของการคาร์บอไนซ์ในช่วง 375-450 องศาเซลเซียสโดยที่อุณหภูมิที่เหมาะสมต่อการคาร์บอไนซ์คือ 400 องศาเซลเซียสเป็นเวลา 90 นาที จากนั้นนำถ่านชาร์ที่ได้ไปกระตุ้นทางเคมีและทางกายภาพโดยศึกษาตัวแปรที่ใช้คืออุณหภูมิ เวลาและขนาดของถ่านชาร์จากกากตะกอนของเสีย จากผลการทดลองพบภาวะที่เหมาะสมในการกระตุ้นคือใช้ ถ่านชาร์จากกากตะกอนของเสียโดยการกระตุ้นทางเคมีด้วย ซิงค์คลอไรด์ด้วยขนาด 1.18-2.36 มิลลิเมตร กระตุ้นที่อุณหภูมิ 350 องศาเซลเซียสเป็นเวลา 1 ชั่วโมง โดยควบคุมปริมาณไนโตรเจน 250 มิลลิลิตรต่อนาที ถ่านกัมมันต์จากกากตะกอนของเสียที่พบมีร้อยละผลิตภัณฑ์ 88.53 ความหนาแน่นเชิงปริมาตร 0.35 กรัม/ตารางเซนติเมตร ค่าการดูดซับไอโอดีน 648.50 มิลลิกรัม/กรัม ค่าการดูดซับเมทิลีนบลู 296.13มิลลิกรัม/กรัม และพื้นที่ผิวรูพรุน 551.23 ตารางเมตร/กรัม ถ่านกัมมันต์ที่ได้จากกากตะกอนของเสียปิโตรเคมีอยู่ในมาตรฐานเกรดการค้า เพราะให้ค่าการดูดซับไอโอดีนมากกว่า 600 มิลลิกรัม/กรัมนั้นเป็นที่ยอมรับโดยทั่วกัน

สาขาวิชา..ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์..ลายมือชื่อนิสิต.............................................
ปีการศึกษา......................2552...……………ลายมือชื่ออ.ที่ปรึกษาวิทยานิพนธ์หลัก...............

# # 507 34203 23 : MAJOR PETROCHEMISTRY AND POLYMER SCIENCE

KEYWORDS: ACTIVATED CARBON / SUPERHEAT STEAM ACTIVATION / CHEMICAL ACTIVATION / SEWAGE SLUDGE.

CHANOKPORN SEAUNG : PREPARATION OF ACTIVATED CARON FROM PETROCHEMICAL WASTE SLUDGE BY CHEMICAL AND PHYSICAL ACTIVATION. THESIS ADVISOR : ASSOC. PROF THARAPONG VITISANT, Ph.D., 93 pp.

The research was the study of the effect of activation by petrochemical waste sludge by physical activation with superheated steam carbondioxide and chemical activation by suitable chemical with potassium hydroxide, phosphoric acid and zinc chloride on properties of activated carbon from sewage sludge. The experiment work included two steps. The first step was carbonization which was carried out in the temperature range of 375-450ºC. It was found that the optimum condition was 400ºC for 90 min. The second step was activation by chemicals and physical activations. The study variables were temperature, time, and, char particle size form waste sludge. The optimum activation condition was chemical activation by zinc chloride; size 1.18-2.36 mm.at temperature 350ºC 1 hr and flow rate of nitrogen of 250 ml/ min. The property of prepared activated carbon from waste sludge was % yield of 88.53, bulk density of 0.35 g/cm$^2$, iodine number of 648.50 mg/g, methylene blue number of 296.13 mg/g, B.E.T. surface area of 551.23 m$^2$/g. The prepared activated carbon from waste sludge from petrochemical could be the commercial grade, because the accepted standard iodine absorption is more than 600 mg/g.

Field of Study:..Petrochemistry and Polymer Science… Student's Signature:..……......
Academic Year..2009………………………………….. Advisor's Signature:……..…

# ACKNOWLEDGEMENTS

The author would like to express her sincere gratitude to advisor, Assoc. Prof. Dr. Tharapong Vitidsant, for their encouraging guidance, supervision and helpful suggestion throughout this research. The author also would to acknowledge Prof. Dr. Pattarapan Prasassarakich, Assoc. Prof. Dr. Wimonrat Trakarnpruk, and. Dr. Suneerat Pipatmanomai for serving as chairman and members of thesis committee, respectively and for their worthy comments and suggestions. Many thanks are going to technicians of the Department of Chemical Technology, Chulalongkorn University. The author gratefully acknowledges the funding support from Program of Petrochemistry and Polymer Science, and National Center of Excellence for Petroleum, Petrochemicals, and Advanced Materials, SCG Chemical Co,Ltd, kindness in supplying waste sludge as a raw material for experiment. Eventually the author would like to express her gratitude to family members for their love, understanding and great support throughout her study. Also, special thanks are expanded to her friends for friendship, encouragements and cheerful moral support.

# CONTENTS

# LIST OF TABLES

# LIST OF FIGURES

# LIST OF ABBREVIATIONS

T : Temperature ( °C)
g : gamme
% Y : % Yield
% M : % Moisture
% VM : %Volatile matter
%FC : % Fixed carbon
BD : Bulk density ($g/cm^3$)
IA : Iodine number (mg/g)
MB : Methylene blue number (mg/g)
B.E.T : B.E.T. surface area ($m^2/g$)
GAC : Granular activated carbon
PAC : Powder activated carbon

# CHAPTER I

# INTRODUCTION

## 1.1 Introduction

Many materials rich in carbon can be used as precursors in the production of activated carbons.[1] The resulting products may have a high adsorption capacity as a result of their physical and/or chemical structure. Activated carbons, which have an enlarged porous structure, are, because of this, very useful in processes involving the separation of mixtures and the cleansing of gases and liquids. They are used in the removal of pollutants which difficult to eliminate owing to their resistance to conventional biological treatments, for example those in some industrial effluents. In this way, adsorption plays an important role in the elimination of non-biodegradable organic pollutants. The activated carbon is the most commonly used as adsorbent because of its versatility and efficiency.

**Table 1.1** Quantity and value of import and export of activated carbon between 2001-2008 (Activated carbon code HS 3802.100-004)

| Year | Import | | Export | |
|---|---|---|---|---|
| | Quantity (kg) | Value (baht) | Quantity (kg) | Value (baht) |
| 2001 | 3,120,594 | 156,116,706 | 3,651,904 | 161,221,372 |
| 2002 | 3,278,957 | 145,201,933 | 3,426,652 | 139,579,749 |
| 2003 | 3,493,984 | 145,810,837 | 4,752,756 | 179,769,321 |
| 2004 | 4,162,058 | 155,816,098 | 6,545,707 | 250,178,784 |
| 2005 | 4,802,834 | 204,881,304 | 8,225,942 | 320,056,852 |
| 2006 | 5,721,970 | 267,327,840 | 30,587,777 | 302,584,339 |
| 2007 | 4,435,887 | 223,121,035 | 9,309,014 | 263,440,875 |
| 2008 | 3,853,152 | 244,428,846 | 10,468,576 | 374,806,960 |

**Source**: Department of Business Economic, Finance Ministry.

The world annual production of activated carbon in all forms is estimated to be in the range of 300,000-400,000 tones. About 55% of this total is in powder form, about 35 % in granular form and the remainder is produced as pellets or extradites,According to one reference ,about 80% of the total production (powder , granular and formed carbon) is used in liquid-phase applications and the remaining 20% (granular and formed carbon only) in gas-phase applications. The highest consumption is in Japan and the USA  per capita annual consumption is 0.5 kg in Japan,0.4 kg in the USA in Europe and 0.03 kg in the rest of the world.Consumption is increasing at a reported rate of about 7 % per annul.[10]  Growth areas are in air purification ,solvent recovery and groundwater treatment and new applications are emerging, particularly those related to environmental protection, that will tend to sustain the level of demand.The approximate average selling price for granular or formed carbon is between US$ 1,500-4,000 per ton. For powder carbon, it is between US$ 500-1,200 per tone. The actual price will vary with the level of activity (surface areas commonly fall in the range 800-1,500 $m^2/g^{-1}$), the strength and attrition resistance and whether impregnates have been added to enhance adsorption selectivity.

Sewage  sludges  are produced as a result of wastewater treatment activity and their production is expected to gradually increase through environmental necessity and legal requirements for wastewater treatment. The conventional disposal options include landfill, application to farmland and forestry, incineration and sea dumping.Sea dumping has recently been banned in many countries due to its pollution to sea incurred by heavy metals, oil, grease and detrimental microorganism. Farmland application is also limited by the uptake capacity of the soil and the potential pollutionby the heavy metals. Landfill has long been a major option in disposal of sewage sludge, but it will not be sustainable due to increasing competition for landfill space,higher costs and more stringent environmental standards applied [2]. Thus, incineration is playing an important role in recent years. However, concerns over its rising energy cost, ash disposal and gaseous emissions continue to be significant constraints on its more widespread use. Therefore, it is pressing to seek a cost-effective and innovative solution to the problem

It is therefore necessary to research the way of making use of sewage sludges. Giving these sludge  carbonaceous nature, the production of activated carbons  from them may be an interesting option. Normally, the starting material for the activated carbons production has to be pyrolysed under certain conditions after an activation treatment [1-4]and the activation may be physical or chemical [3-9]. In the case of chemical activation, the starting material is impregnated with an activating agent before pyrolysis. Among the most commonly used agents are $ZnCl_2$ and $H_2SO_4$. Sewage sludge was impregnated with the corresponding agent, each of them having a different effect on sludge during the pyrolysis-carbonization step. $ZnCl_2$ is a depolymerizer that favors cracking in the liquid phase, more char being formed than tar. It also works as a dehydration reagent and dehydration induces the charring and aromatization of carbonaceous materials during pyrolysis $H_2SO_4$ is also a dehydrator, affecting pyrolytic decomposition and giving rise to reactions of acid hydrolysis. It also promotes depolymerization and makes it easier to obtain products richer in carbon, for, as a dehydrator, it facilitates the loss of hydrogen and oxygen. In both cases, the obtained final products have a developed porous structure that allows for its use as an adsorbent. This is the usual way of obtaining porous materials by chemical activation, and many works have been published using very different waste starting materials. However, if the chemical activators are not completely washed before using neither retained in the adsorbent surface, they may be liberated to the environment when using the produced adsorbents.

This work shows the studies of optimum condition in the production of activated carbon from sewage sludge by physical and chemical activations in an activator, which reduce problem from industry. It would also improve sludge management and give economic value to waste as a cheap raw material for making adsorbents.

## 1.2 Objectives

The objectives of this work are following:

1. To study the production of activated carbon from activated sludge by physical and chemical activation.
2. To study the parameters and find the suitable conditions of activated carbon preparation.

## 1.3 Scope of the research

For the production of activated carbon from sewage sludge by physical and chemicals activations, the appropriate condition such as temperatures, activation times, sizes of the raw material were studied. The necessary procedures are following:

1. Literature survey and in-depth study of this research work.
2. Characterization of sewage sludge.
3. Carbonization changing the following parameters

    Temperature : 375, 400, 425 and 450ºC

    Time : 30, 60, 90 and 120 minutes.

4. Production of activated carbon from sludge by physical activation by superheat steam and $CO_2$ changing the following :

    Temperature : 150 250 350 and 450ºC

    Size : 0.5-0.8, 1.18 -2.00 mm

    Time : 1 and 2 hrs.

5. Production of activated carbon from sludge by chemical activation changing the following :

    Type of chemical solution :KOH, $H_3PO_4$, $ZnCl_2$

    Temperature : 150, 250, 350 and 450ºC

    Size : 0.5-0.8, 1.18 -2.00 mm

    Time : 1 and 2 hrs.

6. Investigation of the properties of the activated carbon such as % yield, bulk density, iodine number, methylene blue number and B.E.T. surface area.
7. Summarize the results and conclusion.

# CHAPTER II

# THEORY AND LITERATURE REVIEWS

## 2.1Activated carbon [11]

Activated carbon is a processed carbon material with a highly developed porous structure and a large internal specific surface area. If you take a look at a cross section of an activated carbon particle, it looks like a beehive. It consists, principally of carbon (87 to 97%) but also contains such elements as hydrogen, oxygen, sulfur and nitrogen, as well as various compounds either originating from the raw material used in its production or generated during its manufacture.

Activated carbon has the ability to adsorb various substances both from the gas and liquid phases. It is widely used for adsorption of pollutants from gaseous and liquid steams, for recovery of solvent and as a catalyst or catalyst support. In the nuclear industry, activated carbon is used for adsorption of iodine and noble gases from gaseous effluents. One of the most important fields in terms of consumption is in water and wastewater treatment. To obtain these activated carbons from cheap and readily available precursors become an interesting objective.

Adsorption on activated carbon is selective, favoring nonpolar over polar substances and in a homologous series, generally improving with increasing boiling point. Absorption is also improved with increased pressure and reduce temperature. Reversal of the physical absorptive conditions (temperature, pressure, or concentration) more or less completely regenerates the carbon activity, and frequently allows recovery of both the carrier fluid and absorbent. Compared with other commercial absorbents. Activated carbon has a board spectrum of absorptive activity, excellent physical and chemical stability, and ease of production from readily available, frequently waste materials.

Large-pore decolorizing carbons are used in liquid phase work. Applications include improving the color of manufactured chemicals, oils, and fats, as well as controlling odor, taste, and color in potable water supplies, beverages, and some foods. Gas-absorbent carbons are generally harder, higher-density, finer pore types useful in gas separations, recovering solvent vapors, air conditioning, gas marks, and supporting metal salt catalysts, particularly in the production of vinyl-resin monomers.

## 2.2 Raw materials for the production of activated carbon [10]

The principal properties of manufactured activated carbons depend on the type and properties of the raw material used. Any cheap substance with a high carbon and low ash content can be used as a raw material for the production of activated carbon. In Europe the most important raw materials used for this purpose are wood(sawdust), charcoal, peat, peat coke, certain types of hard and brown coal, and the semi-coke of brown coal. To produce activated carbon, which should exhibit high adsorption capacity and a large volume of the smallest pores (micropores), coconut shells are usually used. In the USA, brown carbons and petroleum products are widely used for manufacturing activated carbons. Source materials that have been studied for the production of activated carbon(10).

Bagasse
Beet-sugar sludges
Bones
Carbohydrates
Cereals
Coal
Coconut shells
Coffee beans
Corncobs and corn stalk
Distillery waste
Fish
Flue dust
Fruit pits
Graphite
Kelp and Seaweed
Leather waste
Lampblack
Lignite
Molasses
Nut shells
Oil shale
Peat
Polymer scrap
Petroleum acid sludge
Potassium ferricyanide
Petroleum coke
Pulp-mill waste
Rice hulls
Rubber waste
Sawdust
Wood

## 2.3 Production of activated carbon

Activated carbon is usually produced by the carbonization and activation of carbonaceous materials.

### 2.3.1 Carbonization (or pyrolysis) [10]

The production of activated carbon by the steam-gas method must meet certain requirements among which the most importances are (i) low content of volatile matter, (ii) high content of elemental carbon, (iii) definite porosity and (iv) sufficient strength of attrition. Of course, raw materials do not meet all these requirements simultaneously and therefore they require carbonization.

This is one of the most important steps in the production process of activated carbons since it is in the course of carbonization that the initial porous structure is formed. During carbonization most of the non-carbon elements, hydrogen and oxygen are first removed in gaseous form by pyrolytic decomposition of the starting material, and the freed atoms of elementary carbon are grouped into organized crystallographic formations known as elementary graphitic crystallites. The mutual arrangement of the crystallites is irregular, so that free interstices remain between them and apparently as the result of deposition and decomposition of tarry substances, these become filled or at least blocked by disorganized (“amorphous”) carbon. There are three clear stages in the carbonization process: (a) loss of water in the 27-197$^0$C range; (b) primary pyrolysis in the 197-497$^0$C range with evolution of most gases and tars with formation of the basic structure of the char; (c) consolidation of char structure at 497-847$^0$C with a very small weight loss. The resulting carbonized product has only a very small adsorption capacity. Presumably, at least for carbonization at lower temperatures (400-600 ºC), part of the tar remains in the pores between the crystallites and on their surface. A carbon with a large adsorption capacity, however, can be produced only by activating the carbonized material under such conditions that the activation agent (steam, carbon dioxide, etc.) reacts with the carbon.

### 2.3.2 Activation [10]

Generally, there are two main types of production of activated carbon :

-By carbonizing material with the addition of activating agents ($ZnCl_2$, $CaCl_2$ $H_3PO_4$). This method is generally known as “chemical activation”.

#### 2.3.2.1 Chemical activation

For chemical activation[11,12] , the common chemicals used are dehydrating agent such as $ZnCl_2$, $CaCl_2$, $MgCl_2$ and some acids such as $H_3PO_4$ and $H_2SO_4$. The activation agent influences the pyrolytic processes so that the formation of tar is restricted to a minimum and the amount of the aqueous phase in the distillate is also less than that in the normal carbonization. The activation agent also changes the chemical nature of the cellulose substance by dehydration, which decomposes the organic substances by the action of heat and prevents the formation of tar.

Chemical activation [12] is usually carried out at temperatures from 400-600 ºC. These temperatures are lower than those needed for activation with gaseous agent (physical activation). An important factor in chemical activation is the degree (coefficient) of impregnation ; this is the weight ratio of the anhydrous activation salt to the dry starting material. The effect of the degree of impregnation on the resulting product is apparent from the fact that the volume of salt in the carbonized material equals the volume of pores which are freed by its extraction. For small degree of impregnation the increase in the total pore volume of the product with increase in the degree of impregnation is due to the increase in the number of small pores. When the degree of impregnation is further raised, the number of larger-diameter pores increases and the volume of the smallest decreases. The most widely used activation agents are:

Aluminum chloride
Ammonium chloride
Borates
Boric acid
**Calcium chloride**
***Calcium hydroxide***
Chlorine
Hydrogen chloride
Iron salt
Nickel salt
**Nitric acid**
***Nitrous gases***
Phosphorus pentoxide
Potassium metal
Potassium hydroxide
Potassium permanganate
**Potassium sulfide**
***Phosphoric acid***
Sodium hydroxide
Sodium hydroxide
Sodium oxide
Sulfur dioxide
**Sulfuric acid**
***Zinc chloride***

### 2.3.2.2 Physical activation [12,14]

The basic method of activating coal-based granules consists of their treatment with oxidizing gases (steam, carbon dioxide, oxygen) at elevated temperatures. In the activation process, carbon reacts with the oxidizing agent and the resulting carbon oxides diffuse from the carbon surface. Owing to the partial gasification of the granules or grains, a porous structure builds up inside them. The structure of the carbonization product consists of a system of crystallites similar to those of graphite bonded by aliphatic type bonds to yield a spatial polymer. The spaces between the neighbouring crystallites constitute the primary porous structure of the carbon. The pores of the carbonized granules are often filled with tar decomposition products and are blocked with amorphous carbon. This amorphous carbon reacts in the initial oxidation step, and as a result the closed pores open and new ones are formed. In the process of further oxidation, the carbon of the elementary crystallites enters into reaction due to wich the existing pores widen. Deep oxidation leads to a reduction in the total volume of micropores due to the burning off of the walls between the neighbouring pores, and in consequence the adsorptive properties and mechanical strength of the material decrease.

In the first stage of activation [13],when burn-off is not higher than 10% (which occurs at low reaction times), this disorganized carbon is burnt out preferentially and the closed and clogged pores between the sheets are freed. In the course of further activation at the second stage, carbon of the aromatic sheets is burnt. When the burn-off is less than 50%, a microporous activated carbon is obtained; when it is large than 75% (which occurs at high reaction times), a macroporous product is obtained; and when the burn-off is between 50 and 75% , the product is of mixed structure and contains both micro-and macropores. Development of macropores due to coalescence or widening of micropores unde fast reaction conditions.

Carbon oxidation [11]is a complex heterogeneous process encompassing the transport of reagents to the surface of the particles, their diffusion into the pores, chemisorption on the pore surface, reaction with carbon, desorption of the reaction products, and diffusion of these products to the particle surface. The concentration profile of the oxidizing agent of the granule volume, and hence the formation of the carbon porous structure, depends of the rate of the particular steps of the process. At low temperatures the rate of the chemical reaction of carbon with the oxidizing agent is small, so it is this reaction that limits the overall rate of the process. This results in a dynamic equilibrium becoming established between the concentration of the oxidizing agent in the pores and that in the inter particle spaces. In such a case the activation process yields a homogeneous product with a uniform distribution of the pores throughout the whole volume of the granule. With increase of the oxidation temperature, the rate of the chemical reaction increases much faster than that of diffusion, and then overall rate of the process becomes limited by the rate of transport of the oxidizing agent into the granule. At very high temperatures the oxidation reaction rate becomes so high that the whole oxidizing agent reacts with carbon on the external surface of the granule. In such a case significant losses of the material occur due to superficial burn-off, and a porous structure is not formed.

The rate of the oxidation process is limited by the reactivity of the initial carbonaceous material towards the oxidizing agent. The greater is the reactivity of the substrates, the lower the optimal temperature of the process at which uniform formation of pores in the granule.

-Activation with steam [11,12]

The basic reaction of carbon with water vapor is endothermic and a stoichiometric equation can be written in the form :

$$C + H_2O \longrightarrow H_2 + CO \qquad \Delta H = +130\ \text{kJ/mol}$$

This process has been studied extensively since it dominates not only the activation reaction but also the production of water-gas. The reaction of carbon with water vapor is inhibited by the presence of hydrogen while the influence of carbon monoxide is practically insignificant. The rate of gasification of carbon by water vapor is given by the formula:

$$V = \frac{k_1 P_{H_2O}}{1 + k_2 P_{H_2O} + k_3 P_{H_2}}$$

Where : $P_{H_2O}$ and $P_{H_2}$ are the partial pressures of water and hydrogen, respectively, $k_1$, $k_2$, $k_3$, are the experimentally determined rate constants. The mechanism of reaction of carbon with water vapor can be presented with reasonable confidence by the following set of equations:

$$C + H_2O \rightleftarrows C(H_2O)$$

$$C(H_2O) \longrightarrow H_2 + C(O)$$

$$C(O) \longrightarrow CO$$

The inhibiting effect due to hydrogen may be assigned to blocking of the active centers by its adsorption.

$$C + H_2 \rightleftharpoons C(H_2)$$

According to Long and Sykes in the first step of the reaction the adsorbed water molecules dissociate according to the scheme :

$$2C + H_2O \longrightarrow C(H) + C(OH)$$

$$C(H) + C(OH) \longrightarrow C(H_2) + C(O)$$

Hydrogen and oxygen are adsorbed at neighboring active sites, which account for about 2% of the surface area.

The reaction of carbon and water vapor is accompanied by the secondary reaction of carbon monoxide with water vapor (the so-called homogeneous water-gas reaction) catalyzed by the carbon surface :

$$CO + H_2O \longrightarrow CO_2 + H_2 \qquad \Delta H = -42\ kJ/mol$$

explained the presence of carbon dioxide and the catalytic surface effect of carbon by the following reaction :

$$CO + C(O) \rightleftharpoons CO_2 + C$$

Activation with steam is carried out at temperatures from 750 to $950^0$ C with the exclusion of oxygen which at these temperatures aggressively attacks carbon and decreases the yield by surface burn-off. It is catalyzed by the oxides and carbonates of alkali metals, iron, copper and other metal; the activation catalyst usually employed in practice are carbonates of alkali metals, which are added in small amounts to the material to be activated. It was shown in Figure 2.1.

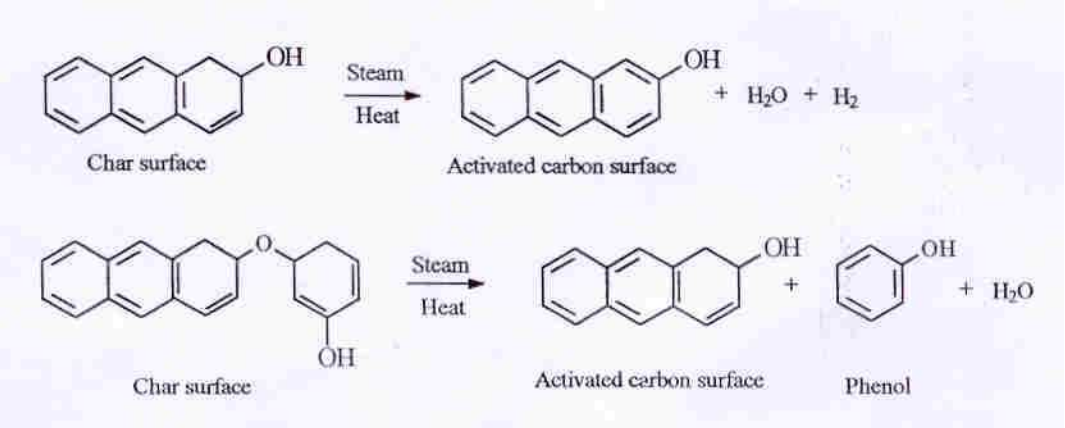

**Figure 2.1** Chemical reaction of char activated by steam[11]

-Activation with Carbon Dioxide [11,12]

The rate of carbon gasification with carbon dioxide is described by an expression analogous to that for the reaction with steam :

$$V = \frac{k_1 P_{co2}}{1 + k_2 P_{co} + k_3 P_{co2}}$$

Where : $P_{co_2}$ and $P_{co}$ are the partial pressures, and $k_1$, $k_2$ , $k_3$ are the experimentally determined rate constants. Two different mechanisms of interaction of carbon dioxide with the carbon surface are proposed :

(1) $C + CO_2 \longrightarrow C(O) + CO$

$C(O) \longrightarrow CO$

$CO + C \longrightarrow C(CO)$

(2) $C + CO_2 \longrightarrow C(O) + CO$

$C(O) \longrightarrow CO$

Activation with carbon dioxide involves a less energetic reaction than that with steam and requires a higher temperature 850 – 1100 $^0$C. The activation agent used in technical practice is flue gas to which a certain amount of steam is usually added, so that actually this is a case of combined activation. The catalyst for the reaction with carbon dioxide are carbonates of alkali metals.

-Activation with Oxygen(air)[11,14]

In the reaction of oxygen and carbon both carbon monoxide and carbon dioxide are formed according to the equations :

$$C + O_2 \longrightarrow CO_2 \qquad \Delta H = -387 \text{ kJ/mol}$$

$$2C + O_2 \longrightarrow 2CO \qquad \Delta H = -226 \text{ kJ/mol}$$

The used of oxygen as activating agent presents particular difficulties which are due to its exothermic reaction with carbon. In this case it is difficult to avoid local overheating in the activation process. In view of its high rate, the carbon burn-off process proceeds chiefly on the surface of the granules, producing high losses of material. In many processes, oxygen activation is conducted at very low temperatures and combined with treatment with water vapor. Such a method is most convenient when materials of low reactivity are activated.

### 2.3.3 Pyrolysis and steam activation[ 15]

Usually the production of activated carbons involves two stages: the carbonization of the raw materials followed by a high temperature activation, at 800-1000 ºC ,of the resulting chars. The method used in this study combines the two stages into a single one, while the treatment temperature is considerably lower, 600-800 ºC. This method is preferable to the two-stage treatment from an economic point of view. The scheme of arrangement of the carbon atom is presented in Figure 2.2.

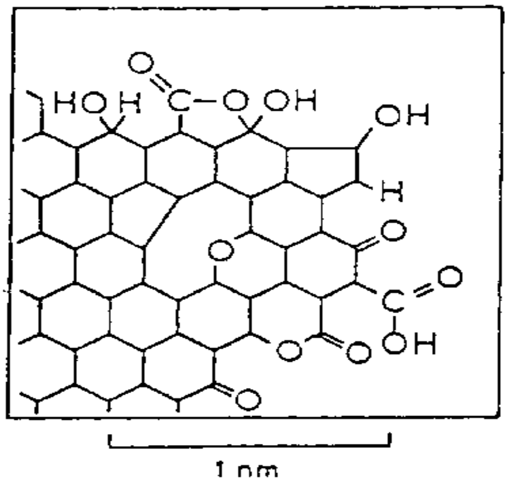

**Figure 2.2** Ordering of carbon atoms [16]

During the pyrolysis and steam activation of carbon-containing materials the following main processes take place.

1. Oxidation-thermolytic conversion of the carbon material leading to the accumulation of oxygen-containing groups.

2. A thermal destruction process including the decomposition of the oxygen containing groups accompanied by the formation of carbon oxides and water.

3. Condensation processes.
4. Deeper penetration of the water molecules and opening up of the initially closed pores into the structure of carbon materials.

### 2.4 Chemical nature of the surface of activated carbon[12]

The chemical nature of activated carbons significantly influences their adsorptive, eletrochemical, catalytic, acid-base, redox, hydrophilic-hydrophobic, and other properties. It is determined decisively by type, quantity and bonding of various heteroatoms, especially oxygen. Heteroatoms may be combined both with peripheral carbon atoms at the corners and edges of crystallites and in intercrystalline spaces and even in defect zones of particular planes constituting the crystallites. Most heteroatoms are grouped at the surface of activated carbon. Apart from their different locations, the heteroatoms are strongly differentiated in terms of their chemical reactivity. Surface-bound heteroatoms are believed to adopt the character of the functional groups typical for aromatic compounds. The surface functional groups often consist of more than one type of heteroatom, e.g. oxygen and hydrogen together as-OH or –COOH.

Surface functional groups can originate from the starting material from which a particular activated carbon is produced. Substantial quantities of oxygen can be introduced during the production process itself, e.g. during activation of carbonaceous materials by oxidizing gases, such as water vapor and air. Activated carbon used predominantly for practical purposes generally includes some percentage by weight of chemically bound oxygen and usually much smaller quantity of hydrogen combines with surface carbon atoms either directly or through oxygen.

Oxygen surface compounds are usually divided into two main types: functional groups of acidic nature and basic group. The first acidic group is exemplified schematically in Figure 2.3 the later basic group is much less well-characterized compared with the first. Usually structures corresponding to chromene or pyrone-like structures are illustrated in Figure 2.4.

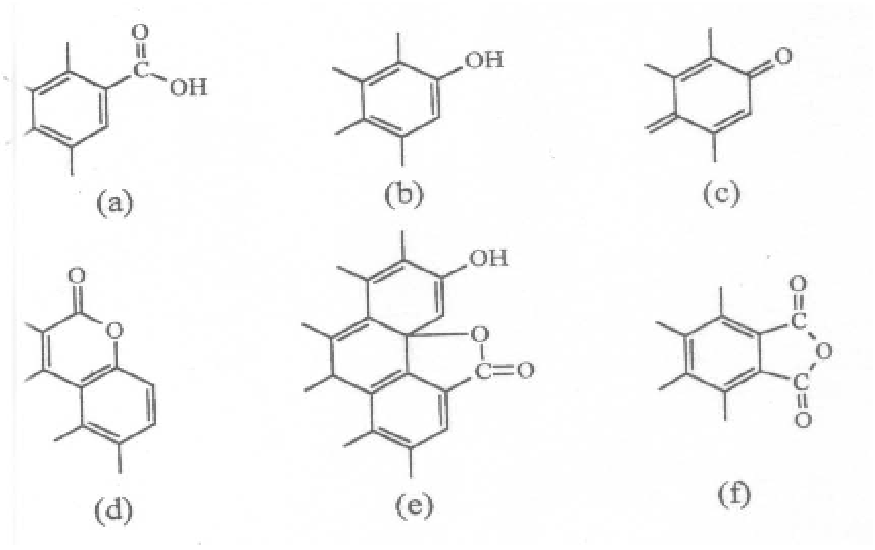

**Figure 2.3** Principal types of acidic oxygen surface functional groups : (a) carboxyl, (b) phenolic, (c) quinonoid, (d) normal lactone, (e) fluorescein-type lactone, (f) anhydride originating from neighbouring carboxyl groups.

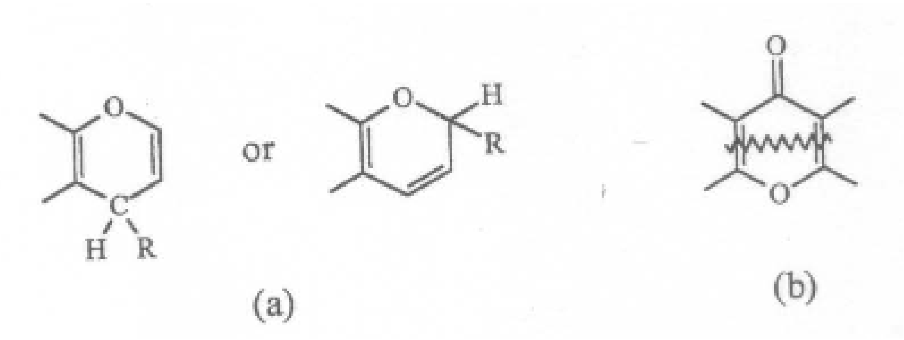

**Figure 2.4** Functional groups of basic character : (a) chromene, (b) pyrone-like

## 2.5 Molecular, crystalline and porous structure of activated carbon [11]

The graphite-like microcrystalline structure is the basic structural unit of activated carbon, as in the case of carbon black. The ordering of carbon atoms in an elementary microcrystallite indicates considerable similarity to the structure of pure graphite, the crystals of which consist of parallel layers of condensed regular hexagonal ring spaced 0.335 nm apart. Such interlayer spacing is diagnostic of interaction by means of van der Waals forces. The length of the carbon-carbon bond in individual layers is 0.142 nm. Each carbon atom bonds with the three adjoining ones by means of covalent bonds, and the fourth delocalized $\pi$-electron may move freely in a system of conjugated double bones of condensed aromatic ring.

The formation of the crystalline structure of activated carbon begins early during the carbonization process of the starting material. Thus sets of condensed aromatic ring of various numbers, which are the nascent centers of graphite-like microcrystallites, are formed. Although their structure resembles that of a crystal of graphite there exist some deviations from that structure. Thus, among other things, the interlayer distances are unequal in crystals of activated carbon and rang from 0.34 to 0.35 nm. Again, the orientations of the respective layers generally display deviations. Such deviations from the ordering characteristic of graphite, called a turbostratic structure. Disordering of the crystal lattice may be caused to a considerable degree both by its defects (vacant lattice sites) and by the presence of built-in heteroatoms. It is resulted from the kind of the raw material used, the nature and quantity of its impurities as well as the methods and conditions of the production processes of the activated carbon.

The average activated carbons have a strongly developed internal structure (the specific surface often exceeds 1000 and sometimes even 1500 $m^2/g$), and they are usually characterized by a polydisperse capillary structure, featuring pores of different shapes and sizes. Bearing in mind the values of the effective radii and the mechanism of adsorption of gases, Dubinin proposed three main types of pore, namely macropores, mesopores and micropores.

Macropores are those having effective radii ≥ 100 – 200 nm and their volume is not entirely filled with adsorbate via the mechanism of capillary condensation (it may occur only for a relative pressure of adsorbate of nearly one). The volumes of macropores are usually in the range 0.2-0.8 $cm^3/g$ and the maxima of volume distribution curves according to the radii are usually in the range 500-2000 nm. The values of their specific surface area not exceeding 0.5 $m^2/g$ are negligibly small when compared with the surface of the remaining type of pore. Consequently macropores are not of great importance in the process of adsorption as they merely act as transport arteries rendering the internal parts of the carbon grains accessible to the particles of adsorbate.

Mesopores, also known as transitional pores, have effective radii falling in the range of 1.5 – 1.6 nm to 100-200 nm. The process of filling their volume with adsorbate take place via the mechanism of capillary condensation. For average activated carbons, the volumes of mesopores lie between the limits 0.1-0.50 $cm^3/g$ and their specific surface area in the range of 20-100 $m^2/g$. The maximum of the distribution curve of their volume versus their radii is mostly in the range of 4 – 20 nm. Mesopores, besides their significant contribution to adsorption, also perform as the main transport arteries for the adsorbate.

Micropores have sizes comparable with those of adsorbed molecules. Their effective radii are usually smaller than 1.5-1.6 nm and for average activated carbons their volumes usually lie between 0.2 – 0.6 cm3/g. The energy of adsorption in micropores is substantially greater than that for adsorption in mesopores or at the nonporous surface, which causes a particularly large increase of adsorption capacity for small equilibrium pressures of adsorbate. In micropores, adsorption proceeds via the mechanism of volume filling. For some activated carbon, the microporous structure may have a complex nature, e.g. two overlapping microporous structure : firstly one for effective pore radii smaller than 0.6-0.7 nm and termed specific micropores, and the secondly one exhibiting pore radii from 0.6-0.7 to 1.5 – 1.6 nm termed supermicropores. It is showed in **Figure 2.5**

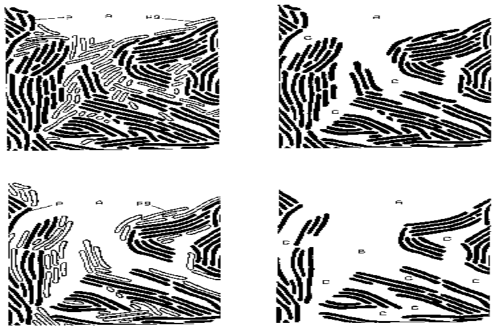

**Figure 2.5** Pores of activated carbon A: micropore B mesopore Cand D macropore.

## 2.6 Estimation of the properties of activated carbon [14]

The commercial use of activated carbons, their transport, storage and sales require knowledge of the properties of these materials. The methods for estimating these properties are approved by the members of the Activated Carbons Sector Group of the European Council of Chemical Manufacturers’ Federations (CEFIC). The tests require highly professional laboratories and advanced equipment. Most of the testing methods have been developed and approved by such organizations as the American Society for Testing method have been developed and approved by such organizations as the American Society for Testing Materials (ASTM), the American Water Works Association (AWWA), the Deutsches Institut fur Normung e.V. (DIN), or the International Organization for Standardization (ISO). In this work ASTM was used for estimating the properties of the resulted activated carbon.

### 2.6.1 B.E.T. Surface area [11]

To measure total surface area, nonspecific physical adsorption is required, but even with physical adsorption the isotherm varies somewhat with the nature of the adsorbent (the solid). Most physical adsorption isotherms may be grouped into five types, as originally proposed by Brunauer, Deming, Deming, and Teller (BDDT). More recently, the grouping has generally been termed the Brunauer, Emmett, and Teller (BET) classification. In all cases the amount of vapor adsorbed increases as its partial pressure is increased, becoming at some point equivalent to a monolayer, but then increasing to a multilayer, which eventually merges into a condensed phase as the relative pressure, P/Po approaches unity.

The most common method of measuring surface area, and one used routinely in most catalyst studies, is that developed by Brunauer, Emmett, and Teller. Early descriptions and evaluations are given by Emmett. In essence, the Langmuir adsorption isotherm is extended to multilayer adsorption. As in the Langmuir approach,for the first layer the rate of evaporation is considered to be equal to the rate of condensation, and the heat of adsorption is taken to be independent of coverage.For layer beyond the first, the rate of adsorption is taken to be proportional to the fraction of the lowest layers still vacant. The rate of desorption is taken to be proportional to the amount present in that layer (These assumptions are made largely for mathematical convenience). The heat of adsorption for all layers except the first layer is assumed to be equal to the heat of liquefaction of the adsorbed gas. Summation over an infinite number of adsorbed layers gives the final expression as follows :

$$\frac{P}{V(P_0 - P)} = \frac{1}{V_m C} + \frac{(C-1)P}{V_m CPo} \qquad (2.1)$$

where V = volume of gas adsorbed at pressure P

$V_m$ = volume of gas adsorbed in monolayer, same units as V

Po = saturation pressure of adsorbate gas at the experimental temperature

C = a constant related exponentially to the heats of adsorption and liquefaction of the gas

$$C = e^{(q1 - qL)/RT} \qquad (2.2)$$

where q1 = heat of adsorption on the first layer
qL = heat of liquefaction of adsorbed gas on all other layers
R = the gas constant

If Equation (2.1) is obeyed, a graph of P/V(Po-P) versus P/Po should give a straight line, the slope and intercept of which can be used to evaluate $V_m$ and C. Many adsorption data show very good agreement with the BET equation over values of the relative pressure P/Po between approximately 0.05 and 0.3, and this range is usually used for surface area measurements. At higher P/Po values, complexities associated with the realities of multilayer adsorption and/or pore condensation cause increasing deviation. With microporous substances such as zeolites, the linear region on a BET plot occurs at much lower values of P/Po, typically around 0.01 or less.

### 2.6.2 Physical test [11]

-*Bulk density.* The bulk density is defined as the mass per unit volume of the activated carbon sample in air including both the pore system and the void between the particles. The bulk density of activated carbon, depending on the shapes, sizes and densities of the individual particles is indispensable for determining the size of unit packages.

### 2.6.3 Adsorption tests [14]

The adsorption properties of activated carbons are generally estimated by determining the isotherms of adsorption from the liquid phase. The determination of the adsorption of one test substance from an aqueous solution is often insufficient for characterizing the adsorption properties of a carbon. Thus the properties of activated carbons are estimated by comparing the results of measurements for different adsorbates, e.g. by comparing the adsorptions of fairyly large molecules of methylene blue or iodine.

-*Iodine adsorption.* The study of the process of iodine adsorption and also the determination of the iodine number is a simple and quick test for estimating the specific surface area of activated carbon. The iodine number is defined as the number of milligrams of iodine adsorbed by 1 g of activated carbon from an aqueous solution when the iodine concentration of the residual filtrate is 0.02 N. If the final values obtained are different from 0.02 N but lie in the range of 0.007-0.03 N, appropriate corrections are necessary. In this method it is assumed that iodine at the equilibrium concentration of 0.02 N is adsorbed on the carbon in the form of a monolayer, and this is the reason why there is a relationship between the iodine number of activated carbon and its specific surface area which may be determined, for example, by the BET method. The specific surface areas of activated carbons with highly developed microporous structures as determined by the iodine number method are too low. This is because iodine is adsorbed chiefly on the surface of pores much larger than 1 nm, while in activated carbons with large specific surface areas the proportion of very fine pores inaccessible to iodine molecules is significant.

-*Methylene blue adsorption.* The methylene blue value gives an indication of the adsorption capacity of an activated carbon for molecules having similar dimensions to methylene blue, it also gives an indication of the specific surface area of the carbon which results from the existence of mesopores of dimensions greater than 1.5 nm.

### 2.6.4 Physico-chemical Test [14]

-*Volatile matter content.* The international standard used for determination of volatile matter in hard coal and coke is also applicable to activated carbon. A sample of powdered (<0.1 nm) activated carbon is heated at 950±25 ºC for 7 min±10 s. Volatile matter content is determined by establishing the loss in mass resulting from heating an activated carbon sample under rigidly controlled conditions.

-*Moisture content.* A simple method of determining the water content is drying activated carbon in a dryer. The sample of powdered (1-2 g) or granular (5-10 g) carbon is dried at 150 ºC to constant weight (usually about 3 hr). The weight loss is expressed as a percentage of the weight of the original sample.

-*Ash content.* The ash content in various types of activated carbon varies over a wide range, depending primarily on the type of raw material. The relative ash content also increases with increase in the degree of burning off the coal during activation. Ash consists mainly of oxides and, in smaller amounts, of sulfates, carbonates, and other compounds of iron, aluminium, calcium, sodium, potassium, magnesium and many other metals. Depending upon the type of raw material, it may comprise different and often fairly large quantities of silicon. The commonly used method of removing ash is to activated carbon with acids. Due to the complex composition of ash, mixture of acids, e.g. hydrochloric or hydrofluoric acid, are often used if ash contains substantial quantities of silicon.

The ash content of activated carbon can be determined by ignition of the crucible in an electric muffle furnace. Ignition is conducted at 650±25 ºC for 3 to 16 hr, depending on the type of activated carbon and dimensions of its particles, to constant mass. The weight of the ashed carbon is expressed as a percentage of the weight of the original carbon sample.

## 2.7 Application for activated carbon [13]

Activated carbon is used for gas- and liquid phase adsorption processes. Nearly 80% of about 300,000 ton per year is used for liquid – phase applications and approximately 60,000 ton per year for gas – phase applications; these tables are based on worldwide usage. Granulated active carbons are mainly employed for gas adsorption and separations (shown in Table 2.1).

**Table 2.1** Application for activated carbon( vapore phase)

| Industry | Description | Typical use |
|---|---|---|
| Solvent recovery | Recovery of organic solvents to optimize process economics and control vapor emissions | Acetate fibres (acetone), pharmaceuticals printing (ethyl acetate), magnetic tape |
| Carbon dioxide | Purification of carbon dioxide from fermentation processes | Adsorption of alcohol, amines and mercaptans |
| Industrial Repirators | Adsorption of organic vapors | |
| Waste disposal | Disposal of domestic, chemical and clinical waste by high temperature incineration | Removal of heavy metals and dioxins from flue gas |
| Cigarettes | Incorporation as either powder or granule in filter tips | Extraction of some harmful elements of cigarette smoke, or taste and flavor control |

**Table 2.2** Application for activated carbon ( liquid phase)

| Industry | Description | Typical use |
|---|---|---|
| Potable water treatment | Granular activated carbon (GAC) installed rapid gravity filters | Removal of dissolved organic contaminants, control of taste and odor problems |
| Soft drinks | Potable water treatment, sterilization with chlorine | Chlorine removal and adsorption of dissolved organic contaminants |

| Industry | Description | Typical use |
|---|---|---|
| Brewing | potable water treatment | Removal of trihalomethanes(THM) and phenolics |
| Semi – conductors | Ultra high purity water | Total organic carbon (TOC) reduction |
| Gold recovery | Operation of carbon in leach(CIL), carbon in pulp (CIP) and heap leach circuits | Recovery of gold from “tailings”solved in sodium cyanide |
| Petrochemical | Recycling of steam condensate for boiler feed water | Removal of oil and hydrocarbon contamination |
| Groundwater | Industrial contamination of ground water reserves | Reduction of total organic halogens (TOX)<br>and adsorbable organic halogens (AOX)<br>Including chloroform, tetrachloroethylene<br>and trichloromethane |
| Industrial waste water | Process effluent treatment to meet environmental legislation | Reduction of total organichalogens (TOX), biological oxygen demand (BOD) and chemical oxygen demand (COD) |

## 2.8 Literature reviews

In 2003, Paul *et al*. [17] Biomass waste in the form of fibrous flax textile waste has been physically and chemically activated to produce activated carbons. The sample was heated at 4ºC /min to the final temperature of 800ºC. The steam/nitrogen ratio was 25%:75%. Chemical processing of the flax to produce activated carbons involved a two-stage process Zinc chloride solutions were used at impregnation ratios of 0.2:1, 1:1 and 2:1. The reactor was continuously purged with nitrogen final temperature of either 450, 550 or 650ºC. The surface area of the physically activated carbons were up to 840 $m^2$ /g and the pores were mainly mesoporous in structure. Chemical activation using zinc chloride activated at 2:1 450ºC produced high surface area activated at 2400 $m^2$ /g and the pore size distribution was mainly microporous.

In 2007, Diana *et al*. [18] Activated carbon was prepared from coconut shells using chemical activation with zinc chloride followed by physical activation. The particles were impregnated with zinc chloride ($ZnCl_2$) at 1:1 wt and the temperature of the pyrolysis oven was 500°C, which was maintained for 3 hrs then also submitted to physical activation temperature 900°C , the samples were then contacted with steam (0.8 kg/h) for 30 mins. The results indicate that the produced carbons show BET surface areas of 2114 $m^2$/g total pore volume 1.307 $cm^3$/g and average pore width 12.40 $A^\circ$

In 2008, Xiaoning *et al*. [ 19] In this work, production activated sludge from wastewater treatment impregnated with KOH in superheated steam. The raw sludge impregnated with a 3M KOH solution (M/V = 1:2.5) for 24 hrs at room temperature. Fifteen grams of SP was pyrolyzed in a heating tube furnace with steam as purge gas. The heating temperature increased at 40ºC /min and the final heating temperature was 600ºC for 1 hr. and the steam flow was maintained at 300 $cm^3$/min. The results obtained showed that the activated carbon produced was mainly microporous and mesoporous in character with specific surface area of 381.62$m^2$/g, and the total pore volume and the micropore volume of 0.25 and 0.11 $cm^3$/g, respectively.

In 2005, Ru-Ling *et al.* [20] Produced activated carbon from corncobs . The processes of carbonization heated at 450ºC for 1.5 hrs and activation with KOH were weight ratio of KOH/char equal to 0, 0.5, 1, 2, 3, 4, and 6 and heated at a rate of 10 ºC /min to 780ºC. Two groups are classified according to the types of adsorption/ desorption isotherms. Group I corncob-derived activated carbons, with KOH/char ratios from 0.5 to 2, exhibited BET surface area ranging from 841 to 1221 $m^2/g$. Group II corncob-derived activated carbons, with KOH/char rations from 3 to 6, showed high BET surface areas, from 1976 to 2595 $m^2/g$. From scanning electron microscopic (SEM) results, the morphology of group I with the KOH/char ratio from 0.5 to 2 shown a cottony, twisted, and deformed surface of honeycomb holes with contracted walls. For group II activated carbons with their KOH/char ratio between 3 and 6, regular honeycomb holes with thick and smooth walls are clearly visible.

In 2005, G.G. *et al.* [21] A study has been performed to produce activated carbon from olive-seed waste residues with chemical activation, using KOH as the activating agent pyrolysis at 800ºC for 1 hr in inert atmosphere (100 cc/min $N_2$ flow). The char was mixed with KOH, in a ratio C/KOH of 1:4 by varying the activation temperature to 800 and 900ºC and time to 1, 2, 3 or 4 hrs. The results indicate that the produced carbons show BET surface areas of 3049 $m^2/g$ at 4 hrs and methylene blue adsorption was 262 mg/g. The pores of the produced carbons are composed of micropores at the early stages of activation and of both micropores and mesopores at the late stages.

In 2007, Donni *et al.* [22] Palm shell was used to prepare activated carbon using potassium carbonate $K_2CO_3$ as activating agent. Palm shells were mixed with saturated solution $K_2CO_3$ with 0.5, 0.75, 1.0, 1.5 and 2.0 impregnation ratios. The carbonization temperature was varied from 600 to 1000ºC with activation duration of 2 h. Specific surface area of activated carbon was maximum about 1170 $m^2/g$ at 850 ºC with activation duration of 2 hrs and at an impregnation ratio of 1.0.

In 2007, Turgay *et al*. [23] The activated carbon was prepared from sunflower oil cake by sulphuric acid activation.The sample was impregnated with sulphuric acid ratio 0,0.85.1.90 and was carbonized at 600ºC under nitrogen ($N_2$) flow of 30 mL min The effects of various process parameters i.e., temperature, pH, initial methylene blue concentration, contact time on the adsorption capacity of each activated carbon were investigated. The optimum impregnation ratio was found to be 0.85 for the maximum adsorption capacity for methylene blue and obtained at 25ºC and pH 6.

# CHAPTER III

# EXPERIMENTAL

## 3.1 Raw material

This research was experimental in laboratory to find out condition in producing activated carbon from sewage sludge by carbonized and activation by superheated steam $CO_2$ and air and chemical activation in fixed bed for study about qualification and potential of the activated carbon. This was used as information for producing or using in other cases and as data. The pictures of sewage sludge and char are shown in Figure 3.1 respectively.

(A)

**Figure 3.1 (A) Sewage sludge.**

(B)

**Figure 3.2 (B) Activated carbon from sludge.**

## 3.2 Chemicals

1. Iodine, ($I_2$)
2. Potassium iodide, (KI)
3. Hydrochloric acid, concentrated, (HCl)
4. Potassium iodate, ($KIO_3$)
5. Sodium thiosulfate, ($Na_2S_2O_3 \cdot 5H_2O$)
6. Sodium carbonate, ($Na_2CO_3$)

7. Hydrochloric acid, concentrated, ($HCl$)
8. Starch
9. Methylene blue, ($C_{16}H_{18}N_3SCl^{\cdot}3H_2O$)
10. Sodium hydroxide, ($NaOH$)
11. Potassium hydroxide, ($KOH$)
12. Potassium phosphate, ($KH_2PO_4$)

## 3.3 Apparatus

1. Muffle furnace : type ESF 12/23 (0-1,200ºC), Carbolite, England.
2. Oven: 0-250 °C, WT binder, Germany.
3. Tube furnace: type21100 (0-1,200°C) Thermolyne Corporation, USA.
4. Desiccator.
5. Laboratory test sieve: s/steel, sizes 0.50,0.85,1.18 and 2.36 mm
6. Shaker.
7. Crucible.
8. Spectrophotometer (Jasco, V 530)
9. Scanning Electron Microscope (Jsm, 5410 LV)
10. Surface area analyzer (Micromeritics , ASAP 2020)
11. C.H.N Analyzer (Leco, 2000)
12. X-ray fluorescence (Eagle 3, 3.2)

Figure 3.3 Activator.

**Figure 3.4** Reactor.

**Figure 3.5** Tube furnace.

## 3.4 Procedures

### 3.4.1 Carbonization of sewage sludge

The variation of temperature and time for carbonization of sewage sludge were studied at 375, 400, 425and 450ºC for the duration of 45, 60, 90 and 120 min of time. The procedures started by weight sample about 70 g in crucible. Next, muffle furnace was heated at the final temperature as 375, 400, 425 and 450ºC and was put the sample for 45, 60, 90 and 120 min, respectively. Finally, the %yield, %ash, bulk density, %volatile matter and %fixed carbon of products have been analyzed as follows ASTM.

### 3.4.2 Activation of physical process

The chars from the carbonization at 400ºC for 90 min were produced to become the activated carbon. They were crushed and sieved to particle sizes of 0.05 – 0.85 mm and 1.18-2.36 mm

In the physical activation process, the samples were prepared by sludge char in flowing two methods used by superheat steam and oxidizing agent with $CO_2$ and air The variables, which have an effect on the activation such as: temperature, activation times and sizes of char were studied in order to determine the optimum conditions. Experimental scheme of the production of activated carbon from sewage sludge was shown in **Figure 3.5.** The procedure was described as follows:

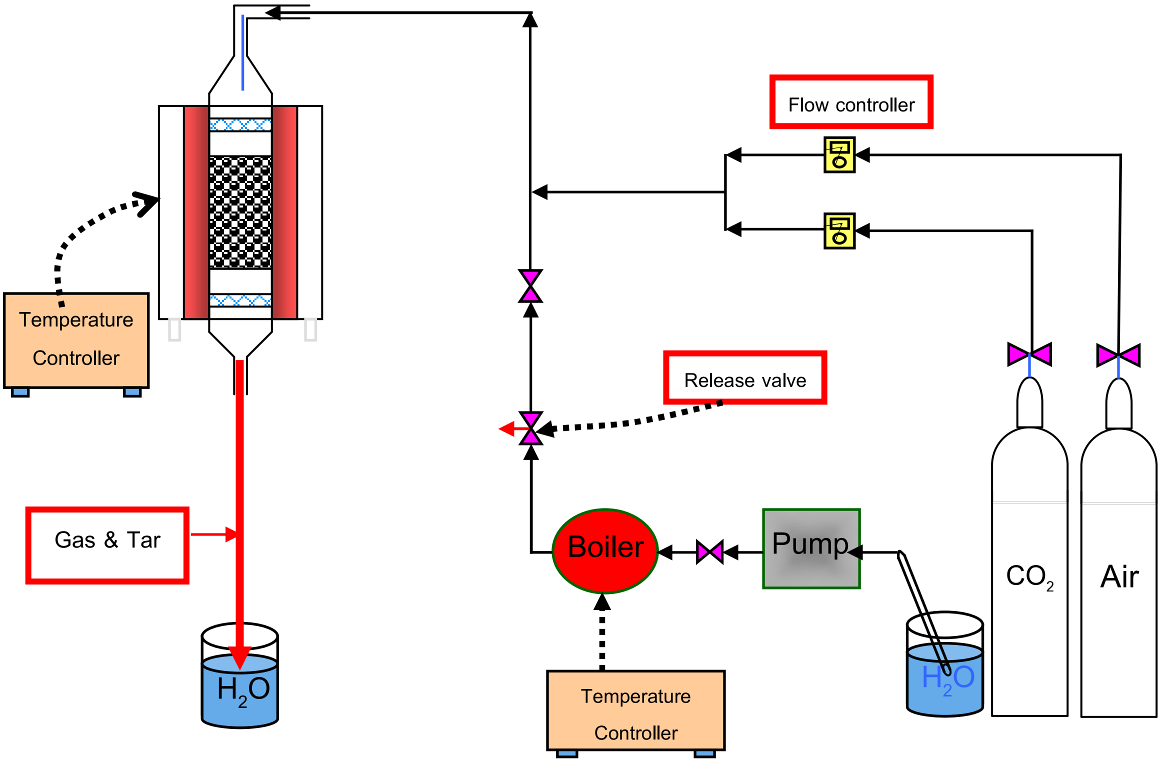

**Figure 3.6** Physical activation process.

#### 3.4.2.1 Activation by superheated steam

##### 3.4.2.1.1 The effect of activation temperature

Four different temperatures were studied for activation. They were 150, 250, 350 and 450ºC. 10 g of sludge char with particle size of 1.18 -2.36 mm was loaded into a stainless tubular reactor. Then the reactor was passed with steam 3 mL/min and air flow through from the top to the bottom at the flow rate of 100 mL/min. Then the reactor was heated to the desired temperature at 150, 250, 350 and 450ºC . The super heated steam and air were charged continuously on, passing up through the reactor for each fixed temperature for 1 hr of reaction time. Finally, the product was characterized by bulk density, iodine number, methylene blue number and B.E.T. surface area.

##### 3.4.2.1.2 The effect of size of sludge char for activation

The sizes of sludge char of 0.05 – 0.85 mm and 1.18-2.36 mm were studied to get the optimum size for preparation of activated carbon . 10 g of sludge char was loaded into a reactor. Then the reactor was passed with steam 3 mL/min and air flow through from the top to the bottom at the flow rate of 100 mL/min. Secondly, the reactor was heated until the optimium temperature. The super heat steam and air were charged continuously on, passing up through the reactor for each fixed temperature for 1 hr of reaction time. Finally, the product was characterized by bulk density, iodine number, methylene blue number and B.E.T. surface area.

##### 3.4.2.1.3 The effect of activation time

Different activation times of 1 and 2 hrs were studied for activation. 10 g of sludge char with optimium size was loaded into the reactor. Then the reactor was passed with steam 3 mL/min and air flow through from the top to the bottom at the flow rate of 100 mL/min. Secondly, the reactor was heated until the optimium temperature. The super heat steam and air were charged continuously on, passing up through the reactor for each fixed temperature for 2 hrs of reaction time.

Finally, the product was characterized by bulk density, iodine number, methylene blue number and B.E.T. surface area.

### 3.4.2.2 Activation by oxidizing agent with $CO_2$

#### 3.4.2.2.1 The effect of activation temperature

Four different temperatures were studied in this work for activation. They were 150, 250, 350 and 450ºC. 10 g of sludge char with particle size of 1.18-2.36 mm were loaded into a stainless tubular reactor. Then the reactor was passed 50 mL/min with $CO_2$ and 50 mL/min with air flow through from the top to the bottom. Then the reactor was heated to the desired temperature to vary at 150, 250, 350 and 450ºC . The $CO_2$ and air were charged continuously on, passing up through the reactor for each fixed temperature for 1 hr of reaction time. Finally, the product was characterized by bulk density, iodine number, methylene blue number and B.E.T. surface area.

#### 3.4.2.2.2 The effect of size of sludge char for activation

The size of sludge char of 0.05 – 0.85 mm and 1.18-2.36 mm studies to get the optimum size for preparation of activated carbon . 10 g of sludge char was loaded into a reactor. Then the reactor was passed 50 mL/min with $CO_2$ and 50 mL/min with air flow through from the top to the bottom . Secondly, the reactor was heated to the optimium temperature. The $CO_2$ and air were charged continuously on, passing up through the reactor for each fixed temperature for 1 hr of reaction time. Finally, the product was characterized by bulk density, iodine number, methylene blue number and B.E.T. surface area.

#### 3.4.2.2.3 The effect of activation time

Different activation times of 1 and 2hrs were studied for activation. 10 g of sludge char with optimium size was loaded into the reactor. Then the reactor was passed 50 mL/min with $CO_2$ and 50 mL/min with air flow through from the top to the bottom Secondly, the reactor was heated until the optimium temperature. The $CO_2$ and air were charged continuously on, passing up through the reactor for each fixed temperature for 2 hrs of reaction time. Finally, the product was characterized by bulk density, iodine number, methylene blue number and B.E.T. surface area.

### 3.4.3 Activation by chemical process[27,28]

The variables, which have an effect on the activation such as: type of alkaline solution such as KOH, $H_3PO_4$ and $ZnCl_2$ temperature, activation time and size of char that used for activation were studied in order to determine the optimum conditions. Experimental schemes of the production of activated carbon from sewage sludge were shown in **Figure 3.7.** The procedures were described as follows:

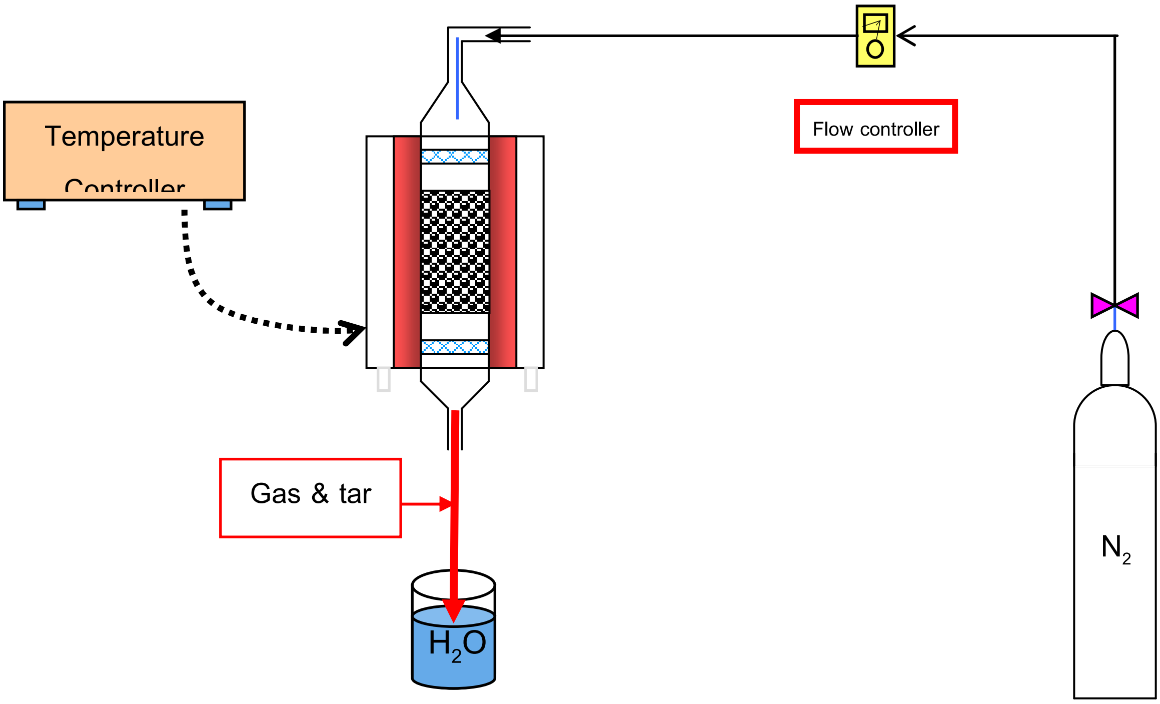

**Figure 3.7** Chemical activation process.

#### 3.4.3.1 The effect of chemical solution such as KOH, $H_3PO_4$ and $ZnCl_2$

The effect of reagent for alkaline solution activation. The three different alkalines as KOH, $H_3PO_4$ and $ZnCl_2$ were studied to determine the effect of activation. 10g of sludge char (1.18 -2.36 mm of particle size) was soaked in different chemicals. The char were impregnated ratio 0.5 : 1 (chemical: char) KOH, $H_3PO_4$ and $ZnCl_2$ for 24 hrs at room temperature. After the supernatant liquid was removed, the sample was subjected to heating at 105ºC to a constant weight., 10 g of char was pyrolyzed in a heating tube furnace with $N_2$ purge gas. The heating temperature increased at the final heating temperature was 350ºC. The dwell time at the final temperature was 1 h. The product was rinsed 10 times with hot deionized water to remove chemical, inorganic matters and subsequently dried to constant weight. The activated carbon were determined the adsorption optimum chemicals.

#### 3.4.3.2 The effect of temperature for activation

Four different temperatures were studied in this work for activation. They were 150, 250, 350 and 450ºC. 10 g of sludge char with particle size of 1.18-2.36 mm was loaded into a stainless tubular reactor. Then the reactor was passed 100 mL/min with $N_2$ flow through from the top to the bottom. Then the reactor was heated to the desired temperature to vary at 150, 250, 350 and 450ºC. The $N_2$ and air were charged continuously on, passing up through the reactor for each fixed temperature for 1 hrs of reaction time. Finally, the product was characterized by bulk density, iodine number, methylene blue number and B.E.T. surface area.

#### 3.4.3.3 The effect of size of sludge char for activation

The sizes of sludge char of 0.05 – 0.85 mm and 1.18-2.36 mm were studied to get the optimum size for preparation of activated carbon . 10 g of sludge char was loaded into a reactor. Then the reactor was passed 100 mL/min with $N_2$ flow through from the top to the bottom and the reactor was heated until the optimum temperature. The $N_2$ were charged continuously on, passing up through the reactor for each fixed temperature for 1 hr of reaction time. Finally, the product was characterized by bulk density, iodine number, methylene blue number and B.E.T. surface area.

#### 3.4.3.4 The effect of time for activation.

Different activation times of 1 and 2 hrs were studied for activation. 10 g of sludge char with optimum size was loaded into the reactor. Then the reactor was passed 100 mL/min with $N_2$ flow through from the top to the bottom and the reactor was heated until the optimum temperature. The $N_2$ were charged continuously on, passing up through the reactor for each fixed for 2 hrs of reaction time. Finally, the product was characterized by bulk density, iodine number, methylene blue number and B.E.T. surface area.

# CHAPTER IV

# RESULTS AND DISCUSSION

## 4.1 Properties of sewage sludge

Sewage sludge was preliminarily analyzed the proximate component as shown in Table 4.1. It was observed that raw sewage sludge was composed of moisture 7.66 %, ash 10.08 %, high volatile matter 65.87% and the % fixed carbon 16.39%. The same fixed carbon of this sludge is observed in coconut or palm oil shell.

The C, H, N composition of the sewage sludge was measured by a C H N analyzer, the results was show in Table 4.2. The major compounds of sewage sludge are carbon and oxygen at 40.86% and 43.98 % respectively followed by hydrogen 6.63%, nitrogen 7.85 % and small amount sulfur 0.68%.

The% heavy metal remained in char shown in Table 4.3 was measured by X-ray Fluorescence. All components were higher than those in sewage sludge, because the tar and volatile removed from raw material during carbonization and activation process.

**Table 4.1** Proximate analysis of sewage sludge

| **Sewage sludge** | **Dry basis** | | |
|---|---|---|---|
| M (%) | Ash (%) | VM (%) | FC (%) |
| 7.66 | 10.08 | 65.87 | 16.39 |

**Table 4.2** Elemental analysis of sewage sludge

| **Type** | **C (%)** | **H (%)** | **O (%)** | **N (%)** | **S (%)** |
|---|---|---|---|---|---|
| Sewage sludge | 40.86 | 6.63 | 43.98 | 7.85 | 0.68 |

**Table 4.3** Components obtained from XRF method

| Composition (%) | Sewage sludge | Carbonization | After Activation |
|---|---|---|---|
| Zn | 3.03 | 10.79 | 37.48 |
| Fe | 4.53 | 15.62 | 33.93 |
| Ca | 1.91 | 9.23 | 9.70 |
| Al | 0.37 | 2.59 | 6.77 |

**Figure 4.1** Sludge before carbonization.

**Figure 4.2** Sludge after carbonization.

### 4.2 Carbonization

Sewage sludge Figure 4.1 was carbonized in order to prepare for activation by superheated steam, oxidizing gas and chemical solution[25,28]. The studied condition was temperature of 375, 400, 425 and 450ºC. Each temperature was carried out at the time of 45, 60, 90 and 120 min.The final products of this step are called (char) in Figure 4.2. The proximate analysis of chars are shown in Table 4.4 and Figures 4.3-4.7.

The suitable condition for carbonization was temperature 400ºC and reaction time of 90 min. This condition contained 20-25% volatile matter, high fixed carbon which was appropriate for activation shown inTable 4.4.

**Table 4.4** Characteristics of sludge from carbonize at different temperatures and times

| Sewage sludge | | | | On dry basis | | |
|---|---|---|---|---|---|---|
| Temperature (ºC) | Time (min) | Y (%wt) | M (%wt) | Ash(%wt) | VM(%wt) | FC(%wt) |
| 375 | 45 | 62.51 | 1.04 | 20.04 | 53.05 | 25.51 |
| | 60 | 48.67 | 0.98 | 21.42 | 39.94 | 37.66 |
| | 90 | 42.43 | 1.06 | 21.83 | 30.78 | 46.33 |
| | 120 | 39.99 | 1.16 | 21.70 | 26.28 | 50.86 |
| 400 | 45 | 49.87 | 0.99 | 21.60 | 37.98 | 39.43 |
| | 60 | 43.48 | 1.01 | 24.08 | 29.47 | 45.44 |
| | 90 | 39.94 | 1.22 | 26.08 | 21.45 | 51.25 |
| | 120 | 39.64 | 1.38 | 26.38 | 20.76 | 51.48 |
| 425 | 45 | 44.99 | 0.69 | 21.03 | 38.47 | 39.81 |
| | 60 | 37.45 | 0.79 | 25.31 | 25.06 | 48.84 |
| | 90 | 40.68 | 0.83 | 26.21 | 20.65 | 52.31 |
| | 120 | 42.21 | 1.08 | 26.82 | 20.49 | 51.61 |
| 450 | 45 | 37.60 | 0.63 | 24.98 | 27.44 | 46.95 |
| | 60 | 33.45 | 0.84 | 27.87 | 19.54 | 51.75 |
| | 90 | 31.70 | 0.76 | 29.18 | 17.85 | 52.21 |
| | 120 | 30.41 | 0.91 | 30.36 | 15.06 | 53.67 |

### 4.2.1 The effect of temperatures and time for carbonization.

Table 4.4 and Figure 4.3 show that the % yields of various carbonization condition decrease with the increased temperature and time, because at high temperature and increase time, the carbon in sludge is progressively gasified and diffused out in the form of volatile, so the % yield in the products decreases .

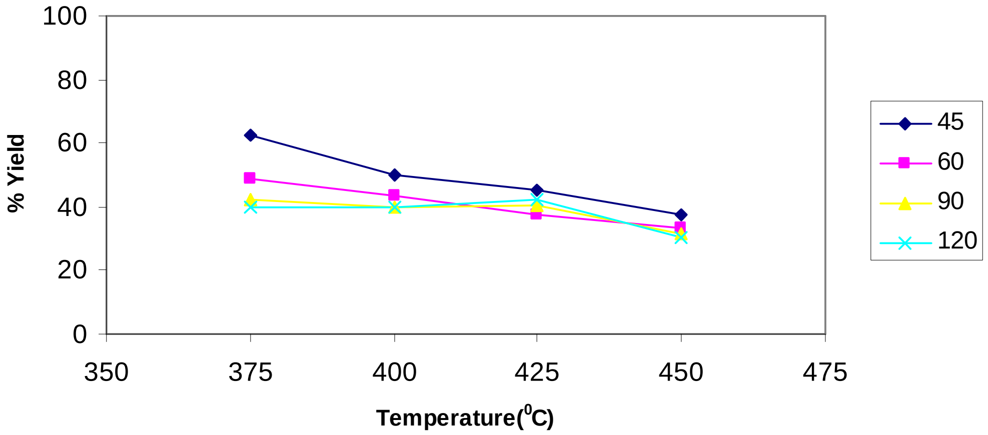

**Figure 4.3** Effect of temperature and time on % yield.

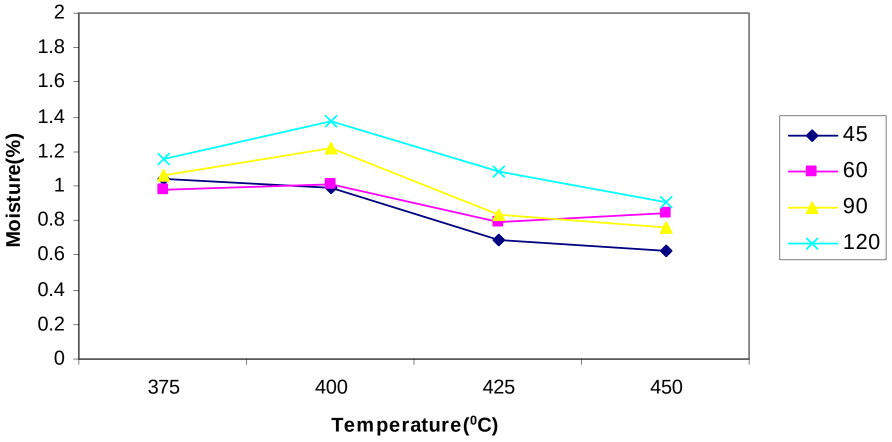

**Figure 4.4** Effect of temperature and time on % moisture.

The change of % ash at 375°C for 45 min is small (20.04%) shown in Table 4.4 and Figure 4.5, because at low temperature and reaction time, only the volatile matter was removed. So, the other components remained in the residue was still high and resulted the lower % ash. When the increased temperature to 450°C, % ash increase from 20.04% to 24.98%, because of some hydrocarbon react to itself and change into ash.

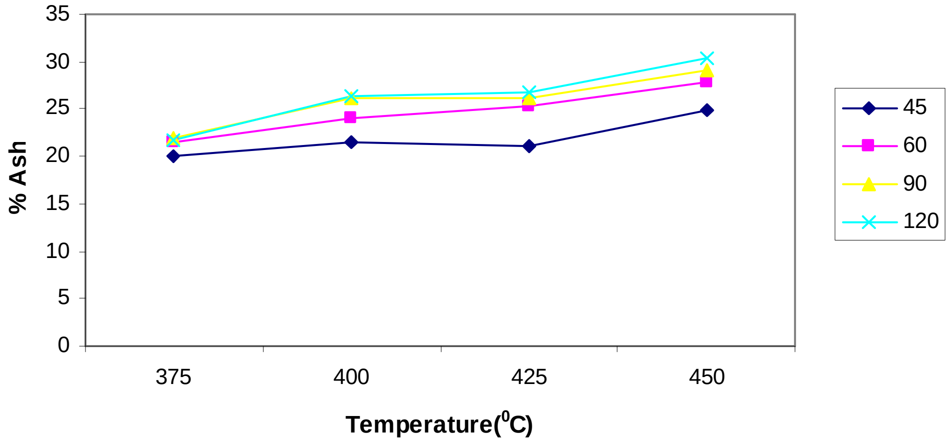

**Figure 4.5** Effect of temperature and time on % ash.

Table 4.4 and Figure 4.6 show that the % volatile matter of various carbonization condition from 375-450ºC decreased quickly from 53.05% to 27.44%, because at low temperature, only the volatile is removed and the carbon in sludge was progressively gasified and diffused out in the form of volatile. When increased temperature to 450ºC, % volatile decreased to 27.44%, because tar and some hydrocarbon react extremely and change into ash.

The decrease of volatile matter in the time range of 45-60 min is faster than at 90-120 min because in the first time range (45-60 min), only volatile at the surface was removed. When time increases above 60 min, volatile in the interior particle would be removed, but with more difficulty than volatile at the surface.

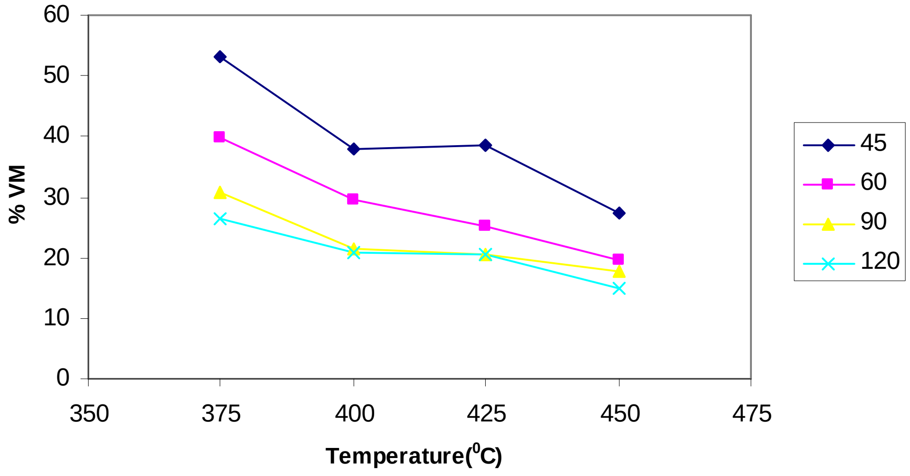

**Figure 4.6** Effect of temperature and time on % volatile matter.

Table 4.2 and Figure 4.7, show the % fixed carbon increase largely from 25.51% to 46.95 % at 375ºC. The carbon in sludge is progressively gasified and diffused out in the form of volatile and change finally into ash. The decrease of % fixed carbon in the time range of 45-60 min is faster than at 90-120 min because in the first time, only volatile at the surface is removed.When time increases above 60 min, tar and carbon the interior particle would be removed and finally changed to ash.

The suitable condition for carbonization of sludge char is 400ºC for 90 min, because % volatile is in range of 20-25% and the char in this condition gives yield of 39.94 %, ash of 26.08%, volatile matter of 21.45% and fixed carbon of 51.25%.

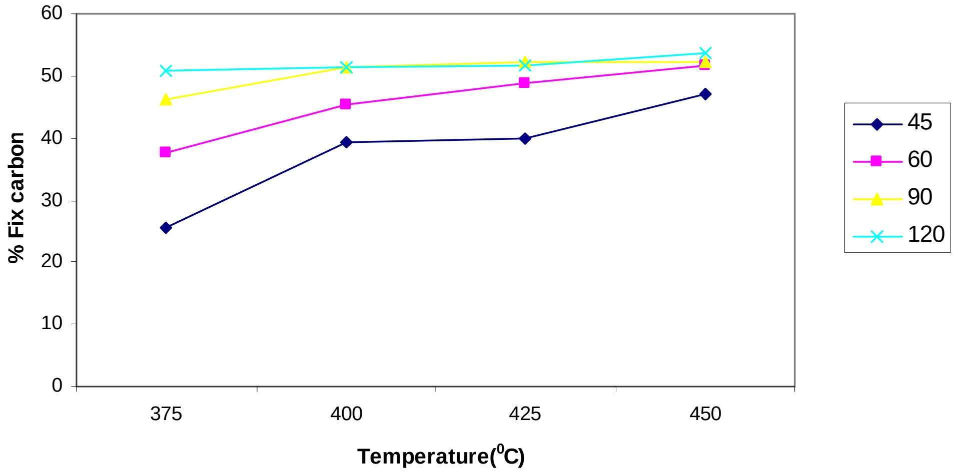

**Figure 4.7** Effect of temperatures and time on% fixed carbon.

## 4.3 Activation

The char from the carbonization at 400ºC for 90 min was prepared for being the raw material to produce activated carbon. It was crushed and sieved to particle sizes of 0.05 – 0.85 mm and 1.18-2.36 mm. The char was activated by physical and chemical activation. [14,27,28]

Figure 4.8 sludge char before activation.

Figure 4.9 Activated carbon.

### 4.3.1 Activation by physical process

In the physical activation process, the samples were prepared by sludge char activating by two method using by superheated steam and oxidizing agent as $CO_2$ and air. The variables, which have an affect to the activation such as: temperature, time and sizes of char were studied in order to determine the optimum conditions. The results are shown in Table 4.5 and Figures 4.10-4.16.

#### 4.3.1.1 Activation by superheated steam

Characteristics of activated carbon from sludge by superheated steam[28] at different temperature, size and times (10 g of char, superheated steam 3 mL/min, air100 mL /min) are expressed in Table 4.5.

**Table 4.5** Characteristics of activated carbon by superheated steam at different temperatures, sizes and times

| Temperature (°C) | Size (mm.) | Time ( hr) | Y (%) | BD (g/cm$^3$) | IA (mg/g) | MB (mg/g) | B.E.T. (m$^2$/g) |
|---|---|---|---|---|---|---|---|
| 150 | 1.18-2.36 | 1 | 97.15 | 0.38 | 624.50 | 293.23 | 531 |
| 250 | 1.18-2.37 | 1 | 94.28 | 0.39 | 623.50 | 281.14 | 518 |
| 350 | 1.18-2.38 | 1 | 88.83 | 0.4 | 615.00 | 289.27 | 502 |
| 450 | 1.18-2.39 | 1 | 64.41 | 0.39 | 356.50 | 279.83 | 303 |
| 150 | 0.50-0.80 | 1 | 88.76 | 0.47 | 549.50 | 285.15 | 467 |
| 150 | 1.18-2.39 | 2 | 92.94 | 0.35 | 533.50 | 299.97 | 480 |

##### 4.3.1.1.1 The effect of temperature and time on activation

Table 4.5 and Figure 4.10 showed the effect of temperature on % yield. When temperature increased to 450ºC, the % yielded of product decreased sharply, tar and volatile matter in the pores disappear. Then char, which partly burned was changed into ashes. The %yield were changed to 64.41 % at 450ºC.

Figures 4.12-4.14 showed the effect of temperature on iodine, methylene blue and B.E.T. surface area, it showed that, when the temperature increased to 450ºC, tar and hydrocarbon in sludge was progressively gasified and diffuse out in the form of volatile and then change to ash, the micropores would be broken to mesopores and macropores and partly burned at wall of pores. While the temperature was decreased from 350 to150ºC, iodine absorption capacity increased dramatically because it seems that the superheated steam diffuse in to pore and produce the large pore size, thus a number of pores were produced at this temperature. The experimented results show that the optimum temperature is 150ºC since it has maximum iodine adsorption and total surface area.

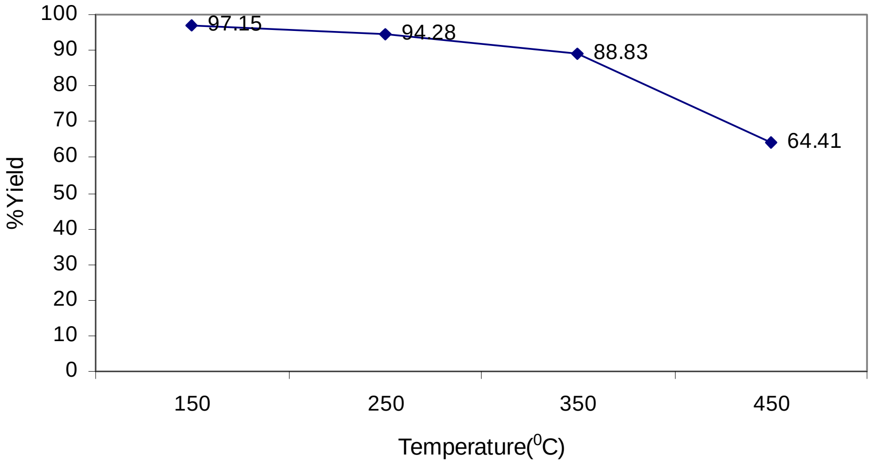

**Figure 4.10** Effect of temperature on % yield at different temperature (size 1.18 – 2.36 mm, 10 g of char, superheated steam 3 mL/min and air 100 mL /min).

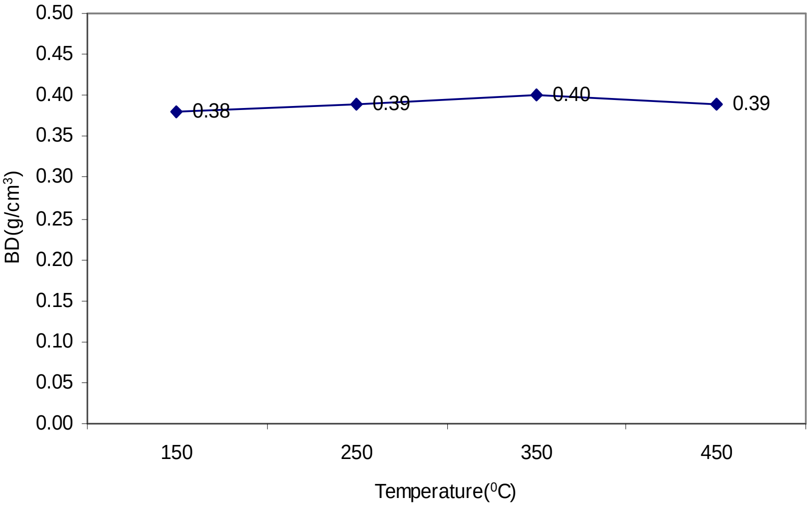

**Figure 4.11** Effect of temperature on % bulk density at different temperature (size 1.18 – 2.36 mm, 10 g of char, superheated steam 3 mL/min and air 100 mL /min)

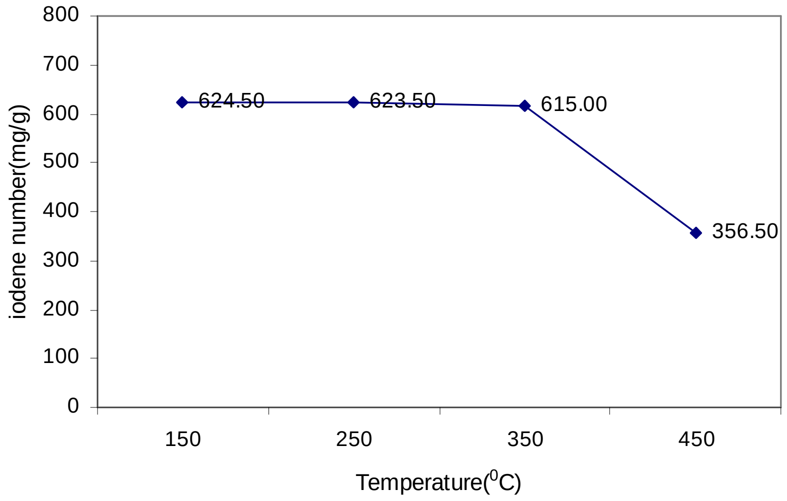

**Figure 4.12** Effect of temperature on iodine number at different temperature (size 1.18 – 2.36 mm, 10 g of char, superheated steam 3 mL/min and air 100 mL /min)

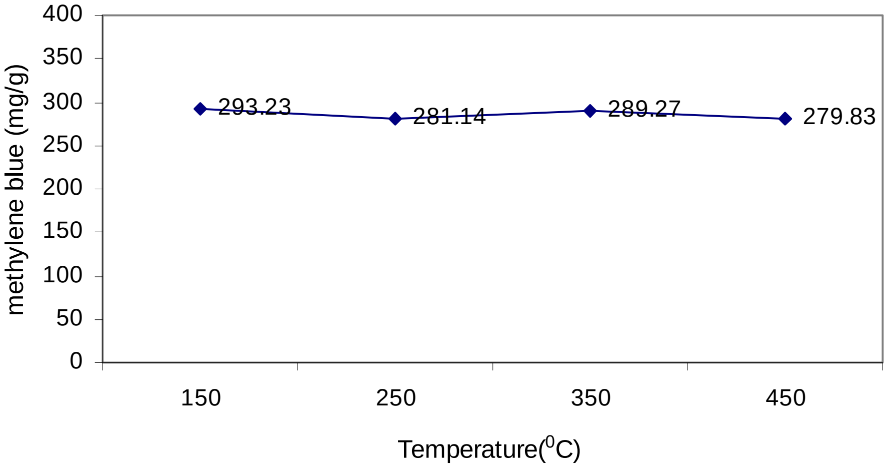

**Figure 4.13** Effect of temperature on methylene blue at different temperature (size 1.18 – 2.36 mm, 10 g of char, superheated steam 3 mL/min and air 100 mL /min)

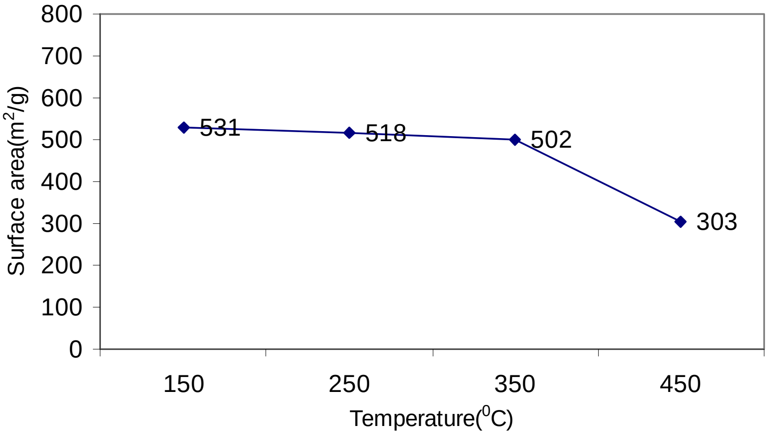

**Figure 4.14** Effect of temperature on surface area at different temperature (size 1.18 – 2.36 mm, 10 g of char, superheated steam 3 mL/min and air 100 mL /min).

### 4.3.1.1.2 The effect of size on activation

Table 4.6 showed the effect of particle size of 1.18-2.36 and 0.50-0.85 mm on property of activated carbon. The experiments were carried out at 1 hr of operation and activation temperature of 150ºC by 3 mL/min superheated steam and 100 mL/min air. The results showed that the iodine number, the methylene blue number and the B.E.T. surface area of 1.18-2.36 mm particle were slightly increased comparing with the results obtained from using 0.50-0.85 mm particle. Because the layer of bigger size of particle can be packed loosly in the fixed bed. So the superheated steam can attack the surface of chars and also diffuse into inner pore easily, resulting in higher amount of pore and increasing of the iodine number, methylene blue number and the B.E.T. surface area were observed.

The optimum size for activation is 0.18-2.36 mm. Because the activated carbon has the highest iodine number, methylene blue and the B.E.T. surface area. The property were % yield of 97.15, bulk density of 0.38 g/cm$^3$ iodine number of 624.50 mg/g, methylene blue number 293.23 mg/g and B.E.T. surface area of 531 m$^2$/g.

**Table 4.6** Characteristics of activated carbon by superheated steam at different sizes

| Temperature (°C) | Size (mm.) | Time ( hr) | Y (%) | BD (g/cm$^3$) | IA (mg/g) | MB (mg/g) | B.E.T. (m$^2$/g) |
|---|---|---|---|---|---|---|---|
| 150 | 1.18-2.36 | 1 | 97.15 | 0.38 | 624.50 | 293.23 | 531 |
| 150 | 0.50-0.80 | 1 | 88.76 | 0.47 | 549.50 | 285.15 | 467 |

#### 4.3.1.1.3 The effect of time on activation

The time for activation step of 1 and 2 hrs were studied for particle size of 1.18-2.36 mm and activation temperature of 150ºC by superheated steam 3 mL/min and air 100 mL/min shown in Table 4.7. When char was activated by taking longer time, the carbon in char structure is more progressively gasified. The micropore was partly changed to mesopores and macropores and some part of pores were burned during activation, thus iodine adsorption was decreased.

The iodine number and B.E.T surface area with the activating time of 1 hr was higher than those acusing acivation time of 2 hrs. Because, at 1 hr, tarry matter and the products of deposition in pores was removed, resulting the porosity development and new pores were produced and old pores were expanded.

The optimum condition for activation by superheated stream was 150ºC for 1 hr. The characteristics of activated carbon are the yield 97.15%, bulk density of 0.38 g/cm$^3$, iodine number of 624.50 mg/g, methylene blue number 293.23 mg/g and B.E.T. surface area of 531 m$^2$/g.

**Table 4.7** Characteristics of activated carbon by superheated steam at different times

| Temperature (°C) | Size (mm.) | Time ( hr) | Y (%) | BD (g/cm$^3$) | IA (mg/g) | MB (mg/g) | B.E.T. (m$^2$/g) |
|---|---|---|---|---|---|---|---|
| 150 | 1.18-2.36 | 1 | 97.15 | 0.38 | 624.5 | 293.23 | 531 |
| 150 | 1.18-2.39 | 2 | 92.94 | 0.35 | 533.5 | 299.97 | 480 |

#### 4.3.1.2 Activation by carbon dioxide

Table 4.8 showed the characteristics of activated carbon from sludge at different temperatures, times and size (size 0.50-0.80 and 1.18-2.36 mm) under $CO_2$ 50 mL/min and air 50 mL /min.

The amount of ten grams of 1.18-2.36 mm sludge was used in each batch. The reactor was heated to the final temperature of 150, 250, 350 and 450°C. After charging, the excess $CO_2$ and the air were passing up through at a fixed flow of $CO_2$ 50 mL/min, air 50 mL/min for 1and 2 hrs. The results were shown in Table 4.8 and Figures 4.15– 4.19.

**Table 4.8** Characteristics of activated carbon by oxidizing agent with $CO_2$ and the air at different temperatures, sizes and times

| Temperature (°C) | Size (mm.) | Time ( hrs) | Y (%) | BD (g/cm3) | IA (mg/g) | MB (mg/g) | B.E.T. ($m^2/g$) |
|---|---|---|---|---|---|---|---|
| 150 | 1.18-2.36 | 1 | 96.76 | 0.39 | 590.50 | 287.61 | 514 |
| 250 | 1.18-2.37 | 1 | 94.37 | 0.37 | 526.00 | 295.25 | 447 |
| 350 | 1.18-2.38 | 1 | 91.37 | 0.41 | 509.00 | 290.95 | 407 |
| 450 | 1.18-2.39 | 1 | 70.05 | 0.41 | 441.00 | 281.4 | 375 |
| 150 | 0.50-0.80 | 1 | 93.79 | 0.47 | 585.50 | 297.89 | 468 |
| 150 | 1.18-2.39 | 2 | 92.94 | 0.42 | 550.50 | 288.99 | 440 |

##### 4.3.1.2.1 The effect of temperature on activation

Table 4.6 and Figure 4.15 showed the effect of temperature on % yield. It showed that the % yield of product decreased sharply when temperature was increased to 450ºC, while tar and volatile matter in the pores disappeared. Then char was burned and changeed to ash. The change in the % yield was about 70.05 % at 450ºC.

Table 4.6 and Figures 4.17-4.19 showed the effect of temperature on iodine, methylene blue and B.E.T. surface area. It showed that when temperature increased to 450ºC, the amount of iodine number was decreased because tar and volatile matter which obstruct in pores disappeared, and then micropores would be broken to mesopores and macropores respectively and partly burned at wall of pores. When temperature was decresed from 350 to150$^o$C, iodine absorption capacity increased dramatically from 441 to 526 mg/g, because the diffusion of volatile matter hindered the penetration of $CO_2$ . Most of volatile matter is diffused from particles then high porosity was developed. The optimum temperature for activation by carbon dioxide is 150$^o$C. At this operated temperature, the product contains high value of iodine number, and B.E.T. surface area.

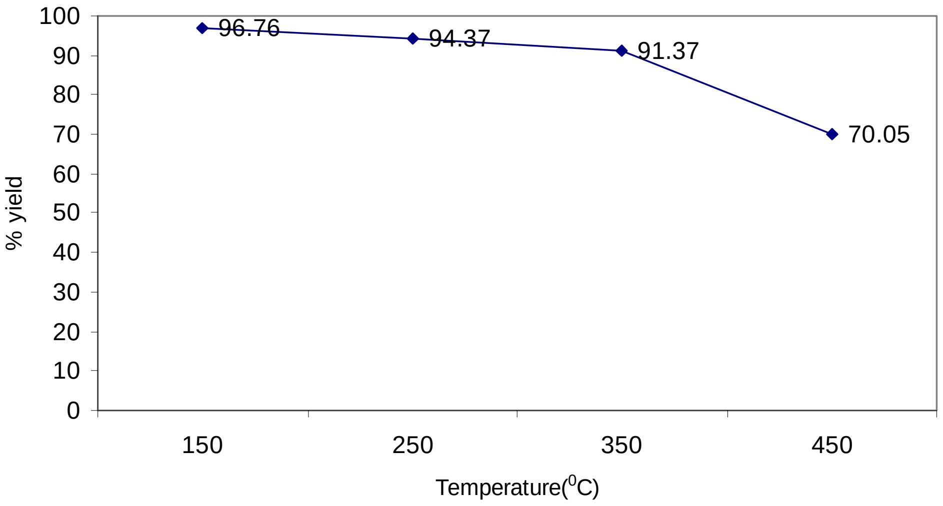

**Figure 4.15** Effect of temperature on % yield at different temperature (size 1.18 – 2.36 mm, 10 g of char, $CO_2$ 50 mL/min, air 50 mL /min).

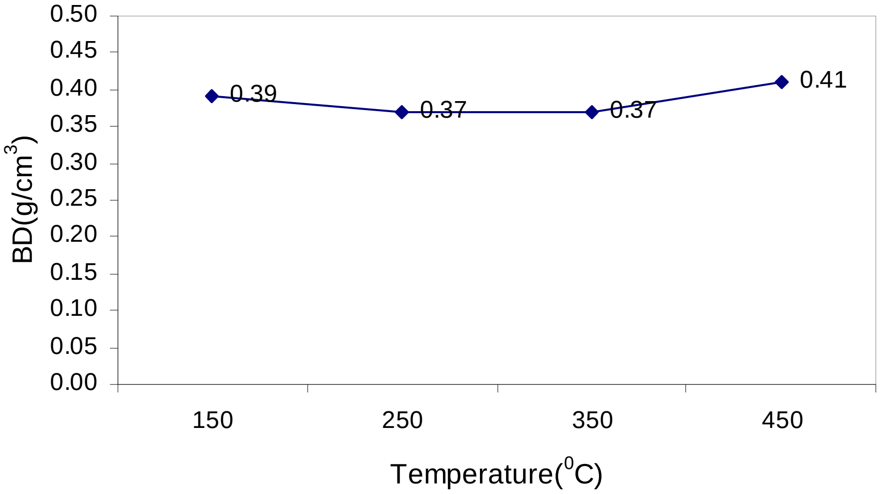

**Figure 4.16** Effect of temperature on bulk density at different temperature (size 1.18 – 2.36 mm, 10 g of char, $CO_2$ 50 mL/min, air 50 mL /min).

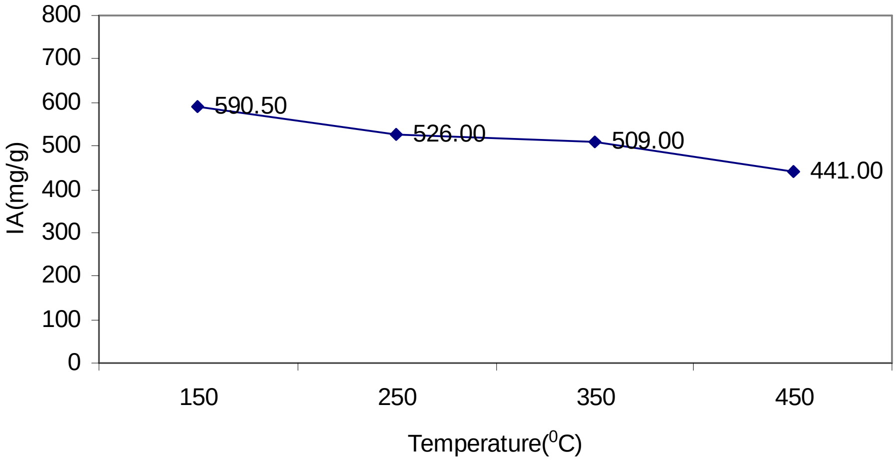

**Figure 4.17** Effect of temperature on iodine number at different temperature (size 1.18 – 2.36 mm, 10 g of char, $CO_2$ 50 mL/min, air 50 mL /min).

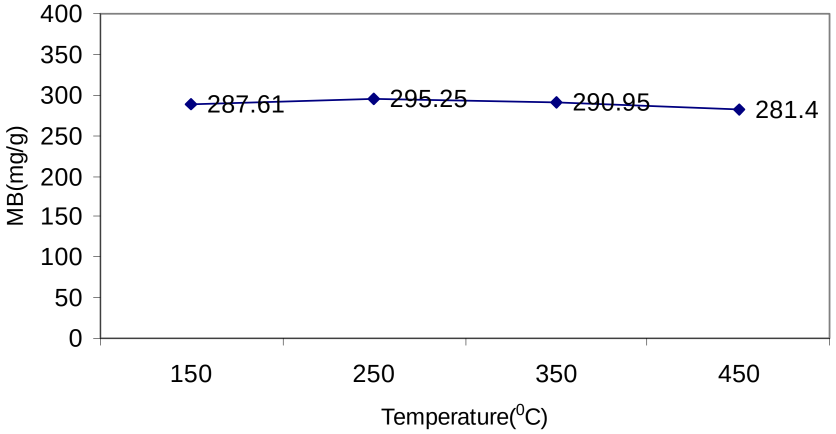

**Figure 4.18** Effect of temperature on methylene blue at different temperature (size 1.18 – 2.36 mm, 10 g, $CO_2$ 50 mL/min, air 50 mL /min).

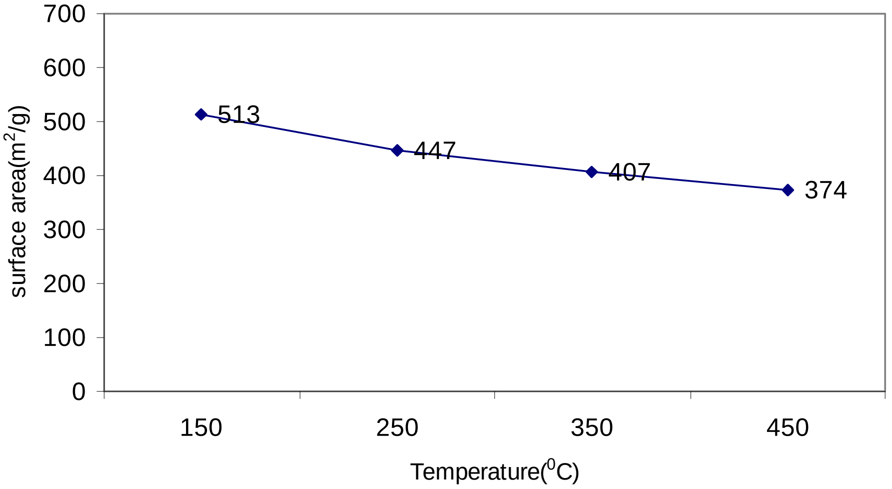

**Figure 4.19** Effect of temperature on surface area at different temperature (size 1.18 – 2.36 mm, 10 g of char, $CO_2$ 50 mL/min, air 50 mL /min).

#### 4.3.1.2.2 The effect of size on activation

Table 4.9 showed the effect of particle size of 1.18-2.36 and 0.50-0.85 mm. The activation step was carried out for 1 hr, temperature of 150ºC, 50 mL/min $CO_2$ and 50 mL/min air. It can be found that the iodine number, the methylene blue number and the B.E.T. surface area of 1.18-2.36 mm. have more increase than the size of 0.50-0.85 mm. Because the layer of bigger size of particle can be packed loosely in the fixed bed. So the $CO_2$ can attack the surface of chars and diffuse into inner pore easily, resulting in higher amount of pore and increasing of the iodine number , methylene blue number and the B.E.T. surface area.

The optimum size for activation is 0.18-2.36 mm., because the activated carbon has the high iodine number, methylene and the B.E.T. surface area. It's property is yield of 96.76 %, bulk density of 0.39 g/cm$^3$ iodine number of 590.50mg/g, methylene blue number 287.61 mg/g and B.E.T. surface area of 514 m$^2$/g.

**Table 4.9** Characteristics of activated carbon by oxidizing agent with $CO_2$ and the air at different sizes

| Temperature (°C) | Size (mm.) | Time ( hr) | Y (%) | BD (g/cm$^3$) | IA (mg/g) | MB (mg/g) | B.E.T. (m$^2$/g) |
|---|---|---|---|---|---|---|---|
| 150 | 1.18-2.36 | 1 | 96.76 | 0.39 | 590.5 | 287.61 | 514 |
| 150 | 0.50-0.80 | 1 | 93.79 | 0.47 | 585.5 | 297.89 | 468 |

#### 4.3.1.2.3 The effect of time on activation

The time for activation step of 1 and 2 hrs were studied for particle size of 1.18-2.36 mm and activation temperature of 150ºC by 50 mL/min $CO_2$ and 50 mL/min air shown in Table 4.9 . When char was activated by taking longer time, the carbon in char structure is more progressively gasified. The micropore was partly changed to mesopores and macropores respectively and some part of pores were burned during activation, thus iodine adsorption was decreased.

The iodine number and B.E.T surface area with the activating time for 1 hours increased higher than those with activation time of 2 hours, because of at the 1 hours, the most of volatile matter is diffusing in the first stage. The $CO_2$ penetrates easily into the surface and inside the particle of sludge char and air helped high partial combustion, therefore, the porosity development was increased.

**Table 4.10** Characteristics of activated carbon by oxidizing agent with $CO_2$ and the air at different times

| Temperature (°C) | Size (mm.) | Time ( hrs) | Y (%) | BD (g/cm$^3$) | IA (mg/g) | MB (mg/g) | B.E.T. (m$^2$/g) |
|---|---|---|---|---|---|---|---|
| 150 | 1.18-2.36 | 1 | 96.76 | 0.39 | 590.5 | 287.61 | 514 |
| 150 | 1.18-2.39 | 2 | 92.94 | 0.42 | 550.5 | 288.99 | 440 |

At the same temperature, the char obtained from superheated steam has higher adsorption and B.E.T surface area compared with this optained from carbon dioxide shown in Table 4.11. Because the smaller molecule of superheated steam which is more reactive than carbon dioxide could diffuse into the pores and reacted with char surface.

**Table 4.11** Compare of activating agent by superheated steam and carbon dioxide

| Activating agent | Size (mm.) | Time ( hrs) | Y (%) | BD (g/cm$^3$) | IA (mg/g) | MB (mg/g) | B.E.T. (m$^2$/g) |
|---|---|---|---|---|---|---|---|
| Superheated steam | 1.18-2.36 | 1 | 97.15 | 0.38 | 624.5 | 293.23 | 531 |
| Carbon dioxide | 1.18-2.37 | 1 | 96.76 | 0.39 | 590.5 | 287.61 | 514 |

### 4.3.2 Activation by chemical process

In the chemical activation process, the sludge char was activated by KOH, $ZnCl_2$ and $H_3PO_4$. The variables, which have an affect to the activation such as: temperature, times and sizes of char were studied in order to determine the optimum conditions. The results are shown in Table 4.12.

The different chemicals such as potassium hydroxide, phosphoric acid and zinc chloride were studied to determine the optimum reagent for activation. The mass of 10 g of sludge char (1.18 – 2.36 mm) were soaked in different reagent and at reagent : char ratio equal to 0.5:1 for 24 hours and then were dried. These samples were used for each batch. The reactor was heated until the temperature in the tube increased at temperature 350°C. The nitrogen gas was passed through the tube reactor at 250 mL/min for 1 hour. The results were shown in Tables 4.12-4.13 and Figures 4.20-4.24

Table 4.12 showed the effect of chemical oxidizing agent on properties of activated carbon. It was found that the iodine number, methylene blue number and B.E.T. surface area of products obtained by using $ZnCl_2$ as activating agent is higher those obtained than KOH and $H_3PO_4$. It is because $ZnCl_2$ penetrated into the pore structure and then resulted a large number of small-scale pores, corresponding to the increasing of iodine adsorption. Meanwhile, $H_3PO_4$ is stronger acid and could react with char more violently and caused larger pores than using $ZnCl_2$ and KOH.

**Table 4.12** Characteristics of activated carbon at diffence chemical **(**size 1.18-2.36 mm**,** 10 g of char, $N_2$ 250 mL /min)

| Chemical | Temperature (ºC) | Size (mm.) | Time ( hr) | IA (mg/g) | B.E.T. ($m^2$/g) |
|---|---|---|---|---|---|
| KOH | 350 | 1.18-2.36 | 1 | 498.00 | 423 |
| $H_3PO_4$ | 350 | 1.18-2.37 | 1 | 522.00 | 454 |
| $ZnCl_2$ | 350 | 1.18-2.38 | 1 | 648.50 | 551 |

The 10 g of 1.18-2.36 mm of chars activation with $ZnCl_2$ were charged into the fixed bed reactor followed with $N_2$ at the flow rate of 250 mL/min at ratio 0.5:1 (chemical:char).The temperature 150, 250, 350 and 450°C and reaction time 1 and 2 hours were studied in order to determine the optimium conditions.

### 4.3.2.1 The effect of temperature on activation

Table 4.13 and Figure 4.20 showed that the temperature increased to 450ºC, the %yield decreased. When the temperature was increased, $ZnCl_2$ could be more spreaded in to the structure of carbon. Then char was activated and partly burnt and finally changed into ashes. The % yield of activated carbon decreased to 64.76% at temperature of 450ºC. When the temperature was decreased, the%yield was increased.

Figures 4.22-4.24 showed that when temperature was increased to 450ºC, the amount of iodine absorption decreased sharply to 434 mg/g, because $ZnCl_2$ could be more spreaded in to the structure of carbon. Then char was changed to ash. At temperature of 350ºC, iodine absorption capacity reached to the maximium at 648.5 mg/g. While temperature was decresed 250 to 150ºC, iodine absorption capacity was decreasesd because temperature was high enough to create the reaction inside the char particle. It is probably caused by high value of zinc chloride inside the particle, which would block volatile matter from passing out of the surface.The optimum temperature for activation by zinc chloride was 350ºC for 1 hr. The characteristics of activated carbon were 88.53 % yield, bulk density of 0.35 g/cm$^3$, iodine number of 648.50 mg/g, methylene blue number 296.13 mg/g and B.E.T. surface area of 551 m$^2$/g.

**Table 4.13** Characteristics of activated carbon by $ZnCl_2$ at temperatures,size and times (size 0.50-0.80, 1.18-2.36 mm, 10 g of char, $N_2$ 250 mL /min)

| Temperature (°C) | Size (mm.) | Time ( hr) | Y (%) | BD (g/cm3) | IA (mg/g) | MB (mg/g) | B.E.T. ($m^2/g$) |
|---|---|---|---|---|---|---|---|
| 150 | 1.18-2.36 | 1 | 97.10 | 0.35 | 546.00 | 279.05 | 464 |
| 250 | 1.18-2.37 | 1 | 94.18 | 0.35 | 578.50 | 272.70 | 492 |
| 350 | 1.18-2.38 | 1 | 88.53 | 0.35 | 648.50 | 296.13 | 551 |
| 450 | 1.18-2.39 | 1 | 64.76 | 0.41 | 434.00 | 284.88 | 369 |
| 150 | 0.50-0.80 | 1 | 87.60 | 0.49 | 592.50 | 282.20 | 504 |
| 150 | 1.18-2.39 | 2 | 93.04 | 0.34 | 450.00 | 295.00 | 383 |

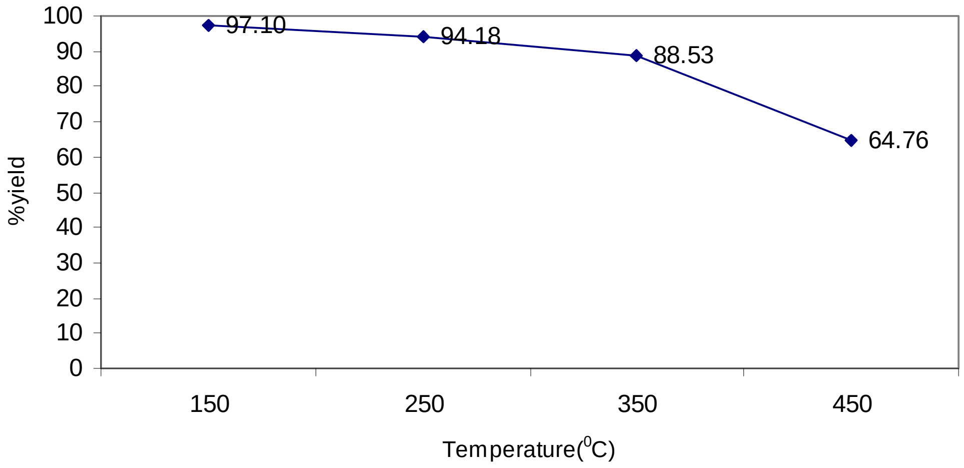

**Figure 4.20** Effect of temperature on % yield at different temperature (size 1.18 – 2.36 mm, 10 g of char, $N_2$ 250 mL /min).

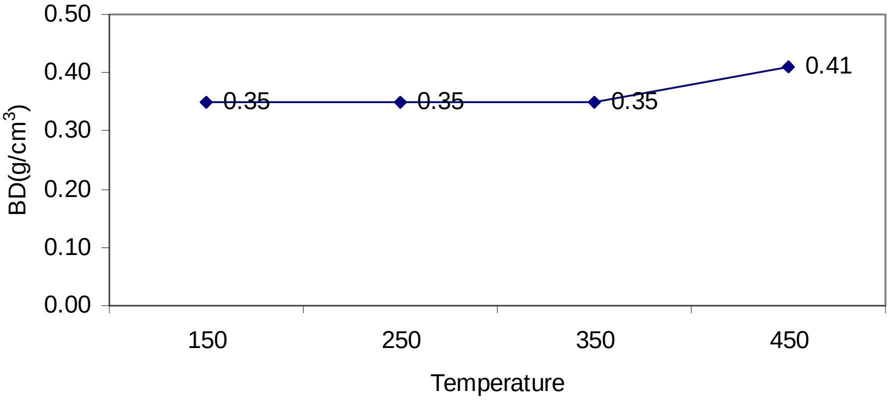

**Figure 4.21** Effect of temperature on bulk density at different temperature (size 1.18 – 2.36 mm, 10 g of char, $N_2$ 250 mL /min).

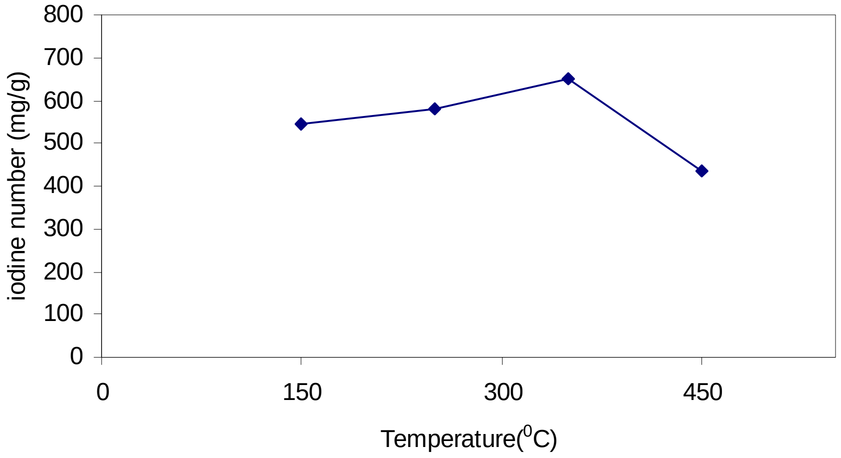

**Figure 4.22** Effect of temperature on iodine number (mg/g) at different temperature (size 1.18 – 2.36 mm, 10 g of char, $N_2$ 250 mL /min).

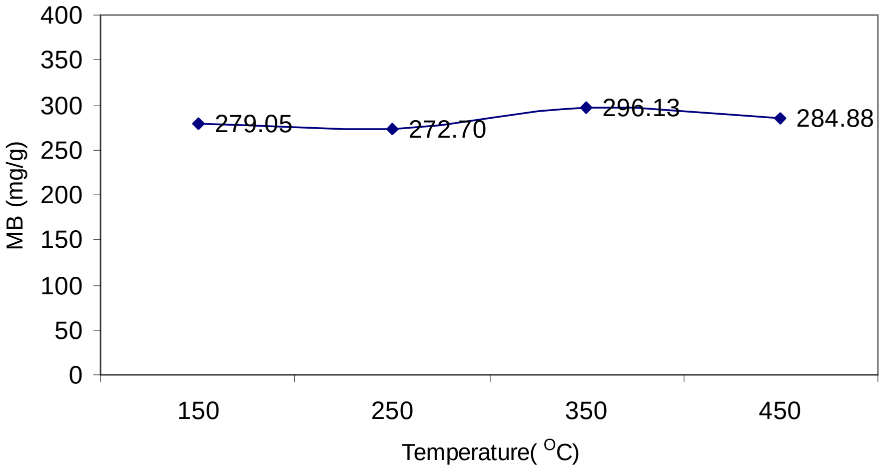

**Figure 4.23** Effect of temperature on methylene blue (mg/g) at different temperature (size 1.18 – 2.36 mm, 10 g of char, $N_2$ 250 mL /min).

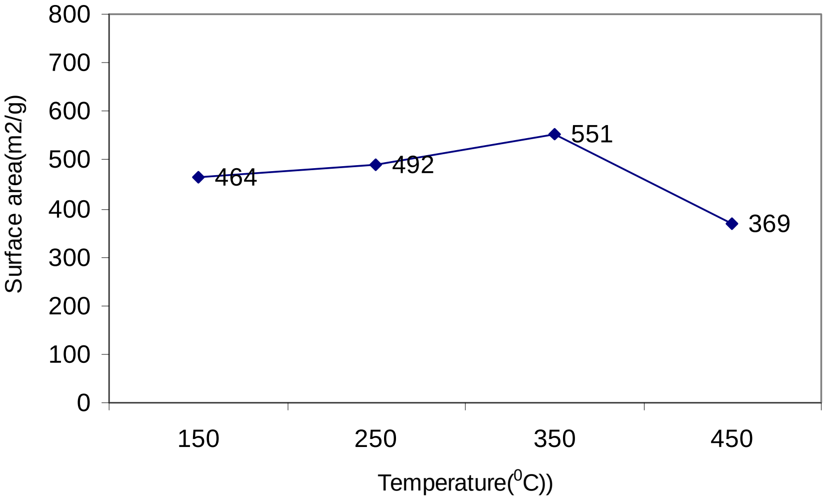

**Figure 4.24** Effect of temperature on surface area (mg/g) at different temperature (size 1.18 – 2.36 mm, 10 g of char, $N_2$ 250 mL /min).

#### 4.3.2.2 The effect of size on activation.

The effect of particle size was studied at 1 hr of activation and temperature of 350ºC by 250 mL/min $N_2$. The results were shown in Table 4.14. It can be seen that the large size of particle give higher products properties than small one. These phenomena could be explained that the former of chars is packed loose in the fixed bed, as a result, the gaps between particles were wide, so the volatile and $ZnCl_2$ were easy to vaporize out of the char by following by $N_2$ gas resulting in more pores development inner particles New pores were produced and old pores were expanded. The optimum size for activation is 0.18-2.36 mm., because the activated carbon had the high iodine number, methylene and the B.E.T. surface area. It's property was yield of 88.53 %, bulk density of 0.35 g/cm$^3$ iodine number of 624.50 mg/g, methylene blue number 296.13 mg/g and B.E.T. surface area of 551m$^2$/g.

**Table 4.14** Characteristics of activated carbon by $ZnCl_2$ at difference size

| Temperature (°C) | Size (mm.) | Time ( hr) | Y (%) | BD (g/cm$^3$) | IA (mg/g) | MB (mg/g) | B.E.T. (m$^2$/g) |
|---|---|---|---|---|---|---|---|
| 150 | 1.18-2.36 | 1 | 88.53 | 0.35 | 648.50 | 296.13 | 551 |
| 150 | 0.50-0.80 | 1 | 87.60 | 0.49 | 592.50 | 282.20 | 504 |

#### 4.3.2.3 The effect of time on activation.

The time for activation 1 and 2 hr were investigated for particle size of 1.18-2.36 mm at 350ºC by $N_2$ 250 mL/min show in Table 4.15 it found that the activation time for 1 hr gave higher iodine adsorption, methylene blue number and B.E.T. surface area than 2 hrs activation. When char sludge was activated longer time, the part of micropores collapsed and became mesopore and macropore.

The optimum activation time was 1 hr at this condition giving highest iodine number of 648.50 mg/g, methylene blue number of 296.13 mg/g and B.E.T. surface area 551 m$^2$/g.

**Table 4.15** Characteristics of activated carbon by $ZnCl_2$ at difference times

| Temperature (°C) | Size (mm.) | Time ( hr) | Y (%) | BD ($g/cm^3$) | IA (mg/g) | MB (mg/g) | B.E.T. ($m^2/g$) |
|---|---|---|---|---|---|---|---|
| 150 | 1.18-2.36 | 1 | 88.53 | 0.35 | 648.50 | 296.13 | 551 |
| 150 | 1.18-2.39 | 2 | 93.04 | 0.34 | 450.00 | 295.00 | 383 |

## 4.4 Study surface morphology of activated carbon with the Scanning electron microscope (SEM)

Scanning electron microscope (SEM) techniques was employed to observe the surface physical morphology of the sludge derived activated carbon. Figure 4.25 shown the scanning electron microscope (SEM) for morphology study of activated carbon from sewage sludge at 1000 enlargement of sludge activated carbon activated by superheated steam, by carbon dioxide and $ZnCl_{2,}$ respectively. The surface structure of the raw sludge is smooth and there are almost no micropores. After the activation process, the structure becomes porous as shown in Figure (b-e). The oxidation and gasification process of organic matter causes form thermal treatment results of the development porosity. The different pore sizes and shapes could be observed after activation with superheated steam at 150°C and 1 hour and carbon dioxide at 150°C and 1 hour. When activation time was increased to 2 hours, the micropores would be broken to mesopores and macropores and partly burnt at wall of pores. However when using $ZnCl_{2,}$ at 350°C and 1 hour, there was a noticeable acattering of salt particles, probably attributed to the remaining zinc chloride or other metal compounds. Some particles were even trapped into the pores and could possibly block the entry of the pores. Therefore, it seems that the adsorptive capacity of the products could be further increased if the washing procedure was improved. In Figure 4.25, the total surface area are 530, 513, 551and 382 $m^2/g$, respectively.

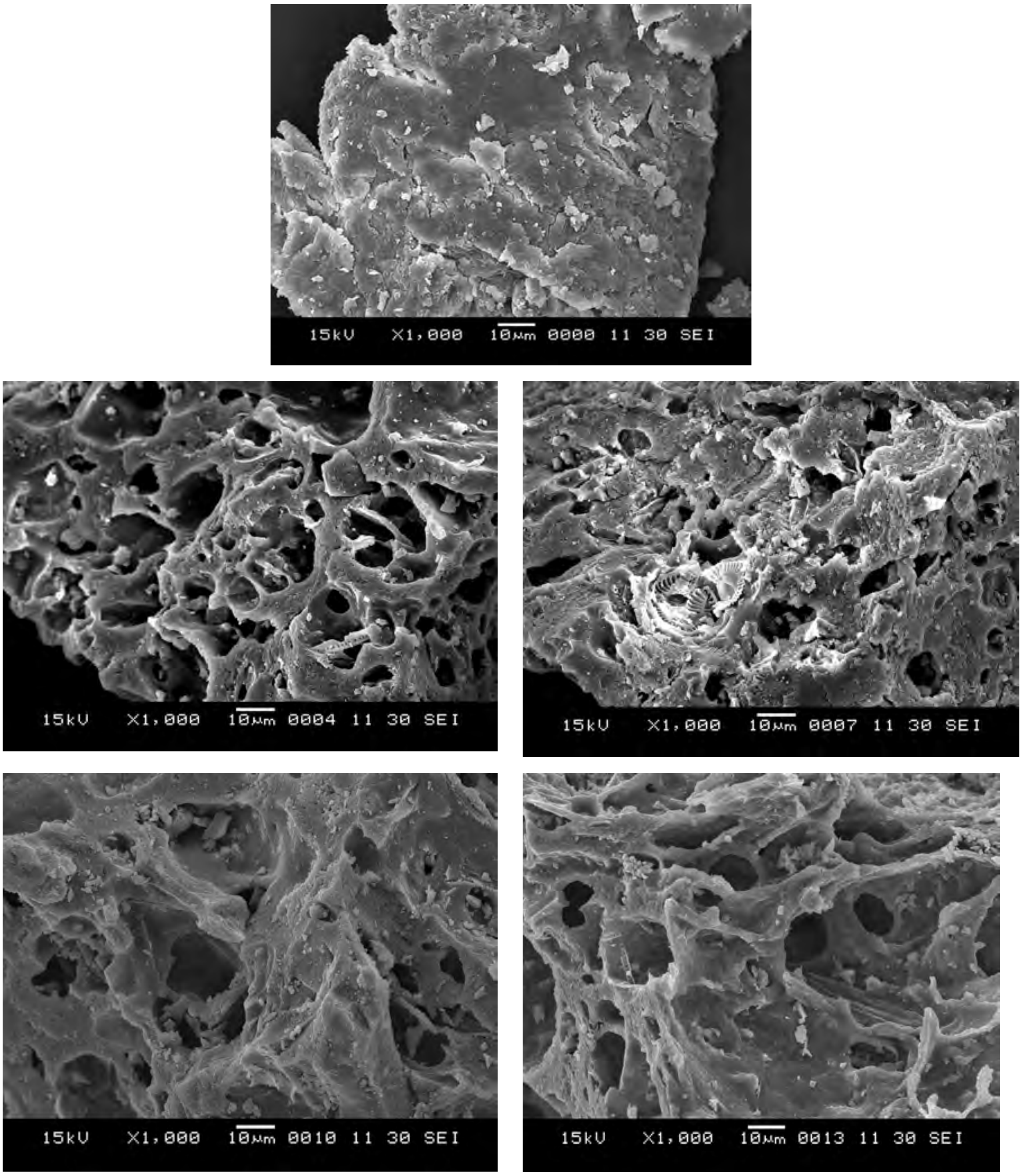

**Figure 4.25** **(a)** SEM photographs of activated carbon from sewage sludge **(a)** sewage sludge **(b)** carbon activated with the superheated steam 1 hr **(c)** carbon activated with the $CO_2$ **(d)** carbon activated with the $ZnCl_2$ **(e)** carbon activated with the superheated steam 2 hr.

## 4.5 Comparison of this work with other works

The comparison of this work with other works was divided into three cases; the first compared with Xiaoning's work (2007)[28] in case of using sewage sludge as raw material and using KOH and steam as oxidizing agent, the second compared with Ru-Ling (2005)[20] in case of using nitrogen as activating agent at different raw material, the last compared with Kiyoshi (2002)[18] in case of using steam as activating agent at different raw material, the characteristics of activated carbon obtained were expressed in Tables 4.16 respectively.

Table 4.16 showed that this work gave high iodine adsorption, methylene blue number and B.E.T. surface area compareed with Xiaoning'work. However, it can be seen that B.E.T. surface area is lower than other's results. This is probably because of different raw material, activating agent and activation condition. Meanwhile, Xiaoning (2007) produced the activated carbon from sewage sludge by using KOH and activating by using nitrogen. The author reported that the optimum condition for activation was 600$^{o}$C and 1 hr which the properties are B.E.T. surface area of 381m$^{2}$/g, and iodine number of 563.10 mg/g. These adsorption capacity research are higher than Xiaoning's work which KOH and high temperature condition during the activation step could collapse micropore to mesopores and macropores. Ru-Ling used corncob as raw material and activated it with KOH at high temperature, 780$^{o}$C. This raw material is harder than sewage sludge, so the porosity development occurred easily and resulted in high B.E.T. surface area of 2,595 m$^{2}$/g.

Kiyoshi (2002) used waste newspaper as raw material, and activated it with steam for 2 hr. The porosity also well develop throughout inside the particles as micropores coresponding to obtain the B.E.T. surface area as 1,090 m$^{2}$/g , less than the work of Ru-Ling. The result obtained from this work, activated carbon with 648.5 mg/g iodine adsorption is acceptable as Thailand activated carbon standard ( at least 600 mg/g of iodine adsorption)

**Table 4.16** Comparison of this work with other work [20,28,29]

| **Description** | **This work (2009)** | **Xiaoning (2007)** | **Ru-Ling (2005)** | **Kiyoshi (2002)** |
|---|---|---|---|---|
| *Raw material* | Sewage sludge | Sewage sludge | corncob | Waste newspaper |
| *Carbonization* | 400ºC for 1.30 hr. | - | 450ºC for1.30 hr. | 850ºC for 2 hr. |
| *Activation* | 250ºC for 1 hr. with nitrogen | 600 for 1 hr. | 780ºC with nitrogen | with nitrogen |
| *Activating agent* | $ZnCl_2$ and nitrogen | KOH and Steam | KOH and nitrogen | steam |
| %yield | 88.53 | 41.80 | - | - |
| IA (mg/g) | 648.50 | 563.10 | - | - |
| MB (mg/g) | 296.13 | - | - | - |
| B.E.T. surface area ($m^2/g$) | 551 | 381 | 2,595 | 1,090 |

# CHAPTER V

# CONCLUSION AND RECOMMENDATION

## 5.1 Conclusions

The experimental results showed the possibility to produce the activated carbon from sewage sludge. In this research, carbonization and activation process were proposed to produce activated carbon from sewage sludge. In the carbonization step, the studied variables were temperature and time at the range of 375-425ºC and 45-120 min respectively. The optimum condition of this step was 400ºC and reaction time of 90 minutes with 39.94 % yield, 52.47% fixed carbon, 21.45 % volatile matter and 26.08 % ash.

In the activation step, 2 method were used. The first is physical activation by superheated steam and carbon dioxide and the second is chemical activation by using chemical solution potassium hydroxide, phosphoric acid and zinc chloride. Studied variables in this process were activation temperature, activation time and size of sewage sludge char. From the results of physical activation process, it was found that the suitable condition was temperature of 150 ºC 1 hr of activation time and char sized 1.18-2.36 mm. The properties of activated carbon obtained from the experiment are 97.15% yield, 0.38 g/cm$^3$ bulk density, iodine number 624.50 mg/g ,methylene blue number 293.23 mg/g and B.E.T surface area 531m$^2$ /g. The optimium condition which is 150ºC in 1 h and 1.18-2.36 mm char paticle size gives 96.76% yield of activated carbon the properties of, 0.39 g/cm$^3$ bulk densitysh, iodine number 590.50 mg/g ,methylene blue number 287.61 mg/g and B.E.Tsurface area 514 m$^2$ /g. Whereas the suitable condition for chemical activation using $ZnCl_2$ at 350ºC for 1 hr and sludge char size of 0.18-2.36 mm gave 88.53 % yield. The product's properties were 0.35 g/cm$^3$ bulk density, iodine number 648.50 mg/g, methylene blue number 296.13 mg/g and B.E.T surface are 551m$^2$/g.

It can be concluded that sewage sludge, which most people think that it is waste, was converted to activated carbon and can be used in adsorption application. It was also proved that $ZnCl_2$ is suitable for the activation process.

In this globalization, recycling was one of the modern know-how. Activated carbon produced from sludge could be solved the pollution problem by keeping the atmosphere clean and greenhouse gas reducing.

## 5.2 Recommendation

For future research work, other modification of process should be studied to observe pore development of activated carbon in one-step carbonized process that might be a promising practical way for activated carbon production for commercial scale.

# REFERENCES

[1] Rodr, F. Activated carbon: structure, characterisation, preparation and applications.Introduction to Carbon Technologies, 1997.

[2] Couillard, D.J. A metallurgical residue for solubilization of metals from sewage sludge, Environmontal System. 22 (1994): 83–89.

[3] Calvo, L.F, Otero, M .Upgrading sewagesludges for adsorbent preparation by different treatments, Bioresource Technology. 80 (2001): 143–148.

[4] Chiang, P.C, You, J.H. Use of sewage sludge for manufacturing adsorbents, Journal of Chemical Engineering 65 (1987) : 922–927.

[5] Graham, N, Chen, X.G. The potential application of activated carbon from sewage sludge to organic dyes removal, Water Science Technology 34 (2001) : 245–252.

[6] Jeyaseelan, S., Lu, G Development of adsorbent/catalyst from municipal wastewater sludge, Water Science Technology 34 (1996): 499–505.

[7] Otero, M., Rozada, L.F. Kinetic and equilibrium modelling of the methylene blue removal from solution by adsorbent materials produced from sewage sludges, Jurnal of Biochemical Engineering 15 (2003): 59–68.

[8] Rozada, F., Calvo, L.F. Dye adsorption by sewage sludge-based activated carbons in batch and fixed-bed systems, Bioresource Technology 87 (2003) : 221–230.

[9] Otero, M., Rozada, F. and Calvo, L.F. Elimination of organic water pollutants using adsorbents obtained from sewage.

[10] Costoms Department, Finance Ministry. Import and exports statistics of activated carbon. Foreign Trade Statistics of Thailand. 1988-1999.

[11] Jankowska, H., Swiatkowski, A., and Choma, J. Active Carbon. Warsaw: Ellis Horwood, 1991.

[12] Hassler, J.W. Purification with Activated Carbon. New York: Mercel Dekker, 1974.

[13] Bansal, R.C., Donnet, J.B., and Stoeckil, F. Active Carbon. New York: Mercel Dekker, 1988.

[14] Hassler, J.W. Activated Carbon. London: Leonard Hill, 1967.

[15] Hussein, M.Z., Zainal, Z., Ibrahim, R., Kheong, K.K., and Muhammad, B. The preparation of activated carbons from chips of oil palm trunk catalysed by $ZnCl_2/CO_2$: Surface area and porosity studies.Biotechnology 64 (1995): 35-40.

[16] Sopanakijkosol, Palut. Production of activated carbon from coconut shell for removing Chromum (IV). Master's Thesis, Department of Chemical Engineering, King Mongkut Institute of Technology Thonbury University, 2000.

[17] Paul, T. W.; Anton R R., Development of activated carbon pore structure via physical and chemical activation of biomass fibre waste Biomass Bioenergy 30 (2006): 144-152.

[18] Diana, C., Azevedo.,J Microporous activated carbon prepared from coconut shells using chemical activation with zinc chloride Microporous and Mesoporous Materials 100 (2007) :361–364.

[19] Xiaoning, W. Preparation of sludge-based activated carbon and its application in dye wastewater treatment Journol of Hazardous Material 153 (2008) : 22-27.

[20] Ru-Ling, T.; Szu-Kung T.; Pore structure and adsorption performance of the KOH-activated carbons prepared from concob Colloid and Interface Science 287 (2005) : 428-437.

[21] G.G S.; A.A Z.; Production and characterization of activated carbons from olive-seed waste residue, Microporus and Mesopore Material 82 (2005): 79-85.

[22] Donni, A., Preparation and characterization of activated carbon from palm shell by chemical activation with $K_2CO$. Bioresource Technology 98 (2007):145–149.

[23] Selhan K.; Turgay T.; Activated carbons from waste biomass by sulfuric acid activation and their use on methylene blue adsorption Bioresource Technology 99 (2008): 6214-6222.

[24] Jerome,O.Mercury removal from water using activated carbons derived from organic sewage sludge Carbon 41 (2003): 1009–1016.

[25] Rozada, F., Otero M. Producing adsorbents from sewage sludge and discarded tyres Characterization and utilization for the removal of pollutants from water Journal of Chemical Engineering 114 (2005): 161–169.

[26] Guillermo, S., Geoffrey,D A study of the characteristics of activated carbons produced by steam and carbon dioxide activation of waste tyre rubber Carbon 41 (2003): 1009–1016.

[27] Rozada ,F., Otero M. Activated carbons from sewage sludge and discarded tyres: Production and optimization Journal of Hazardous Materials B124 (2005) :181–191.

[28] Xiaodan, F., Xiangkai Z.Adsorption properties of activated carbon from sewage sludge to alkaline-black Materials Letters 62(2008): 704–1706.

[29] Kiyoshi,O.;Nobuo Y.; Yoshikazu K.; Atsuo Y.; Adsorption properties of activated carbon from waste newspaper prepared by chemical and physical activation Colliod and Interface Science 262(2003): 194-199.

[30] American Standard of Testing Material. Standard practice for proximate analysis of coal and coke. Annual book of ASTM standards D 3172-89: 288.

[31] American Standard of Testing Material. Standard test method for moisture in the analysis sample of coal and coke. Annual book of ASTM standard D 3173-87: 289-290.

[32] American Standard of Testing Material. Standard test method for ash in the analysis sample of coal and coke from coal. Annual book of ASTM standard D 3174-93: 291-294.

[33] American Standard of Testing Material. Standard test method for volatile matter in the analysis sample of coal and coke. Annual book of ASTM standard D3175-89a (Reapproved 1993): 295-297.

[34] American Standard of Testing Material. Standard test method for determination of iodine number of activated carbon. Annual book of ASTM standard D 4607-94: 542-545.

[35] Japanese Standard Association. Standard testing method of methylene blue number of activated carbon. Japanese industrial standard test method for activated carbon. JIS K 1470-1991.

[36] American Standard of Testing Material. Standard test method for apparent density of activated carbon. Annual book of ASTM standard D 2284-89 (Reapproved 1993): 491-493.

[37] American Standard of Testing Material. Standard test method for carbon black-surface area by multipoint B.E.T. nitrogen adsorption. Annual book of ASTM standard D 4820-96a: 756-762.

[38] American Standard of Testing Material. Standard test method for chemical analysis of wood charcoal. Annual book of ASTM standard D 1762-84 (Reapproved 1995): 281-282.

# APPENDICES

## Appendix A

**Table A.1** Properties of commercial activated carbons limit by TIS 900-1989

| Types | Size | % Moisture | BD (cm$^3$/g) | IA (mg) |
|---|---|---|---|---|
| Powdered activated carbon | <150 μm | - | 0.20-0.75 | >600 |
| Granular activated carbon | >150 μm | <8 | >0.36 | >600 |

**Table A.2** Properties of commercial powdered activated carbon

| Trade names | Raw material | Ash (%) | BD (g/cm$^3$) | $S_{BET}$ (m$^2$/g) | MB (mg/g) | LA (mg/g) |
|---|---|---|---|---|---|---|
| **UDP CHEMICAL (Thailand)** | | | | | | |
| MDP 1-7325 | Coconut shell | 3 | 0.40-0.55 | 1200-1300 | 230 | 1050 |
| PN3 | - | 8 | 0.46 | - | - | 800 |
| Taiko PKW | Sawdust | 2 | - | - | - | - |
| Shirasagi | Sawdust | 3 | - | - | - | - |
| KW | - | 3-5 | 0.37-0.40 | - | - | 900 |
| Nuchar SA | - | 3-5 | 0.37-0.40 | - | - | 900 |
| Nuchar SN | | | | | | |
| **PITTSBURGH ACTIVATED CARBONS** | | | | | | |
| RB | Bituminous | 23 | - | 1250-1400 | - | 1200 |
| RC | Bituminous | 21 | - | 1100-1300 | - | 1100 |
| BL | Bituminous | 8.5 | - | 1000-1100 | 300 | 1000 |
| C | Bituminous | 14 | - | 1000-1100 | - | 900 |
| GW | Bituminous | 12 | - | 1000-1100 | 180 | 700 |

**Table A.3** Properties of commercial granular activated carbon.

| Trade names | Raw material | Ash (%) | BD (g/cm$^3$) | $S_{BET}$ (mg/g) | MB (mg/g) | IA (mg/g) |
|---|---|---|---|---|---|---|
| **UDP CHEMICAL (Thailand)** | | | | | | |
| MD-G 7746 | Coconut shell | 3 | 0.40-0.45 | 1100-1200 | 200 | 1050 |
| MD-W 7830 | Coconut shell | 3 | 0.50-0.55 | 1150-1250 | 220 | 1050 |
| **SUTCLIFFE SPEAKMAN (England)** | | | | | | |
| | Coal | 6-16 | 0.40-0.56 | 600-1250 | - | - |
| | Coconut shell | 1-4 | 0.40-0.59 | 700-1500 | - | - |
| **NORIT ACTIVATED CARBON** | | | | | | |

| | | | | | | |
|---|---|---|---|---|---|---|
| PK1-3 | Peat | 6 | - | 800 | - | 800 |
| Nuchar 681 | Bituminous | - | 0.43-0.46 | 1100 | - | - |
| AG-5 | - | 6 | 0.38-0.45 | 900-1100 | - | - |
| **PJAC( Japan)** | | | | | | |
| CG-4X10 | Coconut shell | 5 | 0.42-0.47 | 1200-1300 | 170 | 1050 |
| CG-6X8 | Coconut shell | 5 | 0.42-0.47 | 1200-1300 | 170 | 1100 |
| CW-8X30 | Coconut shell | 5 | 0.45-0.50 | 1050-1150 | 170 | 1050 |
| SYBRON | Bituminous | - | 0.50-0.55 | 900 | 220 | 900 |
| **IONAC P-50(USA)** | | | | | | |
| Calgon Filtrasorb | Bituminous | - | - | 850-900 | - | 850 |
| 100-200 CALGON SGL | Bituminous | 10 | 0.48 | 950-1050 | - | 900 |
| **PITTSBURGH ACTIVATED CARBONS** | | | | | | |
| *Vapor phase* -PCB | Bituminous | 4.0 | 0.44 | - | - | 1200 |
| *Liquid phase* -CAL | Bituminous | 8.5 | 0.44 | - | - | 1000 |

# Appendix B

**Appendix B.1** Standard test method for chemical analysis of wood charcoal (ASTM D 1762-84).

**Appendix B.2** Standard test method for apparent density of activated carbon (ASTM D 2884-89).

**Appendix B.3** Standard test method for moisture in activated carbon (ASMT D 2867-95).

**Appendix B.4** Standard test method for total ash content of activated carbon (ASTM D 2866-94).

**Appendix B.5** Standard test method for determination of iodine number of activated carbon (ASMT D 4607-94).

**Appendix B.6** Standard testing method of methylene blue number of activated (JIS K 1470-1991).

**Appendix B.7** Standard test method for carbon black-surface area by multipoint B.E.T. nitrogen adsorption (ASTM D 4820-96a).

## Appendix B.1

## Standard test method for chemical analysis of wood charcoal (ASTM D 1762-84)

This test method covers the determination of moisture, volatile matter, and ash in charcoal made from wood. The sample is ground in a specified manner and the moisture determined as loss in a drying oven at 105$^{o}$C. Volatile matter is determined as loss in weight at 950$^{o}$C under specified conditions. Ash is determined as the residue after burning to constant weight 750$^{o}$C.

**Procedure** (for Activated carbon passing A No. 50 Sieve)

**1.** Make duplicate determinations.

**2.** ***Moisture*** Heat the muffle furnace to 750$^{o}$C and place previously ignited porcelain crucible (*Note1*) and covers in the furnace for 10 min. Cool the crucibles in a desiccator for 1 hr. Weigh the crucibles and add to each approximately 1 g, weighed to the nearest 0.1 mg, of the ground sample. Place the Samples in the oven at 105$^{o}$C for 2 hr. Place the dried samples in a desiccator for 1 hr and weight (*note2*).

*Note1* In practice, a crucible from a previous determination is used

*Note2* The sample shall be considered oven-dry when, the decrease in weight of consecutive weightings is 0.0005 g or less. Succeeding dry periods shall be not less than 1 hr.

**3.** ***Volatile matter*** Heat the muffle furnace to 950$^{o}$C. Preheat the crucibles used for the moisture determination, with lids in place and containing the sample, as follows: with the furnace door oven, for 2 min on the outer ledge of the furnace (300$^{o}$C) and then for 3 min on the edge of the furnace (500$^{o}$C) (*Note3*). Then move the samples to the rare of the furnace for 6 min with the muffle door closed. Watch the samples through a small peep-hole in the muffle door. If sparking occurs, results will be in error (*Note4*). Cool the samples in a desiccator for 1 hr and weigh.

*Note3* Individual nichrome wire baskets to hold the crucibles are convenient.

*Note4* If the speaking sample dose not check the results of its nonsparking duplicate within ±0.5%, the analysis shall be repeated.

**4.** ***Ash*** Place the lids and the uncovered crucible used for the volatile matter determination, and containing the sample in the muffle furnace at 750 C for 6 hr.

Cool the crucibles with lids in place in a desiccator for 1 hr and weigh. Repeat burning of the sample until a succeeding 1 hr period of heating results in a loss of less than 0.0005 g.

**Calculation**

1. Calculate the percentage of moisture in the sample as follows:

   Calculate the moisture content as follows:

$$\text{Moisture, } \% = [(A - B) / A] \times 100$$

Where:

$A$ = grams of air-dry sample used, and

B = grams of sample after drying at $105^{o}$C

2. Calculate the percentage of volatile matter content in the sample as follows:

$$\text{Volatile matter, } \% = [(B - C) / B] \text{ X } 100$$

where:

$C$ = grams of sample after drying at $950^{o}$C.

3. Calculate the percentage of ash in the sample as follows:

$$\text{Ash, } \% = (D / B) \times 100$$

Where

$D$ = grams of residue.

## Appendix B.2

## Standard test method for apparent density of activated carbon (ASTM D 2884-89)

This test method covers the determination of the apparent density (bulk density) of granular activated carbon. It is determined on granular sample by measuring the volume packed by a free fall from a vibrating feeder into a 10 mL graduated cylinder and weighing the known volume. For purposes of this test method, granular activated carbon is defined as a minimum of 90% being larger than 80 mesh.

### Procedure

Dry an adequate sample of the carbon to be tested to constant weight at 150 ± 5°C.

Carefully place a representative sample of the activated carbon into the feed funnel so that the material does not prematurely flow into the graduated cylinder.

Fill the cylinder at a uniform rate up to 10 mL mark.

Transfer the contents from the cylinder to a balance pan and weight to the nearest 0.1 g.

### Calculation

Calculate the bulk density as follows :

Bulk density, g/ml = weight of activated carbon/10

## Appendix B.3

### Standard test method for moisture in activated carbon (ASMT D 2867-95)

These test methods for the determination of the moisture content of activated carbon, for this work used the oven-drying method. The oven-drying method is used when water is the only volatile material present and is in significant quantities, and the activated carbon is not heat-sensitive (some activated carbons can ignite spontaneously at temperatures as low as 150$^{o}$C) and weighed accurately. The capsule is opened and placed with the lid in a preheated oven. The sample is dried to constant weight then removed from the oven and with the capsule closed, cooled to ambient temperature. The closed capsule is weighed again accurately. The weight loss expressed as a percentage of the weight of the original sample.

**Procedure** (for Activated carbon Passing A No. 50 Sieve)

1. Dip out with a spoon or spatula from the sample bottle a 1 to 2 g representation sample. Put this into a predried tared capsule with lid, close and weight at once to the nearest 0.5 mg. The depth of the carbon in the capsule must not exceed 1.25 cm.
2. Remove the cover and place the capsule and cover in a preheated forced circulation oven (at 145 to 155$^{o}$C). Close the oven and dry to constant weigh (3 hr normally sufficient). Open the oven and cover the capsules quickly. Cool in desiccator to ambient temperature and weigh.

### Calculation

Calculate the moisture content as follows:

$$\text{Moisture, weight } \% = [ ( C - D ) / ( C - B ) ] \times 100$$

Where:

$B$ = weight of capsule with cover, g

C = weight of capsule with cover plus original sample, g, an

$D$ = weight of capsule with cover plus dried sample, g.

## Appendix B.4

## Standard test method for total ash content of activated carbon (ASTM D 2866-94)

This test method describes a procedure for the determination of total ash content of activated carbon. An accurately weighed sample of dried activated carbon is placed in a controlled-temperature muffle furnace for a period of several hours. When content weight has been achieved, the crucible is cooled to ambient temperature in a decentage of the weight of the original carbon sample.

### Procedure

1. Ignite the crucible in the muffle furnace at 650 ± 25 $^{o}$C for 1 hr Place the crucible in the desiccator. Cool to room temperature and weight to the nearest 0.1 mg.

2.Dry an adequate sample of activated carbon to constant weight at 150 ± 5 $^{o}$C (3 hr is usually sufficient).

3.Weigh out to the nearest 0.1 mg. Sufficient dried activated carbon, so that the estimated amount of ash will be 0.1 g, into the ignited crucible and place the crucible in the furnace at 650 ± 25$^{o}$C. Ashing will require from 3 to 16 hr, depending on the size and type of activated carbon. Ashing can be considered complete when constant weight is achieved.

4.Place the crucible in the desiccator and allow to cool to room temperature. After the sample has cooled in the desiccator, admit air slowly to avoid loss of ash from the crucible. Weigh to the nearest 0.1 mg.

### Calculation

Calculate the ash content as follows:

$$\text{Total ash, \%} = [ ( D - B ) ] / ( C - B ) ] \times 100$$

Where:

$B$ = weight of crucible, g,

C = weight of crucible plus original sample, g, and

$D$ = weight of crucible plus ashed sample, g .

## Appendix B.5

## Standard test method for determination of iodine number of activated carbon (ASMT D 4607-94)

This test method covers the determination of the relative activation level of unused of reactivated carbons by adsorption of iodine from aqueous solution. The amount of amount of iodine absorbed (in milligrams) by 1 g of carbon using test conditions listed herein is called the iodine number.

This test method is based upon a three-point adsorption isotherm. A standard iodine solution is treated with three different weights of activated carbon under specified conditions. The carbon treated solution are filtered to separate the carbon from the treated iodine solution (filtrate). Iodine remaining in the filtrate is measured by titration. The amount of iodine removed per gram of carbon is determined for each carbon dosage and the resulting data used to plot an adsorption isotherm. The amount of iodine adsorbed (in milligrams) per gram of carbon at a residual iodine concentration of 0.02 *N* is reported as the iodine number.

### 1. Preparation of solutions

1.1 *Hydrochloric Acid Solution* (5 % by weight). Add 70 ml of concentrated hydrocholic

acid to 500 ml of distilled water and mix well. A graduated cylinder may be used for measurement of volume.

1.2 *Sodium Thiosulfate* (0.100 N). Dissolve 24.820 g of sodium thiosulfate in appropximately 75 ± 25 ml of freshly boiled distilled water. Add 0.10 ± 0.01 g of sodium carbonate to minimize bacterial decomposition of the thiosulfate solution. Quantitatilvely transfer the mixture to a 1 L volumetric flask and dilute to the mark. Allow the solution to stand at least 4 days before standardizing. The solution should be stored in an amber bottle.

1.3 *Standard Iodine Solution* (0.100 ± 0.001 N). Weigh 12.700 g of iodine and 19.100 g of potassium iodine (KI) into a beaker. Mix the dry iodine and potassium iodine. Add 2 to 5 ml of water to the beaker and stir well. Continue adding small increment of water (approximately 5 ml each) while stirring until the total volume is 50 To 60 ml. Allow the solution into stand a minimum of 4 to ensure that all crystals are thoroughly dissolved. Occasional stirring during this 4 hr period will aid in the dissolution. Quantitatively transfer to a 1 L volumetric flask and fill to the mark with distilled water. It is important that the standard iodine solution has an iodine-to-iodine weight ratio of 1.5 to 1. Store the solution in an amber bottle.

1.4 *Potassium Iodate solution* (0.1000 N). Dry 4 or more grams of primary standard grads potassium iodate ($KIO_3$) at 110 ± 5°C for 2 hr and cool to room temperature in a desicator. Dissolve 3.5667 ± 0.1 mg of the dry potassium iodate in about 100 ml of distilled water. Quantitatively transfer to a 1-L volumetric flask and fill to the mark with distilled water. Mix thoroughly and store in a glass- stoppered bottle.

1.5 *Starch Solution.* Mix 1.0 ± 0.5 g of starch with 5 to 10 ml of cold water to make a paste. Add an additional 25 ± 0.5 g of water while stirring to the starch paste. Pour the mixture, while stirring, into 1 L of boiling water add boil for 4 to 5 min. This solution should be made fresh daily.

**2. Standardization of solutions**

2.1 *Standardization of 0.100 N Sodium Thiosulfate*. Pipet 25.0 ml of potassium iodate ($KIO_3$) solution from 1.2 into a 250-ml titration (or wide-mouthed Erlenmeyer) flask. Add 2.00 ± 0.01 g of potassium iodide (KI) to the flask and shake the flask to dissolve the potassium iodide crystals. Pipet 5.0 ml of concentrated hydrochloric acid into the flask. Titrated the free iodine with sodium thiosulfate solution until a light yellow color is observed in the flask. Add a few drops of starch indicator (1.5) and continue the titration dropwise until one dropwise until one drop produces a colorless solution. Determine sodium thiosulfate normality as follows:

$$N_1 = (P \quad R)/S$$

Where :

$N_1$ = sodium thiosulfate, *N*,

P = potassium iodate, ml,

$R$ = potassium iodate, *N*, and

$S$ = sodium thiosulfate, ml.

The titration step should be done in triplicate and the normality results averaged. Additional replications should be done if the range of values exceeds 0.003 *N*.

2.2 *Standardization of 0.100 ±0.001 N Iodine solution.* Pipet 25.0 ml of iodine solution

(1.3) into a 250-mL wide mouthed Erlenmeyer flask. Tritrate with standardized sodium thiosulfate (2.1) until the iodine solution is a light yellow color. Add a few drops of starch indicator (1.5) and continue the titration dropwise until one drop produces a colorless solution. Determine iodine solution normality as follows:

$$N_2 = ( S \quad N_1) / \quad I$$

Where :

$N_2$ = iodine, *N*,
$S$ = sodium thiosulfate, ml,
$N_1$ = sodium thiosulfate, *N*, and
$I$ = iodine, ml.

The titration step should be done in triplicate and the normality results averaged. Additional replications should be done if the range of values exceed 0.003 *N*. The iodine solution concentration must be 0.100 ± 0.001 *N*. If this requirement is not met, repeat 1.3 and 2.2.

## 3. Procedure

3.1 The procedure applies to either powdered or granular activated carbon. When granular carbon is to be tested, grind a representative sample of carbon until 60 wt % (or more will pass through a 325-mesh screen) and 95 wt % or more will pass through a 100-mesh screen (U.S. sieve series, see specification E 11). Carbon received in the powdered from may need additional grinding to meet the particle size requirement given above.

3.2 Dry the ground carbon from 3.1 in accordance with test method D 2867. Cool the dry carbon to room temperature in a desiccator.

3.3 Determination of iodine number requires an estimation of three carbon dosages. Section 4 and **Table B.5.1** describes how to estimate the carbon dosages to be used.

After estimating carbon dosages, weight three appropriate amounts of dry carbon to the nearest milligram. Transfer each weighed sample of carbon to a clean, dry 250-mL. Erlenmeyer flask equipped with a ground glass stopper.

3.4 Pipet 10.0 ml of 5 wt % hydrochloric acid solution into each flask containing carbon.

Stopper each flask and swirl gently until the carbon is completely wetted. Loosen the stoppers to vent the flasks, place on a hot plate in a fume hood, and bring the contents to a boil. Allow to boil gently for 30 ± 2 s to remove any sulfur which may interfere whit the test results. Remove the flasks from hot plate and cool to room temperature.

3.5 Pipet 100.0 ml of 0.100 *N* iodine solution into each flask. Standardize the solution just prior to use. Stagger the addition of iodine to the three flasks so that no delays are encountered in handling. Immediately stopper the flasks, and shake the contents vigorously for 30 ± 1 s. Quickly filter each mixture by gravity through one sheet of folded filter paper (Whatman No. 2V or equivalent) into a beaker. Filtration equipment must be prepared in advance so no delay is encountered in filtering the samples.

3.6 For each filtrate, use the first 20 to 30 ml to rinse a pipet. Discard the rinse portion. Use clean beakers to collect the remaining filtrates. Mix each filtrate by swirling the beaker and pipet 50.0 ml of each filtrate into a clean 250-mL Erlenmeyer flask. Titrate each filtrate with standardized 0.100 *N* sodium thiosulfate solution until the solution is a pale yellow. Add 2 mL of the starch indicator solution and continue The titration with sodium thiosulfate until one drop produces a colorless solution. Record the volume of sodium thiosulfate used.

## 4. Calculation

4.1 The capacity of carbon for any adsorbate is dependent upon the concentration of the adsorbate in solution. The concentrations of the standard iodine solution and filtrate must be specified or known. This is necessary to determine an appropriate carbon weight to produce final concentrations agreeing with the definition of iodine number. The amount of carbon sample to be used in the determination is governed by the activity of the carbon. If filtrate normalities (C) are not within the range of 0.008 *N* to 0.040 *N*, repeat the produre using different carbon weights.

4.2 Two calculations are required for each carbon dosage, as *X/M* and *C*

4.2.1 To calculate the value of *X/M*, first derive the following values:

$$A = (N_2)\ (12693.0)$$

Where:

$N_2$ = iodine, $N$ (from 2.2)

$$B = (N_1)(126.93)$$

Where:

$N_1$ = sodium thiosulfate, $N$ (from 2.1)

$$DF = (I + H) / F$$

Where:

$DF$ = dilution factor,

$I$ = iodine, ml (from 2.2),

$H$ = 5% hydrochloric acid used, ml, and

$F$ = filtrate, ml.

For example, if 10 ml of HCI and 50 ml of filtrate are used:

$$DF + (100+10) / 50 = 2.2$$

4.2.1.1 Calculate the value of X/M as follows:

$$X/M = [A - (DF)(B)(S)] / M$$

Where:

$X/M$ = iodine absorsed per gram of carbon, mg/g,

$S$ = sodium thiosulfate, $N$, and

$M$ = carbon used, g.

4.2.2 Calculate the value of C as follows:

$$C = (N_1 S) / F$$

Where:

$C$ = residual filtrate, $N$,

$N_1$ = sodium thiosulfate, ml, and

$F$ = filrate, ml.

4.3 Using logarithmic paper, plot $X/M$ (as the ordinate) versus $C$ (as the abscissa) for each

of the three carbon dosages. Calculate the least squares fit for the three points and plot. The iodine number is the $X/M$ value at a residual iodine concentration ($C$) of 0.02 $N$. The regression coefficient for the least squares fit should be grater than 0.995.

4.4 Carbon dosage may be estimated as follows:

$$M = [A - (DF)(C)(126.93)(50)] / E$$

Where:

$M$ = carbon, g,
$A$ = ($N_2$) (12693.0),
$DF$ = dilution factor (see 4.2.1)
$C$ = residual iodine, and
$E$ = estimated iodine number of the carbon.

Three carbon dosage are calculated using three values of $C$ (usually 0.01,0.02 , and 0.03)

4.4.1 Calculate the value of C as follows:

$$C = (N_1 S) / F$$

Where:

$C$ = residual filtrate, $N$,
$N_1$ = sodium thiosulfate, ml and,
$F$ = filtrate, ml.

**Table B.5.1** Find M for calculation iodine number by using ASTM D4607-86.

## Appendix B.6

## Standard testing method of methylene blue number of activated (JIS K 1470-1991)

### 1. Preparation of solutions

1.1 *Potassium dihydrogen phosphate solution* – Dry of potassium dihydrogen phosphate ($KH_2PO_4$) in the oven at 110-120$^oC$ for 2 hr and cool to room temperature in a desicator. Dissovle 9.07 g of $KH_2PO_4$ dry with distilled water. Quantitatively transfer to a 1-L volumetric flask and fill to the mark with distilled water.

1.2 *Disodium hydrogen phosphate solution*- Dry of disodium hydrogen phosphate ($NA_2HPO_4$) in the oven at 110-120$^oC$ for 2 hr and cool to room temperature in a desicator. Dissolve 23.88 g of dry $NA_2HPO_4$ with distilled water. Quantitatively transfer to a 1-L volumetric flask and fill to the mark with distilled water. Quantitatively transfer to a 1-L volumetric flask and fill to the mark with distilled water.

1.3 *Buffer solution* – Mix 400 ml of 1.1 and 600 ml of 1.2. The pH of this solution is approximately 7.

1.4 *Standard methylene blue solution* – Dry of methylene blue in the oven at 105 $\pm$ 5 $^oC$. For 4 hr and cool to room temperature in a desicator. Dissolve 1.2 g of dry methylene blue with buffer solution. Quantitatively transfer to a 1-L volumetric flask and fill to the mark with buffer solution.

### 2. Procedure

2.1 Dry of activated carbon at 150 $\pm$ 5$^oC$ (3 hr is usually sufficient).

2.2 Weigh the specified amount (note 1) of activated carbon to the nearest 1 mg, transfer to an Erlenmeyer flask with ground-in stopper 100 ml, and add methylene blue solution 25 ml.

2.3 Shake at room temperature using a shaker for 30 min.

2.4 Take methylene blue solution 10 ml into one mark volumetric flask 50 ml, and add buffer solution up to the marked line. Further, take its 5 ml into other one mark volumetric flask 500 ml, and add buffer solution up to the marked line. In this case the concentration of methylene blue solution is 0.24 mg/l.

2.5 Measure the absorbance at wavelength of 665 nm with contrasting to buffer solution.

> *Note 1* Weight the sample by dividing into three stage degree so that the mass interval dose not exceed 0.02 g corresponding to anticipated methylene blue adsorption performance to the sample 0.1 to 0.3 g.

**3.Preparation of calibration curve**

3.1 Take methylene blue solution 10 ml into one mark volumetric flask 50 ml, and add
buffer solution up to the marked line. From this solution, take 5, 10, 25 and 50 ml into respective one mark volumetric flask 500 ml, and add buffer solution up to the marked line.

3.2 For these solution, prepare the relation curve between the concentration of methylene
blue solution (0.24 to 2.4 mg/I) and the absorbance at 665 nm in wavelength and obtain from this the remaining concentration of methylene blue.

**4.Calculation** Using the remaining concentration of methylene blue obtain in **3**, the methylene blue amount (mg/g) shall be calculated using the following formula.

$$Q = \frac{(1200-C)\ (25/1000)}{S}$$

Where : Q = Methylene blue adsorption amount (mg/g),
C = remaining concentration of methylene blue (mg/I),
S = mass of activated carbon (g) and

.

**5.Preparation of adsorption isotherm in methylene blue solution.** Plot the remaining
concentration of methylene blue solution obtained in **3** on the abscissa and the adsorption amount of methylene blue obtained using the calculation method of **4** on the ordinate of both logarithm graph and prepare the adsorption isotherm. From the adsorption isotherm obtain the methylene blue amount (mg/g) of sample when the remaining concentration of methylene blue as the methylene blue adsorption performance is 0.24 mg/l.

## Appendix B.7

## Standard test method for carbon black-surface area by multipoint B.E.T. nitrogen adsorption (ASTM D 4820-96a)

A carbon sample is placed in a known volume cell and evaluated to less than 5 milliliter of vacuum. Using the ideal gas equation, the volume of nitrogen required to give a predetermined relative pressure is calculated and dosed into the sample cell. Any additional nitrogen required to attain this relative pressure is due to adsorption by the carbon. Based on the volume of nitrogen adsorbed at various relative pressures, the surface area is calculated.

### Theory of Test Method

The determination of surface area from the B.E.T. theory is a straight forward application of the B.E.T. equation :

$$\frac{1}{V\,[(Po/P)-1]} = \frac{1}{V_M C} + \frac{C-1}{V_M C} \times \frac{P}{Po}$$

Where :

V = volume of nitrogen adsorbed, cm3

P = pressure, kPa,

Po = saturation vapor pressure of nitrogem, kPa,

$V_M$ = volume of nitrogen that cover one monomolecular layer, cm$^3$, and

C = B.E.T. constant.

A plot of 1 / V [(Po/P) – 1] versus P / Po will usually yied a straight line in the range 0.05 to 0.35 Solving the B.E.T. equation for $V_M$ gives:

$$V_M = \frac{1}{M + B}$$

Where:

M = slop of straight line, and

B = y-intercept.

### Sample Preparation

1. Place a clean sample tube on the degassing station and heat at 150 $^{o}$C for 0.5 hr at a Pressure below 2.7 pa (20 umHg). The insection of a glass rod into the sample

tube stem will reduce the void volume of the stem, thus improving testing precision.

2. Cool the sample tube to room temperature, then backfill, preferably with helium to atmospheric pressure. Place a stopper on the sample tube and weight it to nearest 0.0001 g and record as mass *A*.
3. For samples of unknown surface area, place approximately 0.1 g of carbon in the sample tube clean the sample tube stem with a pipe cleaner.
4. Place the sample tube containing the carbon on the degassing station and open the vacuum valve
5. Place the heating mantle on the sample cell and heat at $150^{o}$ C for 1 hr or longer to obtain and hold a pressure less than 2.7 Pa (20 umHg).
6. Remove the heating mantle and allow the sample sell to cool to room temperature. Backfill the sample tube with helium to atmospheric pressure, remove from the degassing station, and close it with a stopper.

**Sample analysis**

1. Place the sample tube containing the carbon on the nitrogen surface area analyzer.
2. Initial the experiment. The following experiment steps, necessary to attain accurate results, can be automatically determined by most automated nitrogen surface area analyzers.

2.1 *Leak Teat* – The vacuum volumetric relies on pressure measurements to determine the surface area of carbon. Any leaks in the system will result in erroneous surface area measurements. A minimum of a 2 min leak teat of this time interval will result in the absorption of the experiment.

2.2 *Transducer Linearization* – If separate sample and transducer manifolds are utilized by the testing equipment, it is necessary to zero and linearize the transducers prior to each experiment.

2.3 *Sample Cell Volume* – In determining the void volume of the sample cell, both warm

zone (section submersed in liquid nitrogen) must be measured prior to each analysis. Non-ideality gas corrections are applied to the volume of gas in the cold zone

2.4 *Saturated Vapor Pressure* (Po) – The saturated vapor pressure of nitrogen is affected by purity of the liquid nitrogen and ambient pressure. Dissolved impurities In the liquid $N_2$ will usually cause the bath temperature to in crease sufficiently to cause a 1.4 to 2.7 kPa (10 to 20 mmHg) increase in theoretical vapor pressure. Often, Po is assumed to be 103 kPa (775 mmHg); however, for maximum accuracy the actual Po should bi measured.

3. Once the above conditions are measured, volumes of pure nitrogen are calculates, measured, and dosed into the sample cell. This process is repeated until equilibrium conditions are satisfied at the desired relative pressure. The summation of the dose volumes required to reach a particular relative pressure constitute the adsorption volume pressures of 0.05 to 0.30. A minimum of 5 relative pressures are recommended
4. Backfill the sample tube at ambient temperature with helium to atmospheric pressure. Remove the sample tube from the instrument, stopper it, and weigh it to the nearest 0.0001 g and record as mass *B*.
5. Nitrogen adsorbed by the carbon at the various relative pressure is used to prepare the

   B.E.T. plot. The data points that give the best straight line are used to calculate the stop and y-intercept. The slope and y-intercept are used to calculate the surface area. For examples of how to select the proper relative pressure range.
6. A B.E.T. plot that yields a negative y-intercept could be indicative of the presence of microprobes (< 3 nm diameter), but other factors can produce a negative y-intercept. The surface area is calculated from the pressure range that yields the highest correlation coefficient and positive y-intercept.

## Calculation

1. Calculate the sample mass as follows :

$$S = B - A$$

Where :

S = sample mass, g,

A = mass of sample tube, stem, and stopper, and

B = mass of sample tube, stem, stopper, and sample after analysis.

2. Calculate the nitrogen surface area (NSA) to the nearest 0.1 x $10^3$ $m^2$/kg (0.1 $m^2$/g)

As follows :

$$NSA = \frac{V_M N A_{CS}}{22\,400 \times S}$$

where :

N = Avagadro’s number, 6.023 x $10^{23}$

$A_{CS}$ = Cross-section area of nitrogen molecule, 16.2 x $10^{-20}$ $m^2$/moleculr, and

22 400 = number of $cm^3$ occupied by one mole of gas at STP.

# VITA

Mrs. Chanokporn Saeung was born on Feb 04, 1972 in Petchaboon, Thailand. She graduated with a Bachelor's degree of science, majoring in chemistry, Rajabhat institute Suan Dusit, in 1994. She has continued her study in Master's degree, majoring in Petrochemistry and Polymer Science, Faculty of Science, Chulalongkorn University, Bangkok, Thailand since 2007 and finished her study in 2009.

## Presentation Experience

Oral presentation from The 2nd Science Research Conference organized by Naresuan University in the topic of "Preparation of activated carbon from petrochemical waste sludge by chemical and physical activations".