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ของถ่านกัมมันต์ชนิดเม็ดที่เตรียมจากเปลือกไม้ยูคาลิปตัส



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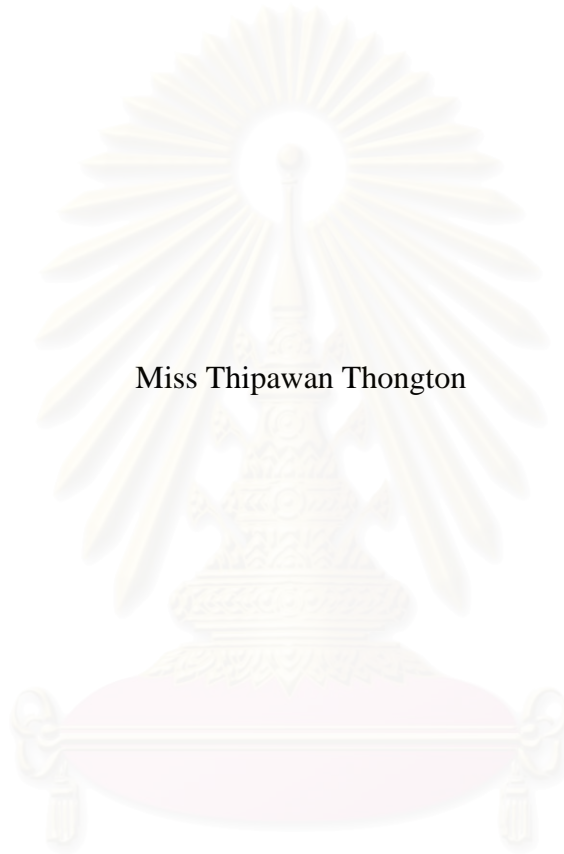
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EFFECTS OF BINDERS AND REINFORCERS ON PHYSICAL AND CHEMICAL
PROPERTIES OF GRANULAR ACTIVATED CARBON
FROM EUCALYPTUS BARK



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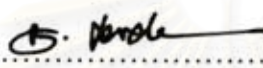
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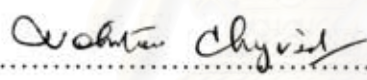
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ทิพวรรณ ทองตัน : ผลของสารตัวเชื่อมและสารเพิ่มความแข็งต่อคุณสมบัติทางกายภาพและทางเคมีของ ถ่านกัมมันต์ชนิดเม็ดที่เตรียมจากเปลือกไม้ยูคาลิปตัส. (EFFECTS OF BINDERS AND REINFORCERS ON PHYSICAL AND CHEMICAL PROPERTIES OF GRANULAR ACTIVATED CARBON FROM EUCALYPTUS BARK) อ. ที่ปริกษาวิทยานิพนธ์หลัก : รศ. ดร.ประเสริฐ ภาวสันต์, 119 หน้า.

งานวิจัยนี้เป็นการศึกษาถึงกระบวนการผลิตเม็ดถ่านกัมมันต์จากเปลือกไม้ยูคาลิปตัส โดยใช้สารเคมีเพื่อทำหน้าที่เป็นตัวเชื่อมและเพิ่มความแข็งแรงให้กับเม็ดถ่านกัมมันต์ พร้อมทั้งตรวจสอบคุณลักษณะของเม็ดถ่านกัมมันต์ที่ผลิตขึ้นได้ ในกระบวนการผลิตขั้นแรกจะทำการเปลี่ยนเปลือกไม้ให้อยู่ในรูปของผงถ่านกัมมันต์ โดยวิธีกระตุ้นด้วยกรดฟอสฟอริก หลังจากนั้นจึงนำผงถ่านกัมมันต์ที่ได้มาผสมกับสารผสมระหว่างสารตัวเชื่อมและสารเพิ่มความแข็ง แล้วจึงขึ้นรูปให้เป็นเม็ด ซึ่งสารเคมีที่นำมาใช้เป็นตัวเชื่อมและเพิ่มความแข็งแรงให้กับเม็ดถ่านกัมมันต์ประกอบด้วย 4 คู่ คือ คาร์บอกซีเมทิล เซลลูโลส/เคาลิน, คาร์บอกซีเมทิล เซลลูโลส/แคลเซียมคาร์บอเนต, เมทิล เซลลูโลส/เคาลิน และ เมทิล เซลลูโลส/แคลเซียมคาร์บอเนต ผลการทดลองพบว่าเม็ดถ่านกัมมันต์ที่ใส่สารคาร์บอกซีเมทิล เซลลูโลส/เคาลิน เป็นตัวเชื่อมและเพิ่มความแข็งมีคุณสมบัติที่ดีที่สุด สัดส่วนของน้ำหนักรวมที่เหมาะสมระหว่างสารตัวเชื่อมและสารเพิ่มความแข็งมีค่าเท่ากับ 0.5 ต่อ 0.5 และสัดส่วนของน้ำหนักรวมที่เหมาะสมระหว่างสารผสมและผงถ่านกัมมันต์มีค่าเท่ากับ 20 ต่อ 80 โดยเม็ดถ่านกัมมันต์ที่ได้มีค่าพื้นที่ผิวแบบบีอีทีเท่ากับ 1,085 ตารางเมตรต่อกรัม ค่าความหนาแน่นรวมเท่ากับ 0.214 กรัมต่อลูกบาศก์เซนติเมตร ค่าความแข็งเท่ากับ 75 เปอร์เซ็นต์ ปริมาณแฉะมีค่าเท่ากับ 12.7 เปอร์เซ็นต์ และค่าพีเอชเท่ากับ 6.67 ค่าไอโอดีนและเมทิลลินบลู้นัมเบอร์มีค่าเท่ากับ 686 และ 310 มิลลิกรัมต่อกรัม ตามลำดับ จากผลการทดลองที่ได้พบว่าเม็ดถ่านกัมมันต์มีประสิทธิภาพในการดูดซับลดลงเมื่อเพิ่มสัดส่วนน้ำหนักรวมของสารตัวเชื่อมและสารเพิ่มความแข็งซึ่งสาเหตุเกิดจากอนุภาคของสารตัวเชื่อมและสารเพิ่มความแข็งเข้าไปอุดภายในรูพรุนของเม็ดถ่านกัมมันต์ จากการเปรียบเทียบพบว่าเม็ดถ่านกัมมันต์ที่ผลิตได้ มีคุณสมบัติต่ำกว่าถ่านเม็ดเกรดการค้าที่นำมาใช้อ้างอิงในงานวิจัยนี้ แต่มีคุณสมบัติผ่านเกณฑ์มาตรฐานอุตสาหกรรม (มอก.900-2004) ของประเทศไทย

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

ภาควิชา.....วิศวกรรมเคมี.....ลายมือชื่อนิสิต.....ทิพวรรณ ทองตัน.....
สาขาวิชา.....วิศวกรรมเคมี.....ลายมือชื่อ อ. ที่ปริกษาวิทยานิพนธ์หลัก.....
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The present study reports the preparation procedure and characterization of the granular activated carbon (GAC) derived from eucalyptus bark using different types of binders and reinforcers. Firstly, eucalyptus bark was converted to powdered activated carbon (PAC) using the chemical method with H_3PO_4 as carbonizing/activating agent. The GAC was then prepared by mixing PAC with a mixture of binder to reinforcer. Four choices of binders to reinforcers were investigated in this work, i.e. CMC:kaolin, CMC:calcium carbonate, MC:kaolin and MC:calcium carbonate. The best choice among these four selected mixture was CMC:kaolin and the results illustrated that the optimal weight proportion of binder to reinforcer was 0.5:0.5, and the weight proportion of the mixture (binder:reinforcer) to PAC of 20:80. With this formula, the properties of the resulting GAC were: BET surface area $1,085 \text{ m}^2 \text{ g}^{-1}$, bulk density 0.214 g cm^{-3} , hardness number 75%, ash content 12.7% and pH 6.67. This condition gave the iodine and methylene blue numbers of 686 and 310 mg g^{-1} , respectively. It was observed that the adsorption capacity of the GAC product decreased with an increasing weight proportion of both binder and reinforcer to PAC. This was because the porous structure of the carbon was being filled by the presence of the binder and reinforcer. Although the final properties of the products were slightly lower than those of commercial GAC, they complied well with the national activated carbon standard (TIS.900-2004).

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Field of Study :.....Chemical Engineering.....Advisor's Signature..... *Prasert Pavasant*.....
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CONTENTS

	Page
ABSTRACT IN THAI.....	iv
ABSTRACT IN ENGLISH.....	v
ACKNOWLEDGEMENTS	vi
CONTENTS.....	vii
LIST OF TABLES.....	x
LIST OF FIGURES.....	xii
CHAPTER I INTRODUCTION.....	1
1.1 Motivations.....	1
1.1.1 Uses of granular activated carbon.....	1
1.1.2 Management of waste from pulp and paper industry.....	1
1.2 Objectives.....	2
1.3 Scopes of the research.....	2
CHAPTER II THEORY AND LITERATURE REVIEWS.....	4
2.1 General knowledge of Eucalyptus wood.....	4
2.2 Activated carbon.....	4
2.3 Types of activated carbon.....	6
2.3.1 Powdered activated carbon.....	6
2.3.2 Granular activated carbon.....	6
2.3.3 Pellets or extruded activated carbon.....	6
2.4 Raw Materials.....	7
2.5 Production of activated carbon.....	16
2.5.1 Dehydration.....	16
2.5.2 Carbonization.....	16
2.5.3 Activation.....	17
2.5.3.1 Physical or gas activation.....	17
2.5.3.2 Chemical activation.....	17
2.6 Production of granular activated carbon.....	20
2.7 Properties of granular activated carbon.....	26

	Page
2.8 Classification of Isotherms	29
CHAPTER III RESEARCH METHODOLOGY.....	30
3.1 Materials.....	30
3.1.1 Equipments.....	30
3.1.2 Glassware.....	31
3.1.3 Chemical reagents.....	31
3.2 Methods.....	32
3.2.1 Precursor raw material.....	32
3.2.2 Preparation of powdered activated carbon.....	32
3.2.3 Preparation of granular activated carbon.....	32
3.2.4 Determination the optimal proportion of mixture of binders and reinforcers.....	33
3.2.5 Determination the optimal proportion of powdered activated carbon and mixture of binder/reinforcer.....	33
3.2.6 Vary type of binders and reinforcers.....	34
3.2.7 Analysis of granular activated carbon.....	34
CHAPTER IV RESULTS AND DISCUSSION.....	36
4.1 Characteristics of powdered activated carbon.....	36
4.2 Characteristics of binders and reinforcers.....	37
4.2.1 Binders (Carboxymethyl cellulose and Methyl cellulose).....	37
4.2.2 Reinforcers (Kaolin and Calcium carbonate).....	38
4.3 Selection of the suitable proportion of binder and reinforcer.....	39
4.4 Characteristics of granular activated carbon (GAC) products.....	41
4.4.1 with Carboxymethyl cellulose (CMC) as binder and Kaolin as reinforcer.....	41
4.4.2 with Carboxymethyl cellulose (CMC) as binder and Calcium carbonate as reinforcer.....	43
4.4.3 with Methyl cellulose (MC) as binder and Kaolin as reinforcer.....	45
4.4.4 with Methyl cellulose (MC) as binder and Calcium carbonate as reinforcer.....	47

	Page
4.5 Comparison of the properties of various GAC products.....	49
CHAPTER V CONCLUSIONS AND RECOMMENDATIONS.....	82
5.1 Conclusions.....	82
5.2 Contributions.....	82
5.3 Recommendations / Future works.....	83
REFERENCES.....	84
APPENDICES.....	93
BIOGRAPHY.....	119

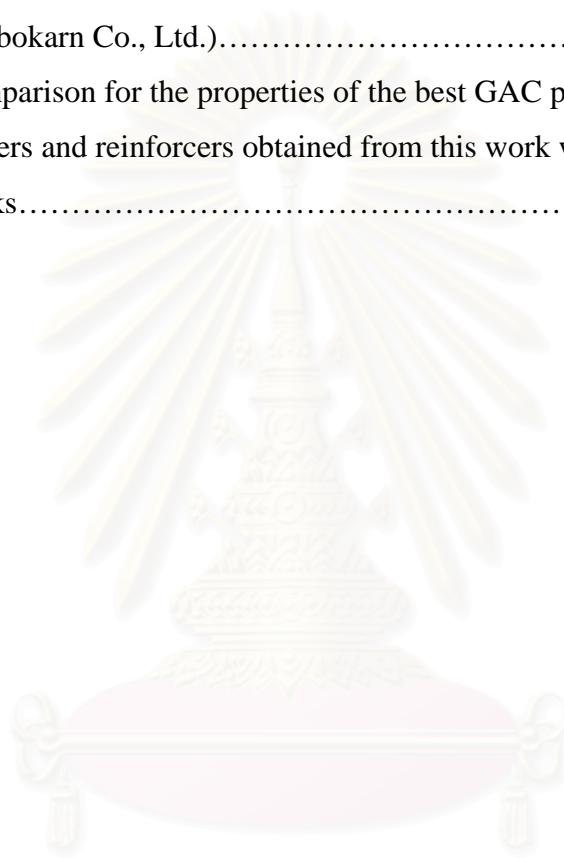


สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

LIST OF TABLES

	Page
Table 2.1 Applications of activated carbon.....	5
Table 2.2 Activated carbon consumption in 1990.....	6
Table 2.3 Carbon content (%) of raw materials.....	8
Table 2.4 Dependency of characteristics of activated carbon on the raw material sources.....	8
Table 2.5 Summary of raw materials and properties of activated carbon in recent works.....	10
Table 2.6 Summary of the properties of activated carbon obtained from physical and chemical activations.....	19
Table 2.7 Recent works on the production of granular activated carbon.....	21
Table 2.8 Organic compounds amenable to adsorption by granular activated carbon.....	25
Table 2.9 Standard value for the properties of granular activated carbon.....	28
Table 4.1 Proximate and ultimate properties of powdered activated carbon.....	50
Table 4.2 Properties of powdered activated carbon.....	50
Table 4.3 FT-IR spectra result from powdered activated carbon.....	51
Table 4.4 Properties of binders (Carboxymethyl cellulose and Methyl cellulose) and reinforcers (Kaolin and Calcium carbonate).....	52
Table 4.5 FT-IR spectra results from binders (Carboxymethyl cellulose and Methyl cellulose) and reinforcers (Kaolin and Calcium carbonate).....	53
Table 4.6 Properties of the GAC products obtained from the fabrication at various proportion of binder (CMC) and reinforcer (Kaolin).....	55
Table 4.7 Properties of the GAC products obtained from the fabrication at various proportion of binder (CMC) and reinforcer (Calcium carbonate).....	56
Table 4.8 Properties of the GAC products obtained from the fabrication at various proportion of binder (MC) and reinforcer (Kaolin).....	57
Table 4.9 Properties of the GAC products obtained from the fabrication at various proportion of binder (MC) and reinforcer (Calcium carbonate).....	58
Table 4.10 Properties of the best GAC products at various binders and reinforcers.	59

	Page
Table 4.11 FT-IR spectra results from the best GAC products at various binders and reinforcers.....	60
Table 4.12 Comparison for the properties of the best GAC products at various binders and reinforcers obtained from this work with Thai Industrial Standard (TIS.900-2004) and commercial grade GAC (Carbokarn Co., Ltd.).....	62
Table 4.13 Comparison for the properties of the best GAC products at various binders and reinforcers obtained from this work with the other recent works.....	63



สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

LIST OF FIGURES

	Page
Figure 2.1 Flow diagram for the production granular activated carbon.....	24
Figure 2.2 Isotherm patterns for the activated carbon.....	29
Figure 4.1 SEM photomicrograph of powdered activated carbon.....	65
Figure 4.2 XRD pattern of powdered activated carbon.....	66
Figure 4.3 FT-IR transmission spectra of powdered activated carbon.....	67
Figure 4.4 N ₂ adsorption and desorption isotherms at -196°C on powdered activated carbon.....	68
Figure 4.5 SEM photomicrographs for binders and reinforcers.....	70
Figure 4.6 XRD patterns for binders and reinforcers.....	72
Figure 4.7 FT-IR transmission spectra for binders and reinforcers.....	74
Figure 4.8 SEM photomicrographs for the GAC products with various binders and reinforcers.....	76
Figure 4.9 XRD patterns for the GAC products with various binders and reinforcers.....	78
Figure 4.10 FT-IR transmission spectra for the GAC products with various binders and reinforcers.....	80
Figure 4.11 N ₂ adsorption isotherms at -196°C on the GAC products with various binders and reinforcers.....	81

CHAPTER I

INTRODUCTION

1.1 Motivations

1.1.1 Uses of granular activated carbon

Granular activated carbon (GAC) has been generally considered more versatile than the powdered activated carbon (PAC) and commanded a large percentage of the carbon market (Activated Carbon Markets, 1994). Adsorption with GAC has been proven successfully for the advanced treatment of municipal and industrial wastewaters and found themselves several long term applications. Although the use of GAC generally involves high investment cost, they were in several cases considered economical since the carbon could be easily reactivated/regenerated. Advantages in using GAC over PAC include: (i) they suitable for system do not require contaminant of the least amount of powdered; vapor and gas phase adsorption; (ii) easily incorporated into an existing waste water treatment; (iii) greater operational flexibility and control; (iv) reasonably good durability due to the added binder in granule form for hardness which refrains them from being broken/decomposed; (v) readily regenerated; reducing solid waste problems caused by the disposal of spent carbon. However, as GAC need binders in order to be in granular form, their adsorption capacity is often not as good as that of PAC as some of the adsorption surface has been taken place by the inert binder agent.

1.1.2 Management of waste from pulp and paper industry

Eucalyptus bark has been generated in large quantity from the process of pulp and paper industry. This bark is often utilized as fuel and/or adapted to other type of energy within the plant or exported as fuel for other industries. However, the remnant of this bark still remains and has to be disposed of. As the bark still consists of high carbon content, they can be converted to several kinds of products such as activated carbon depending on the condition of the conversion processes.

Activated carbon has been produced mainly from high carbon content materials such as wood, sawdust, nutshells, coconut shells, coal, other agricultural by-product, and other materials with high carbon content. Raw materials for activated carbon are chosen depending on their purity, price, potential extent of activation, and stability of supply (Kim et al., 2001). Eucalyptus wood has been reported in previous

studies to be a good alternative as feedstock for the production of activated carbon (Tancredi et al., 1996). The type of raw material is important in determining its suitability for granular activated carbon (Ahmedna et al., 2000) and these properties are also influenced by production techniques (Bansode, 1998).

In our previous work, it has been shown that there was potential in turning the eucalyptus bark into activated carbon in powdered form (Patnukao and Pavasant, 2006). The PAC product had reasonably attractive properties compared with commercial activated carbons. In this work, the production of GAC will be investigated. Granular form of powdered activated carbon will be obtained using different types of binders and reinforcers. Good binders and reinforcers should be substances that do not liquefy when carbonized and should swell sufficiently to give a porous structure (Bansode, 1998). Typically carboxymethyl cellulose (CMC) was used as binder as it can act as a viscosity modifier or thickener. Kaolin has good plasticity and strength properties such as hardness (Tancredi et al., 2004). Examples of some other binders and reinforcers are given in Chapter 2.

1.2 Objectives

In the present study, the objectives are:

- to produce granular activated carbon using suitable binders and reinforcers when compared with several types of binders and reinforcers
- to compare the properties of granular activated carbon obtained from this work with the commercially available GAC

1.3 Scopes of the research

1.3.1 The production of the powdered activated carbon was from eucalyptus bark.

1.3.2 Choices of binders and reinforcers were:

- carboxymethyl cellulose (CMC) and kaolin
- carboxymethyl cellulose (CMC) and calcium carbonate (CaCO_3)
- methyl cellulose (MC) and kaolin
- methyl cellulose (MC) and calcium carbonate (CaCO_3)

1.3.3 Experimental conditions include the following parameters:

- proportion of binder to reinforcer

- proportion of mixture (binder : reinforcer) to powdered activated carbon

1.3.4 Properties of granular activated carbon are indicated by:

- iodine number
- methylene blue number
- hardness number
- specific surface area (BET method)
- apparent (bulk) density
- ash content
- pH
- yield
- surface morphology (SEM)
- fourier transform infrared (FT-IR)
- x-ray diffraction (XRD)



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CHAPTER II

THEORY AND LITERATURE REVIEWS

2.1 General knowledge of Eucalyptus wood

Eucalyptus trees are widely grown in the Southeast of Asia. Eucalyptus can be found in almost every part of the Thailand, as it can adapt to all types of climatic conditions. The eucalyptus tree is a large, fast-growing, some can grow to 375-480 feet (125-160 meters). Eucalyptus belongs to the myrtle (Myrtaceae) family. There are more than 300 species of eucalyptus, and Eucalyptus globulus is the most well known species. One species (E. amygdalin) is the tallest tree known in the world. The tree grows best in areas with an average temperature of 60°F (15°C). The whole eucalyptus tree could be used from its roots to its crown, from its bark to its foliage. The eucalyptus has served humankind in many ways. It not only provided fuel, windbreaks, medicine, shade and beauty, it also was lumber for implements, nectar for bees, pulp for paper, charcoal and chemical for boiler cleaning. Its oils have been extracted and used in medicine and in scented products.

The eucalyptus bark consists of two part, smooth-bark and rough-bark. The smooth-bark is the outer part leaving a smooth surface. This part remains on the tree even it is dead. The rough-bark is the inner layer which is the focus of this work for the production powder and granular form respectively.

2.2 Activated carbon

Activated carbon is a material known to human from ancient times. Recent attempts have been devoted towards the selection of raw materials and production conditions. Activated carbon is a porous carbonaceous material where a good activated carbon should have the following characteristics:

- high porosity (microporous structure)
- large internal surface area
- high total surface area
- large pore volume

Activated carbon is widely used as an adsorbent for several purposes, such as air purification, waste water treatment, catalysis and chemical recovery (Pendyal et al., 1998). The various applications of the use of activated carbon are summarized in

Table 2.1. The two main parameters of activated carbon are related to the adsorption performance, including the surface area and pore volume. The pore volume indicates the size of molecules whilst the surface area reflects the amount of materials which activated carbon can absorb. Usually, the surface areas of activated carbon are ranging from 500-1400 m²/g. The pore size is often classified into three groups: macropores (diameter > 20 nm), mesopores (diameter 2-20 nm) and micropores (diameter < 2 nm). Micropore is the most important for adsorption and is used to indicate the quality of activated carbon.

Table 2.1 Applications of activated carbon

Application utilities	Usage Percentage (%)
<i>Liquid phase adsorption</i>	
- potable water	19.2
- waste water	16.9
- sweetener decolourisation	16.9
- chemical process	6.8
- food, beverages, oils	5.1
- pharmaceuticals	4.6
- mining	4.4
- groundwater	3.4
- household uses	2.4
- other	1.8
<i>Gas phase adsorption</i>	
- solvent recovery	4.8
- petrol recovery	4.4
- industrial of gas control	3.4
- catalysis	2.9
- other	3.0

Due to its versatile applications, the global consumption of activated carbon increased every year (Clarke et al., 1989; Bansal and Goyal, 2005). Table 2.2 illustrates the distribution of the global consumption of activated carbon. New technologies for supporting the manufacture of activated carbon have been proposed

enormously in literature. In addition, the regeneration of spent activated carbon has also been given active attention as an alternative for the reuse of the activated carbon.

Table 2.2 Activated carbon consumption in 1990

Country	Consumption (ton/year)
United States of America	175,000
Western Europe	155,000
Japan	145,000
China	85,000
Asia	65,000
Other	75,000
Total	700,000

2.3 Types of activated carbon

There are three main forms of activated carbon.

2.3.1 Powdered activated carbon

Powdered forms are the type of activated carbon where small pores and large internal surface area are the main features (Usmani et al., 1993). After activation, carbon is pulverized to a suitable size normally in the range less than 0.18 mm (US Mesh 80). These are mainly used in liquid phase applications and for flue gas treatments.

2.3.2 Granular activated carbon

Granular activated carbon is generally produced by grinding the raw material, adding suitable binders for hardness, re-compacting, and crushing to the required mesh size and generally associated with smaller pore diameter and larger internal surface area (Usmani et al., 1993). This forms irregular shaped particles with size ranging from 0.2-5 mm and they are considered more versatile and command a larger percentage of the carbon market (Activated Carbon Markets, 1994). This type is used in both liquid and gas phase applications.

2.3.3 Pellets or extruded activated carbon

The production is the same as that of granular form, they are generally produced by grinding the raw material, adding a suitable binder for hardness, re-

compacting, and crushing to the required mesh size (Bourke and Mazzoni, 1989). The extrude is generally cylindrical shaped with diameters from 0.8-5 mm. These are mainly used for gas phase applications because of their low pressure drop, high mechanical strength and low dust content.

2.4 Raw Materials

Activated carbon can be prepared from various carbonaceous materials such as wood, coal, petroleum coke, other wood products including agricultural by-products. Recently, activated carbon was reported to also be obtained from municipal and industrial wastes such as fly ash (Li et al., 2006). Agricultural by-products can also make a good precursor for the production of granular activated carbons and these are generally classified in two groups. Group 1 materials consist of soft compressible waste products of low density, such as sugarcane bagasse, rice straw, soybean hulls, peanut shells, and rice hulls. Materials in Group 1 must be mixed with suitable binder and compressed into briquettes or pellets to increase the density of the final product (Johns et al., 1998). In contrast, Group 2 materials such as nut shells from pecan and walnut, are hard, dense and not easily compressed. The materials from this group can be made granular activated carbon precursors without the use of binder or briquette formation (Ahmedna et al., 2000).

The type of raw materials has a very large influence on the characteristics and performance of activated carbon. Almost any organic matter with a large percentage of carbon could theoretically be activated to enhance its sorption characteristics. However, the best candidates for activated carbon contain a minimum amount of organic material which will lead to a long storage life, and they should be hard enough to maintain their properties under usage conditions. The manufacture should be low cost, and obviously is capable of producing a high quality activated product when processed.

The fixed carbon contents of various raw materials used for the production of activated carbon are shown in Table 2.3.

Table 2.3 Carbon content (%) of raw materials

Raw materials	Carbon content (%)
Soft wood	35
Hard wood	40
Coconut shell	35
Grain and agro products	40
Lignite	60
Bituminous coal	75
Anthracite	90

The raw material from which a given activated carbon is produced often has a large effect on its porosity distribution and surface area. As a result, activated carbons produced from different raw materials may have much different adsorbent qualities. **Table 2.4** illustrates some of the differences between the qualities of the activated carbon obtained from different raw materials.

Table 2.4 Dependency of characteristics of activated carbon on the raw material sources

Raw materials	Density (kg L ⁻¹)	Texture of ACs	Applications
Soft wood	0.40-0.50	Soft, large pore volume	Aqueous phase adsorption
Nut shells	1.40	Hard, large micropore volume	Vapor phase adsorption
Hard coal	1.50-1.80	Hard, large pore volume	Gas phase adsorption

Some of the properties of raw materials suitable for the production of activated carbon are summarized below:

- low organics volatile content
- high carbon content
- inexpensive and efficient use of resources
- high and stable properties

This summary was obtained from the results of unique surface properties of carbonaceous adsorbents such as surface area and high pore volume along with particular surface chemistry obtained from the various raw materials. Modifications to the raw materials have also been reported for the enhanced properties of activated carbon. The modification often aimed at a decrease in porosity, especially in the micropore volume. **Table 2.5** shows examples of raw materials used in the production activated carbon and their associated properties.



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Table 2.5 Summary of raw materials and properties of activated carbon in recent works

Raw materials	Method of Activation	Properties of activated carbons			References
		Iodine number (mg g ⁻¹)	Methylene blue number (mg g ⁻¹)	Surface area (m ² g ⁻¹)	
- Coal pitch	Chemical	-	-	400	Boudou et al., 1996
- Synthetic crude coke	Chemical	200	100	318	Dipanfilo and Egiebor, 1996
- Bituminous coal	Physical	-	-	1000	Sun et al., 1996
- Eucalyptus wood	Physical	-	-	1440	Tancredi et al., 1996
- Eucalyptus globulus	Physical	-	-	801	Arriagada et al., 1997
- Peach stones	Physical	-	-	1247	Arriagada et al., 1997
- Coir pith	Chemical	768	-	752	Namasivayam and Kadirvelu, 1997
- Coir pith	Physical	414	-	507	Namasivayam and Kadirvelu, 1997
- White oak	Chemical	-	-	-	Jagtoyen and Derbyshire, 1998

Table 2.5 (Continued)

Raw materials	Method of Activation	Properties of activated carbons			References
		Iodine number (mg g ⁻¹)	Methylene blue number (mg g ⁻¹)	Surface area (m ² g ⁻¹)	
- Yellow poplar	Chemical	-	-	-	Jagtoyen and Derbyshire, 1998
- Olive-seed waste residue	Physical	-	-	-	Khalid et al., 1998
- Autoshredder light fraction	Physical	-	-	211	Laszlo et al., 1998
- Auto tyre	Physical	-	-	142	Laszlo et al., 1998
- Sugarcane, bagasse	Physical	-	-	524	Pendyal et al., 1998
- Bituminous coal	Physical	-	-	988	Teng and Lin, 1998
- Cotton stalks	Chemical	-	-	1032	Girgis and Ishak, 1999
- Palm-oil shells	Physical	620	177	559	Vitidsant et al., 1999
- Sugarcane bagasse	Chemical	746	258	1132	Cartro et al., 2000
- Bituminous coal	Physical	-	-	1200	Solano et al., 2000
- Municipal solid waste	Physical	-	-	828	Tamon et al., 2000

Table 2.5 (Continued)

Raw materials	Method of Activation	Properties of activated carbons			References
		Iodine number (mg g ⁻¹)	Methylene blue number (mg g ⁻¹)	Surface area (m ² g ⁻¹)	
- Almond shells	Chemical	-	-	1152	Toles et al., 2000
- Sapwood	Physical	1409	-	415	Abe et al., 2001
- Sugar cane bagasse	Physical	1140	-	1579	Darmstadt et al., 2001
- Pyrolytic char	Physical	276	-	272	Helleur et al., 2001
- Coconut shells	Chemical	532	-	492	Khuysangaain, 2001
- Walnut shells	Chemical	1297	-	-	Kim et al., 2001
- Waste tyre rubber	Physical	-	-	1070	Miguel et al., 2001
- Corncobs	Chemical	2209	-	960	Nasser et al., 2001
- Coconut charcoal	Physical	1110	-	1237	Shawwa et al., 2001
- Petroleum coke	Physical	28	-	9	Shawwa et al., 2001
- Grain sorghum	Chemical	-	-	528	Diao et al., 2002
- Apricot stone	Physical	580	-	486	Galiatsatou et al., 2002
- Olive	Physical	550	-	474	Galiatsatou et al., 2002
- Peach	Physical	600	-	660	Galiatsatou et al., 2002
- Chickpea husk	Chemical	-	-	1778	Hayashi et al., 2002

Table 2.5 (Continued)

Raw materials	Method of Activation	Properties of activated carbons			References
		Iodine number (mg g ⁻¹)	Methylene blue number (mg g ⁻¹)	Surface area (m ² g ⁻¹)	
- Bagasse	Physical	-	-	607	Juang et al., 2002
- Corn cob	Physical	-	-	943	Juang et al., 2002
- Plum kernel	Physical	-	-	1162	Juang et al., 2002
- Coconut shell	Chemical	1055	164	1097	Sirichote et al., 2002
- Pericarp of rubber fruit	Chemical	1063	276	1508	Sirichote et al., 2002
- Almond shells	Chemical	638	-	736	Aygün et al., 2003
- Apricot stones	Chemical	754	-	783	Aygün et al., 2003
- Hazelnut shells	Chemical	965	-	793	Aygün et al., 2003
- Walnut shells	Chemical	905	-	774	Aygün et al., 2003
- Coffee bean husks	Chemical	-	-	1402	Baquero et al., 2003
- Rayon cloth	Physical	-	-	1185	Boudou et al., 2003
- Coal pitch	Physical	-	-	1130	Fuertes et al., 2003
- Phenolic Resin	Physical	-	-	1920	Fuertes et al., 2003
- Polymeric fibres	Physical	-	-	1100	Fuertes et al., 2003
- Pecan shells	Physical	-	-	-	Ng et al., 2003

Table 2.5 (Continued)

Raw materials	Method of Activation	Properties of activated carbons			References
		Iodine number (mg g ⁻¹)	Methylene blue number (mg g ⁻¹)	Surface area (m ² g ⁻¹)	
- Coal tar pitch	Chemical	-	-	3033	Agullo et al., 2004
- Coal tar pitch	Physical	-	-	2487	Agullo et al., 2004
- Rice husk	Chemical	-	-	376	Daifullah et al., 2004
- Sawdust	Chemical	1050	-	1100	Gan et al., 2004
- Polyaramid fibers	Chemical	-	-	1688	Garcia et al., 2004
- Peach Stones	Chemical	-	-	-	Kim, 2004
- Acrylic textile fibres	Physical	-	-	1397	Nabais et al., 2004
- Refuse derived fuel	Physical	-	-	520	Nakagawa et al., 2004
- Waste PET	Physical	-	-	1200	Nakagawa et al., 2004
- Waste tires	Physical	-	-	1000	Nakagawa et al., 2004
- Olive stones	Physical	-	157	677	Sheikh et al., 2004
- Biomass natural fibres	Chemical	-	-	900	Williams and Reed, 2004
- Oat hulls	Chemical	-	-	-	Chuang et al., 2005
- Palm shells	Chemical	-	-	1014	Guo et al., 2005

Table 2.5 (Continued)

Raw materials	Method of Activation	Properties of activated carbons			References
		Iodine number (mg g ⁻¹)	Methylene blue number (mg g ⁻¹)	Surface area (m ² g ⁻¹)	
- Palm shells	Physical	-	-	1062	Guo et al., 2005
- Teak sawdust	Physical	-	-	1150	Ismadji et al., 2005
- Sago waste	Chemical	-	-	725	Kadirvelu et al., 2005
- Rubber wood sawdust	Chemical	795	255	1674	Karthikeyan et al., 2005
- Apricot stone	Chemical	548	-	566	Kobya et al., 2005
- Rubberwood sawdust	Chemical	835	255	822	Kumar et al., 2005
- Rubberwood sawdus	Chemical	1052	375	954	Kumar et al., 2005
	followed by				
	Physical				
- Rubberwood sawdus	Physical	765	255	1092	Kumar et al., 2005
- Lignin	Chemical	-	-	-	Montane et al., 2005
- Coffee grounds	Chemical	440	-	640	Namane et al., 2005
- Rice husk	Chemical	-	92	-	Rahman et al., 2005

2.5 Production of activated carbon

The production process of activated carbon is mainly divided into three steps, dehydration, carbonization and activation.

2.5.1 Dehydration

Dehydration is a drying process for the removal of moisture from raw materials. Raw materials such as sawdust, peat, brown coal and coconut shells; usually, contains carbohydrate compounds in their structure and therefore require heating during the dehydration. Common dehydrate agents are sulphuric acid, phosphoric acid and aqueous solution of zinc chloride.

2.5.2 Carbonization

Carbonization or pyrolysis consists of slow heating of the raw materials at temperature usually below 800°C in the absence of air. During the pyrolysis, organics contained in raw material change into primary carbon and the volatile products are removed from the starting material. In addition, the carbonization can be controlled by an addition of dehydrating agents such as zinc chloride or phosphoric acid, for which they are recovered or recycled for reuse.

There are three steps of the carbonization process:

1. First step, the loss of water from raw material structures between temperature from 27-197° C.
2. Second step, the formation of pyrolysis products such as gas and tar oils in the structure under the temperature range from 197-497° C.
3. Finally, the formation of char structure lowering the density of the material, this occurs under the temperature range from 497-847° C.

The factors controlling the effectiveness in carbonization process are:

1. Temperature
2. Heating of the raw materials temperature
3. Intermediate of the catalyst
4. The nature of raw materials

Generally, dehydration and carbonization processes involve slow heating of the sources in anaerobic condition. The raw materials are carbonized to obtain the char or carbonaceous material, which is activated to yield the highly porous final products.

2.5.3 Activation

Activation consists of treating the pyrolyzed char with activating agents such as steam or carbon dioxide at elevated temperatures of 800-900°C, and this transforms the char into numerous pores which are systematically developed and enlarged, thus enabling the production of a well defined pore system in the activated carbons. During activation, temperature must be high enough to provide a reasonable rapid rate of activation, but temperatures above 1000 °C are to be avoided as it begins to impair adsorption. The stage of activation requires exposure to additional chemicals or other oxidizing agents such as a mixture of gases. The newly activated carbon can be classified according to density, hardness and other characteristics (AWWA, 1971). Activation which is the main step in the process of production activated carbon, is generally carried out in two ways, depending upon the starting material and whether a low or high density, powder or granular carbon. The main steps of activation include gas or physical activation and chemical activation.

2.5.3.1 Physical or gas activation

Gas activation is a physical process in which raw material passes through carbonization, which is a selective oxidation of the carbonaceous matter with air at low temperature, steam, carbon dioxide, or flue gas at high temperature. In the physical activation method, the three steps process was applied: (i) coal oxidation in air at 225°C, (ii) devolatilization of oxidized coal in nitrogen at 400-500°C, and (iii) char activation in 50% steam or 50% CO₂. Activation with steam or carbon dioxide is conducted at temperature from 800-850°C. Activation with air involves an exothermic reaction and measures must be taken to keep the temperature from rising above proper limits, usually not over 850 °C. Steam activation is generally used for coal-based, coconut shells and grain based activated carbon.

The most widely used type of gas activating process is the one utilizing steam as the activating gas under high temperature and long treatment conditions. The disadvantages of the gas activation process include low yield and lack of the homogeneity of the final product.

2.5.3.2 Chemical activation

Chemical activation is generally used for the production of activated carbon from sawdust, wood, peat where chemicals are used for activation. The chemical activation involves mixing inorganic chemical compounds with the carbonaceous raw

material at high temperature (400 °C). The activating chemicals are used with the carbon to form the pore structure and also to alter the carbon surface. Examples of activating agents are usually strong acids, bases or corrosives such as phosphoric acid, sulfuric acid, potassium hydroxide, zinc chloride, potassium sulfide and potassium thiocyanate (Mozammel et al., 2002). The most widely used agents are phosphoric acid and zinc chloride. Although phosphoric acid is known to be the most environmentally benign chemical for the activation process, most studies have used zinc chloride due to its effective activating capability. However, zinc chloride could be left-over as a dangerous trace in the end product. In any case, chemical activation depended upon the action of the selected inorganic chemical compounds.

The factors controlling the effectiveness of the pore structure of the activated carbon include:

1. The proportion of lignin to cellulose in raw materials
2. The proportion of activating agents to raw materials
3. The temperature that used in activation process
4. Heating in the activation process

The factors controlling the characteristics of pore structure in the activation process are:

1. carbon structure or char structure used in activation
2. amount of inorganic contaminant in carbon
3. types of oxidizing gas
4. reaction temperature
5. pressure of gas
6. time for reaction
7. particle size of char carbonaceous

As the activation temperature increased, the iodine value increased. However, a temperature higher than 400 °C resulted in a thermal degradation, and the activation longer than 1 h at 375 °C could result in the destruction of microporous structure of activated carbon. In general, carbonization and activation temperature are known to have influence on the micropore structure and usually the optimal must be determined simultaneously to yield activated carbon with increased specific surface area.

Table 2.6 Summary of the properties of activated carbon obtained from physical and chemical activations

	Chemical activation	Physical activation
Advantages	<ul style="list-style-type: none"> - high surface area (Diao et al., 2002) - high yields of carbon product (Castro et al., 2000; Diao et al., 2002; Sirichote et al., 2002) - good porous structure (Redriguez-Reinoso, 1997; Pendyal et al., 1999; Maciá-Agulló, 2004) - suitable pore size (Qiao et al., 2001) - high adsorption (Carvalho et al., 2006) - lower temperature of activation (Redriguez-Reinoso, 1997; Martin-Gullon, 2004; Maciá-Agulló, 2004) - easily recover chemicals (Philip, 1996) - possible to recycle chemical reagents (Jagtoyen and Derbyshire, 1998) 	<ul style="list-style-type: none"> - no contamination of chemical (Laine and Yunes, 1992)
Disadvantages	<ul style="list-style-type: none"> - contaminant with hazardous chemical i.e zinc chloride (Girgis et al., 2002; Daifullah, 2004) - impurities coming from the activating agent, which may affect the chemical properties of the activated carbon (Gómez-Serrano et al., 2005) 	<ul style="list-style-type: none"> - low yield (Kim et al., 2001) - carbonized at high temperature (El-Hendawy, 2001) - lack of homogeneity of the product (Kim et al., 2001) - used water steam or carbon dioxide (Hayashi et al., 2002)

2.6 Production of granular activated carbon

Powdered activated carbon usually possesses good adsorbing properties but they have operating constraints in actual applications due to its handling difficulties. In practice, granular activated carbon (GAC) is proposed as alternative. GAC is produced by grinding the raw material, adding a suitable binder for hardness, re-compacting and crushing to the correct mesh size (Usmani et al., 1993). The pattern as illustrated in Figure 2.1 is the basis for the production of granular activated carbon. However, there might be differences in details of the production methods such as the exact location of the addition of binder/reinforcer agents. Generally, the step of carbonization is followed by the addition of suitable binder/reinforcer, and re-compaction but a reverse step could also be possible as carbonization was also employed to destroy organic structure contained in binder/reinforcer agents (Li et al., 2006). Although the term granular activated carbon is used in general, they are not identical adsorbents. Depending on raw materials, method, degree of activation and other factors, the final activated carbon can be different in properties and performs differently in various applications. The type of raw materials and binders commonly used for the production of GAC are summarized in Table 2.7.

Table 2.7 Recent works on the production of granular activated carbon

Raw materials	Binder	Reinforcer	Properties of activated carbons			Characteristics of GAC	References
			Iodine number (mg g ⁻¹)	Methylene blue number (mg g ⁻¹)	Hardness number (%)		
- Coke	tar	-	-	-	-	- better adsorption - suitable pore	Taylor and Hennah, 1991
- Rice husk	zinc chloride	-	1232	375	>95	- hardness - balance micro-, meso- and macropores	Usmani et al., 1994
- Rice hulls, rice straw, sugarcane bagasse	mixture of four binders (coal tar, corn syrup, sugarcane molasses, sugar beet molasses)	-	953	-	90	- small pore - high pore volume - high total surface area	Pendyal et al., 1998

Table 2.7 (Continued)

Raw materials	Binder	Reinforcer	Properties of activated carbons			Characteristics of GAC	References
			Iodine number (mg g ⁻¹)	Methylene blue number (mg g ⁻¹)	Hardness number (%)		
- Sugarcane bagasse	coal tar	-	970	-	90	- high porous	Pendyal et al., 1998
- Sugarcane bagasse	corn syrup	-	986	-	80	- high pore volume	Ahmedna et al., 1999
- Coal	commercial binder pitch	-	-	-	99	- hardness - high pore volume - high surface area	Rubio et al., 1999
- Coke	pitch	-	-	-	-	- hardness - large pore volume	Rubio et al., 1999
- Tar	polyvinyl-butyrac (PVB)	dibutyl phthalate (DBP)	-	-	99	- hardness - large surface area	Qiao et al., 2001

Table 2.7 (Continued)

Raw materials	Binder	Reinforcer	Properties of activated carbons			Characteristics of GAC	References
			Iodine number (mg g ⁻¹)	Methylene blue number (mg g ⁻¹)	Hardness number (%)		
- Eucalyptus grandis sawdust	carboxymethyl cellulose (CMC)	kaolin	-	-	-	- high porosity - high adsorption - micro- and mesopore volume	Tancredi et al., 2004
- Cork waste	clays	-	903	-	>95	- high porous - large surface area	Carvalho et al., 2006
- Fly ash	water	coal tar	835	-	95	- high specific surface area - better adsorption ability	Li et al., 2006

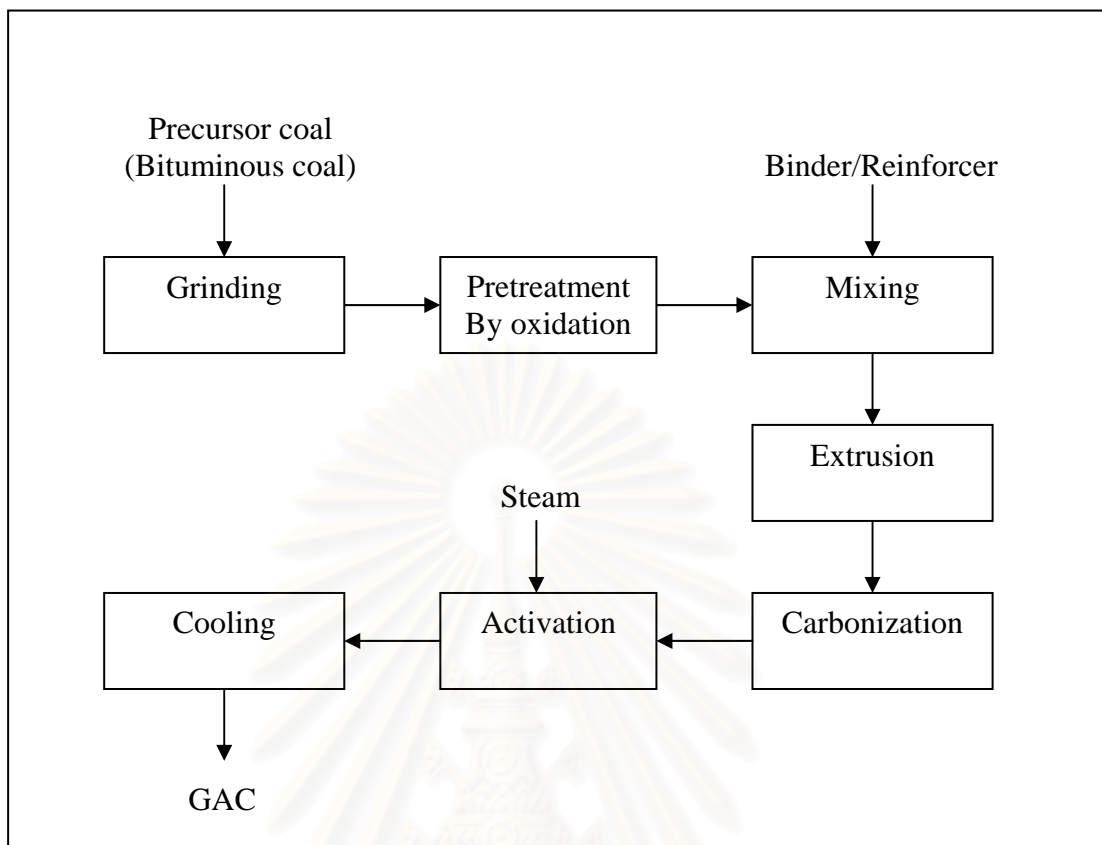


Figure 2.1 Flow diagram for the production granular activated carbon (Degel, 1990)

Granular activated carbon is used to adsorb the relatively small quantities of soluble organics (see Table 2.8) and inorganic compounds such as nitrogen, sulfides and heavy metals remaining in the waste water following biological or physical-chemical treatments.

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Table 2.8 Organic compounds amenable to adsorption by granular activated carbon

Types of raw materials	Class	Examples
- Soft wood	- Aromatic solvents	- Benzene, toluene, xylene
- Soft wood and hard wood	- Polynuclear aromatics	- Naphthalene, biphenyl
- Soft wood	- Chlorinated aromatics	- Chlorobenzene, PCBs, endrin, toxaphene, DDT,
- Soft wood and hard wood	- Phenolics	- Phenol, cresol, resorcinol, nitrophenols, chlorophenols, alkyl phenols
- Soft wood	- Aromatic amines & high molecular weight aliphatic amines	- Aniline, toluene diamine
- Soft wood	- Surfactants	- Alkyl benzene sulfonates
- Soft wood	- Soluble organic dyes	- Methylene blue, textiles dyes
- Hard coal	- Fuels	- Gasoline, kerosene, oil
- Hard wood and hard coal	- Chlorinated solvents	- Carbon tetrachloride, perchloroethylene
- Hard wood and hard coal	- Aliphatic & aromatic acids	- Tar acids, benzoic acids
- Soft wood	- Pesticides/herbicides	- 2,4-D, atrazine, simazine, aldicarb, alachlor, carbofuran

2.7 Properties of granular activated carbon

Granular activated carbon has certain chemical (bulk density, hardness, surface area) and physical (ash, pH, conductivity) properties depending on the basic material source, precursor and activation (Gergova et al., 1994). These are delineated below.

2.7.1 Ash content

Ash content of granular activated carbon can be significant as it is the inorganic, inert, amorphous and unusable part present in the activated carbon. This ash consists mostly of calcium salts and metal oxides and comes initially from the basic material. In general, good activated carbon should have low ash content. It is noted that reactivation of the carbon will increase the ash content.

2.7.2 BET-surface area

The internal surface is measured by a method developed by Brunauer, Emmett & Teller, by setting up the adsorption-isotherms of liquid nitrogen at -196°C . The BET-surface can reach up to $1200\text{ m}^2\text{ g}^{-1}$ (average $1000\text{ m}^2\text{ g}^{-1}$ for a good quality).

2.7.3 CTC or tetrachloride number

This number indicates the amount of tetrachloride adsorbed on granular activated carbon. This value is significant as indicator for air applications and varies between 35 to 120%.

2.7.4 Density

Density of the activated carbon is the weight (kg) for 1 litre of activated carbon. The value ranges from ± 300 to 500 g l^{-1} , depending on the raw materials (wood-coal). A simple calculation for determining the volume activity of activated carbon is to multiply the bulk density by the Iodine Number.

2.7.5 Hardness

Granular activated carbon's ability to withstand degradation during handling and expressed as value is the resistance of the particle to pressure drop and carbon loss and measured by means of a ball pan. This property is mainly determined by the raw material and hardness value typically varies from $\pm 99\%$ (coconut shells), $\pm 95\%$ (coal), to $\pm 75\%$ (wood).

2.7.6 Iodine number

Iodine number is commonly used to indicate total surface area available for adsorption. It is defined as milligrams of iodine adsorbed by one gram of activated

carbon and it approximates the internal surface area (micropores) in square meters per gram. Iodine number can be up to 1300 mg g⁻¹ and a good quality should be not lower than 1000 mg g⁻¹.

2.7.7 Methylene blue number

This value is measured by the amount of adsorbed iodine of activated carbon and is used to indicate the adsorption capacity for large molecules (like color, detergents). Methylene blue number can be up to 270 mg g⁻¹ and a good quality is 200 mg g⁻¹.

2.7.8 Moisture content

This is the amount of water on the granular activated carbon under normal condition. A high moisture content indicates poor quality and a normal value varies between 1 and 5%.

2.7.9 Particle size distribution

The size of most granular activated carbon is used by the U.S (United States) standard sieve. For granular activated carbon, often is described by the sieve range method or by diameter of the pellets.

2.7.10 pH

The pH of the carbon is a measure of surface acidity or basicity of the oxygen containing groups. Granular activated carbons are typically close to neutrality and the pH range can vary between 6-10.

2.7.11 Phenol number

This value is measured by the amount of adsorbed phenol and used to indicate the adsorption capacity for products causing odor and taste.

Table 2.9 shows the properties the standard value for Thai Industrial Standard 900-2004.

Table 2.9 Standard value for the properties of granular activated carbon

Standard	Properties of granular activated carbon						
	Iodine number (mg g ⁻¹)	Methylene blue number (mg g ⁻¹)	Hardness number (%)	BET surface area (m ² g ⁻¹)	Bulk density (g cm ⁻³)	Ash content (%)	pH
Thai Industrial Standard 900-2004	≥600	-	≥70	900-1100	≥0.200	-	-

2.8 Classification of Isotherms

The quantification of the porosity of granular activated carbon is often carried out by physical adsorption of liquid nitrogen at -196°C . The standard isotherm of granular activated carbon according to the International Union of Pure and Applied Chemistry (IUPAC) classification as illustrated in **Figure 2.2**. Six patterns presenting these isotherms with different features which could be correlated with porosity development.

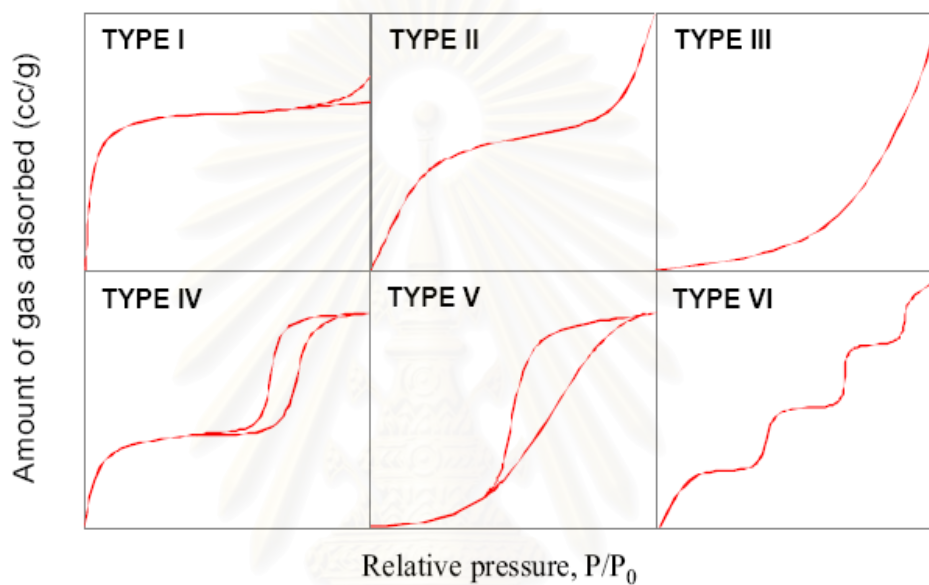


Figure 2.2 Isotherm patterns for the activated carbon (Sing, 1998)

- Type I : Langmuir Type (mono layer), physisorption by microporous adsorbent
- Type II : S-shape, monolayer-multilayer isotherm, in non-porous or macroporous adsorbent
- Type III : Non-porous or macroporous carbon, stronger gas-gas interaction than gas-solid
- Type IV : Hysteresis Loop, 15-1000 Å, in mesoporous adsorbent
- Type V : Modification of Type II, 15-1000 Å
- Type VI : Stepwise isotherm

CHAPTER III

RESEARCH METHODOLOGY

3.1 Materials

3.1.1 Equipments

- Analytical Balance 2 digit (Sartorius, BP 3100S)
- Analytical Balance 4 digit (Sartorius, BP2215)
- Desiccators
- Filter paper (Whatman No. 42)
- Rotary Shaker
- Muffle furnace: type ESF 12/23 (0-1200 °C), Carbolite, England.
- Spectrophotometer, Spectronic® UV/VIS Helios Alpha spectrophotometer with Vision32 software –v1.25
- Micropipette 5 ml
- Conical tube
- X-ray Diffraction Spectroscopy (SIEMENS XRD D5000)
- Scanning Electron Microscopy (SEM), Jeol, JSM-5800LV
- Surface area analyzer : Micrometrics FlowSorb 2300
- Fourier Transform Infrared Spectrometer (FT-IR), Perkin Elmer, Model 1760X
- pH-meter, HACH, SensIon 1 and SensIon 3
- Horizontal shaker
- Magnetic stirrer, Clifton UK, MSU-3 and magnetic bar
- Water purification system (For making DI-water)
- Hot plate
- Gloves
- Standard Sieve number 10, 100, 325
- Syringe
- Extruder
- Vernier caliper
- Ball mill
- Universal Testing Machine

- Oven

3.1.2 Glassware

- Beakers
- Burette
- Pipettes
- Graduated cylinders
- Dropper
- Funnels
- Erlenmeyer flasks
- Volumetric flasks
- Thermometer
- Crucible
- Mortar

3.1.3 Chemical reagents

- Phosphoric acid (H_3PO_4)
- Carboxymethyl cellulose
- Methyl cellulose
- Kaolin
- Calcium carbonate (CaCO_3)
- Hydrochloric acid (HCl)
- Methylene blue ($\text{C}_{16}\text{H}_{18}\text{N}_3\text{S}_3\text{O}_7 \cdot 3\text{H}_2\text{O}$)
- Iodine (I_2)
- Starch solution
- Potassium iodine (KI)
- Potassium iodate (KIO_3)
- Potassium phosphate (KH_2PO_4)
- Sodium carbonate (Na_2CO_3)
- Sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$)
- Sodium hydrogen phosphate (Na_2HPO_4)
- Deionized water (DI water)

3.2 Methods

3.2.1 Precursor raw material

1. Wash the eucalyptus bark with tap water
2. Dry the eucalyptus bark in oven at 105°C for 4 h
3. Crush and sieve pass through mesh number 10 (2 mm)
4. Store in closed bottle

3.2.2 Preparation of powder activated carbon

1. Weigh 100 g of raw material (eucalyptus bark) and impregnate into a 100 ml of phosphoric acid
2. Stir thoroughly until well mixed at room temperature
3. Carbonize in a muffle furnace at 500°C for 1 h
4. Wash the char with hot distilled water until the final pH reaches 6-8
5. Dry in oven at 105°C for 4 h
6. Crush and sieve in the size ranged between mesh number 100 (0.150 mm) and 325 (0.045 mm)
7. Store powdered activated carbon in the desiccator

3.2.3 Preparation of granular activated carbon

1. Mix carboxymethyl cellulose (CMC) as binder and kaolin as reinforcer at a weight proportion of 30:0 (impregnation ratio of CMC and kaolin is 1:0), stir thoroughly until well mixed at room temperature
2. Weigh 60 g of powdered activated carbon following the same procedure as Section 3.2.2 and impregnate into 40 g of the mixture of binder/reinforcer (weight proportion of powder activated carbon and mixture of binder/reinforcer is 60:40)
3. Add 2 ml g⁻¹ of DI water
4. Stir thoroughly until well mixed at room temperature
5. Wet the mixture of binder/reinforcer and powdered activated carbon and send it through the extruder
6. Dry in oven at 105°C for 2 h
7. Store the obtained granular activated carbon in desiccator

8. Repeat this section with other binders and reinforcers

3.2.4 Determination the optimal proportion of mixture of binders and reinforcers

Repeat Steps 1-7 in Section 3.2.3 by changing the weight proportion of carboxymethyl cellulose (CMC) and kaolin (or other binders and reinforcers) as follows:

Carboxymethyl cellulose (CMC) (g)	Kaolin (g)	Impregnation ratio
30	0	1 : 0
70	30	0.7 : 0.3
50	30	0.625 : 0.375
70	50	0.583 : 0.417
30	30	0.5 : 0.5
50	70	0.417 : 0.583
30	50	0.375 : 0.625
30	70	0.3 : 0.7
0	30	0 : 1

3.2.5 Determination the optimal proportion of powdered activated carbon and mixture of binder/reinforcer

Repeat Steps 1-7 in Section 3.2.3 by changing the weight proportion of powdered activated carbon and the mixture of binder/reinforcer at the following ratio:

Powder activated carbon (g)	Mixture of binder/reinforcer (g)
60	40
70	30
80	20

3.2.6 Vary type of binders and reinforcers

Repeat Steps 1-7 in Section 3.2.3 by changing type of binder and reinforcer as follows:

No.	Binders	Reinforcers
1	Carboxymethyl cellulose (CMC)	Kaolin
2	Carboxymethyl cellulose (CMC)	Calcium carbonate (CaCO ₃)
3	Methyl cellulose (MC)	Kaolin
4	Methyl cellulose (MC)	Calcium carbonate (CaCO ₃)

3.2.7 Analysis of granular activated carbon

Characteristics of granular activated carbon analysed in this work include:

1. Iodine number: determined according to the standard method ASTM D 4607-94 and see details in [Appendix A.1](#).

2. Methylene blue number: determined according to the standard method, Gergova et al., 1993 and see details in [Appendix A.2](#).

3. Surface area: calculated from adsorption isotherms using the method of Brunauer, Emmet and Teller (BET method) and see details in [Appendix A.3](#).

4. Ash content: determined by using standard method according to ASTM D 2866-94 and see details in [Appendix A.4](#).

5. Apparent (bulk) density: calculated as the ratio between weight and volume of packed dry material and see details in [Appendix A.5](#).

6. Moisture content of granular activated carbon: determined according to the standard method ASTM D 2867-95 and see details in [Appendix A.6](#).

7. Weight loss: calculated as the ratio of the weight of final powder activated carbon to that of initial raw materials according to the following :

$$\text{Weight loss \%} = \frac{(W_2 - W_0)}{(W_1 - W_0)} \times 100 \quad (3.1)$$

where W_0 is the weight of capsule with cover (g), W_1 is the weight of capsule with cover plus original sample (g), and W_2 is the weight of capsule with cover plus dried sample (g).

8. The surface morphology of granular activated carbon is visualized via scanning electron microscopy (SEM), and the corresponding SEM micrographs are obtained using a XL 30 ESEM FEG scanning electron microscope.

9. Yield of granular activated carbon: The yield is defined as the ratio of the weight of the resultant granular activated carbon to that of the original powder activated carbon with both weight on a dry basis, i.e.

$$\text{Yield} = \frac{W_1}{W_0} \times 100 \quad (3.2)$$

where W_0 is the original mass of powder activated carbon on a dry basis and W_1 is the mass of the granular activated carbon product.

10. X-ray diffraction (XRD) patterns: obtained in a X-ray Diffraction Spectroscopy using Cu K α radiation ($\lambda=0.154056$ nm), with a step size of 0.004° and a step time of 1.5 s.

11. Chemical analysis of wood charcoal: examined according to the standard method ASTM D 1762-84 and see details in [Appendix A.7](#).

12. Ultimate analysis of eucalyptus bark: performed in CHNS/O analyzer (Perkin Elmer PE2400 Series II), using gaseous products feed by pyrolysis in high purity oxygen and are chromatographically detected with a thermal conductivity detector. The proximate analysis is developed following ASTM standards for chemical analysis of wood charcoal (ASTM D 1762-84).

13. Ball-Pan Hardness of granular activated carbon: determined according to the standard method ASTM D 3802-79 and see details in [Appendix A.8](#).

14. pH of granular activated carbon: determined according to the standard method ASTM D 3838-80 and see details in [Appendix A.9](#).

15. Fourier Transform Infrared Spectrophotometer (FT-IR) analysis. For this, the granular activated carbon samples are brought to constant weight in a drying oven at 50°C for 24 h and kept in the desiccators. Then 1 mg of dried granular activated carbon is mixed with 100 mg of KBr, which is initially dried at 110°C , in the sample disk. FT-IR spectra in the range of $450\text{-}4000\text{ cm}^{-1}$ were obtained on a Perkin-Elmer, Model 1760X.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Characteristics of powdered activated carbon

Table 4.1 shows proximate and ultimate analyses of the powdered activated carbon obtained from this chemical method with H_3PO_4 as carbonizing/activating agent. The results demonstrate that the powdered activated carbon product had a higher fixed carbon (65.3%) and lower volatile matter (22.8%). This relatively high fixed carbon exerts significant influence on the characteristics and performance of carbon product. In general, the raw material is heated during the activation step to $500^\circ C$ under inert atmospheric conditions, and at this condition, the volatile matters and moisture content decomposed while the residue char took place at this step (Patnukao and Pavasant, 2006). The results demonstrated in **Table 4.2** are the properties of the powdered activated carbon product obtained from this work. The overall yield (dry basis) was only 30.5% which is quite small and expected to be due to the loss of a great amount of char carbons during the washing step. Nevertheless, this yield was considered moderate when compared with reported values such as *Eucalyptus camaldulensis* Dehnh (33%) (Jindaphunphairoth, 2000), *Eucalyptus* wood (37%) (Amen-Chen et al., 1997), *Eucalyptus globulus* (36%) (Arriagada et al., 1997) and *Eucalyptus grandis* sawdust (31%) (Tancredi et al., 1996). The apparent (bulk) density was 0.251 g cm^{-3} and the lowest ash content was 4.88%. As illustrated in **Table 4.2**, a relatively high iodine number of 917 mg g^{-1} was obtained whereas a relatively moderate level of methylene blue number of 427 mg g^{-1} was resulted which indicated that the pore size of the PAC product was more in a micropore range ($d < 2 \text{ nm}$) rather than mesopore range ($2 \text{ nm} < d < 50 \text{ nm}$).

The microstructures of the powdered activated carbon were observed by Scanning electron micrograph (SEM) and are shown in **Figure 4.1**. This image shows that the carbon product had an irregular structure and highly porous surface, indicating relatively high surface areas. X-ray diffraction (XRD) patterns in **Figure 4.2** illustrates that the powdered activated carbon had amorphous carbon structure. FT-IR was used to analyze the functional groups of powdered activated carbon. **Figure 4.3** shows the FT-IR transmission spectra in the range of $500\text{-}4000 \text{ cm}^{-1}$ for the PAC product. The main functional groups, for instance, amine, amide and carboxyl

groups (see Table 4.3) exerted negatively charged on the surface of the carbon product. The dominant peaks were found in the wave number 3390.59 cm^{-1} for N-H stretching in amine, 2943.07 cm^{-1} for O-H stretching in carboxylic acids, 1693.14 cm^{-1} for C-O stretching in amide, and also as 1590.93 cm^{-1} for COO^- stretching-asymmetric in carboxylic acid groups.

The specific surface area (up to $1239\text{ m}^2\text{ g}^{-1}$) was calculated by applying the BET method, where the shape of the adsorption-desorption of nitrogen isotherms as demonstrated in Figure 4.4 indicated that the product was Type I. according to IUPAC classification. The Type I isotherm is mostly associated with microporous structure, as there is a large amount of nitrogen adsorbed at low relative pressure and an increase in the adsorbed nitrogen at higher relative pressure revealed the mesoporous structure (corresponding well to the results displayed in Table 4.2 where 88.5% was micropore and 11.5% mesopore). This is an indication of uniform microporosity development during the activation and these are primarily responsible for adsorption (Fuertes et al., 2003).

4.2 Characteristics of binders and reinforcers

4.2.1 Binders (Carboxymethyl cellulose and Methyl cellulose)

Carboxymethyl cellulose

Carboxymethyl cellulose (CMC) is a chemical compound derived from cellulose. It is often used as a binding agent which is basically a substance that when added to a mixture, increases its viscosity. The results in Table 4.4 illustrate the properties of CMC in this work where iodine and methylene blue numbers were 53 and 5 mg g^{-1} , respectively. The ash content in CMC (18.2%) shows that this material is an oxide salt. The morphology of CMC surface obtained by SEM as shown in Figure 4.5(a) demonstrates that the structure was agglomeration of cellulose chain. The XRD pattern in Figure 4.6(a) identified the crystallinity structure. Figure 4.7(a) shows the FT-IR transmission spectra for CMC which suggested the existence of the following functional groups: alkanes, alcohols, carboxylic acids and amino acids groups (Table 4.5). Detail of the wave numbers and the alcohol groups are as follows: 3435.03 cm^{-1} representing O-H stretching, $1418.19\text{-}1267.68\text{ cm}^{-1}$ representing O-H bending-in plane, 595.81 cm^{-1} representing O-H bending-out of plane and 1052.51 cm^{-1} representing C-O stretching. The alkane group represented by the wave number 2922.19 cm^{-1} represents C-H stretching whereas the amino acid group in the wave

number of 2146.93 cm^{-1} represents O-H stretching. The carboxylic acids group contained with minor groups in the following wave numbers: 1606.55 cm^{-1} representing COO^- stretching-asymmetric and as 897.38 cm^{-1} representing OC-OH bending-out of plane vibration.

Methyl cellulose

Methyl cellulose (MC) is a methyl ether of cellulose and a white powder in pure form. It is often used as a binder on the capsule or tablet in pharmaceuticals. MC has similar function to carboxymethyl cellulose, which is to enhance the viscosity. Some important properties of MC are shown in **Table 4.4**, e.g. iodine and methylene blue numbers of 23 and 2 mg g^{-1} , respectively, and the lowest ash content of 0.50%. **Figure 4.5(b)** shows the morphology of MC surface measured by SEM whereas **Figure 4.6(b)** displays its corresponding XRD pattern where the MC surface was shown to have crystalline structure. **Figure 4.7(b)** shows FT-IR transmission spectra of MC, where main functional groups are alkane, alcohol, amino acid and ether groups (**Table 4.5**). Other dominant peaks indicated several alcohol groups as follows: 3465.75 cm^{-1} representing O-H stretching, $1408.58\text{-}1375.57\text{ cm}^{-1}$ representing O-H bending-in plane, 567.48 cm^{-1} representing O-H bending-out of plane and as 1064.00 cm^{-1} representing C-O stretching. Alkane groups in wave number of 2837.18 cm^{-1} represents C-H stretching. The amino acid groups are contained the minor groups in wave numbers following: $2399.21\text{-}2059.96\text{ cm}^{-1}$ representing O-H stretching and 1633.52 cm^{-1} representing COO^- stretching-asymmetric vibration. Lastly the wave number of 945.09 cm^{-1} represents C-O-C stretching in ether groups.

4.2.2 Reinforcers (Kaolin and Calcium carbonate)

Kaolin

Kaolin is a typically of fine clay minerals with the chemical composition of $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$. It is widely used in ceramics industry to improve mechanical properties, such as tensile strength and rigidity of the product. In this work, kaolin used as a reinforcing agent to increase the hardness of the final granule. **Table 4.4** demonstrates most important properties on kaolin, where rather high iodine (206 mg g^{-1}) and methylene blue (51 mg g^{-1}) numbers were noticed when compared with other agents (CMC, MC and Calcium carbonate). A relatively high ash content of 88.5% was observed which should be caused by the metal oxides in the structure. The morphology by SEM shown in **Figure 4.5(c)** illustrates the higher crystallinity structure which is consistent with the XRD pattern (**Figure 4.6(c)**) where high

intensities (sharp) in dominant peaks indicating crystallized structure. Furthermore, the transmission spectra in [Figure 4.7\(c\)](#) were analyzed by FT-IR method, indicating the existence of the following functional groups: alcohol, peroxide, aluminum and silicon compounds groups (see [Table 4.5](#)). The alcohol groups are contained with minor groups in the following wave numbers: 3695.86-3442.19 cm^{-1} representing O-H stretching, 696.98-470.38 cm^{-1} representing O-H bending-out of plane and 1031.66 cm^{-1} representing C-O stretching. The wave number of 1823.51-1629.67 cm^{-1} represents Al-O stretching in aluminum compounds. Dominant peaks at wave number 1112.51-1008.20 cm^{-1} represents Si-O stretching in silicon compounds and at wave number 912.60 cm^{-1} represents O-O stretching in peroxide compounds.

Calcium carbonate

Calcium carbonate (CaCO_3) is a common substance used in the construction industry, especially used as an ingredient of cement. The calcium carbonate is used to replace kaolin in the production of glossy paper. Some important properties of this compound are summarized in [Table 4.4](#), which indicates that calcium carbonate had rather poor adsorption capacity (10 for iodine and only 1 mg g^{-1} methylene blue numbers), and contains extremely high ash content (95.4%). [Figure 4.5\(d\)](#) and [Figure 4.6\(d\)](#) demonstrate a high crystallization on the carbon structural, which may also explain the high XRD intensity. The functional groups on surface of calcium carbonate measured by FT-IR in [Figure 4.7\(d\)](#) are summarized in [Table 4.5](#). Main functional groups are carbonyl and inorganic (calcium) compounds. Dominant peaks at wave number 1797.29 cm^{-1} represents C=O stretching in carbonyl compounds, and at 1462.81 cm^{-1} represents Ca-O stretching of inorganic compounds.

4.3 Selection of the suitable proportion of binder and reinforcer

The selection of the suitable proportion or weight ratio between binder and reinforcer was carried out by mixing the binder/reinforcer mixture with powder activated carbon at 20:80. The weight proportions of binder and reinforcer were varied from 1:0, 0.7:0.3, 0.625:0.375, 0.583:0.417, 0.5:0.5, 0.417:0.583, 0.375:0.625, 0.3:0.7 and 0:1, respectively. Good GAC products are indicated using the following parameters: i.e. iodine number, surface area, hardness number and bulk density (according to the TIS. 900-2004 GAC standard).

The results summarized in [Table 4.6](#) illustrate the properties of the GAC products with various the proportion of CMC as binder and kaolin as reinforcer. This

illustrates that the iodine number increased with increasing proportion of kaolin and reached the maximum where reached to 1 (by weight). At the proportion of 0.5:0.5 (CMC : Kaolin), it was observed that the iodine number has the lower than at the proportion of 0.417:0.583, 0.375:0.625, 0.3:0.7 and 0:1. In contrast, those the proportion had the low hardness and also bulk density and their still could not complied with TIS. 900-2004 standard. Thus, the GAC product obtained by used CMC as binder and kaolin as reinforcer had the suitable weight proportion was 0.5:0.5 and their details the explanation in [Section 4.4.1](#).

[Table 4.7](#) demonstrates the properties of GAC product at various proportions of CMC and calcium carbonate. It was found that the iodine number decreased with increasing proportion of calcium carbonate (reinforcer) and the highest occurred at the CMC:calcium carbonate ratio of 1:0. At this condition, the GAC also had the highest values of hardness and bulk density. It was clear that this was an appropriate proportion of CMC and calcium carbonate. The properties of GAC obtained from this condition are shown in [Section 4.4.2](#).

In the case with MC as binder and kaolin as reinforcer, [Table 4.8](#) demonstrates that, similar to the case with CMC and kaolin as binder and reinforcer, iodine number and surface area increased with increasing proportion of kaolin but the opposite was found for the hardness and bulk density. The selected condition was at the proportion of 0.5:0.5 as this provided relatively high iodine value whereas its other properties (hardness and bulk density) still could comply with the standard. Details of the GAC produced from this condition are given in [Section 4.4.3](#).

Finally, [Table 4.9](#) demonstrates the properties of GAC using MC and calcium carbonate as binder and reinforcer. In this case, the iodine number decreased with increasing proportion of calcium carbonate (reinforcer) close to 1 (by weight) while the highest iodine number was obtained at the MC:calcium carbonate ratio of 1:0. This condition also yielded the highest hardness and bulk density, and therefore it was concluded that an appropriate proportion of MC and calcium carbonate was 1:0. The properties of GAC obtained from this condition are described further in [Section 4.4.4](#).

4.4 Characteristics of granular activated carbon (GAC) products

4.4.1 with Carboxymethyl cellulose (CMC) as binder and Kaolin as reinforcer

In this case, the optimal weight proportion of binder and reinforcer (impregnation ratio) was 0.5:0.5 and the optimal weight proportion of mixture (binder : reinforcer) to powdered activated carbon was 20:80. Properties of the GACs using in these conditions are summarized in [Table 4.10](#) and are described below.

Iodine and methylene blue numbers

[Table 4.10](#) demonstrates that iodine and methylene blue numbers (686 mg g^{-1} and 310 mg g^{-1} , respectively) obtained from the GAC product with this condition, were not as good as those obtained from the original powdered activated carbon in [Section 4.1](#) (917 mg g^{-1} iodine and 427 mg g^{-1} methylene blue numbers). Within this experiment, CMC and kaolin were added in the step of the granule production, and thus, filled in the pore structure of the activated carbon, which then decreased the sorption capacities for both iodine and methylene blue. The image morphology for this GAC product obtained by SEM shown in [Figure 4.8\(a\)](#) displays the dispersion of CMC and kaolin on the pore structure of GAC product whereas the XRD pattern of this product is shown in [Figure 4.9\(a\)](#). [Figure 4.10\(a\)](#) illustrates the existence of functional groups (FT-IR spectra) of the product. Generally, the functional groups on surface of activated carbon are mostly negative charged such as amine, amide and carboxyl groups ([Patnukao and Pavasant, 2006](#)) as discussed in [Section 4.1](#). From [Figure 4.10\(a\)](#) can be used to identify the transmission spectra in [Table 4.11](#). It was observed that dominate peaks on this GAC product changed from the original powdered form to include some additional functional groups including amine and carboxylic acid groups. Moreover, increasing wave numbers for dominant peaks indicated functional groups of CMC and kaolin, e.g. N-H stretching at the wave number from 3390.59 cm^{-1} of original powdered activated carbon to 3418.56 cm^{-1} of this GAC. For carboxylic acid group, there was a shift in the wave number for O-H stretching from 2943.07 cm^{-1} of original powdered activated carbon to 2915.51 cm^{-1} of this GAC. In addition, the GAC still exhibited O-H stretching of alcohol groups which was overlapped with N-H stretching groups of amine in wave number 3418.56 cm^{-1} . Kaolin caused this GAC to exhibit the peak of silicon and peroxide compounds at wave numbers of $1100.13\text{-}1008.59 \text{ cm}^{-1}$ (silicon Si-O stretching) and 912.07 cm^{-1} (peroxides O-O stretching vibration). This implied that there was an increase in the

positively charged functional groups on the surface structure of the product, leading to a reduction of the sorption capacity of iodine and methylene blue.

Specific surface area

The results summarized in [Table 4.10](#) illustrate that the BET surface area was $1085 \text{ m}^2 \text{ g}^{-1}$ on the GAC product using CMC as binder and kaolin as reinforcer. It was observed that the surface area decreased when compared with the original powdered activated carbon (up to $1239 \text{ m}^2 \text{ g}^{-1}$) in [Section 4.1](#). As stated in the previous section, this reduction in the surface area could occur as the porous structure of the carbon was being filled by the addition of CMC and kaolin. [Figure 4.11](#) illustrates N_2 adsorption-desorption isotherms at $-196 \text{ }^\circ\text{C}$ on the GAC product where the shape of isotherm can be identified as Type I. This indicates that the product contained mostly development of small pores where the corresponding % micro- and mesopore volume were 80.9% and 19.1%, respectively ([Table 4.10](#)).

Hardness number

Hardness was ability to resist the degradation of the carbon granule. In this experiment, kaolin was used as a reinforcing agent to increase hardness of the final granule. The result in [Table 4.10](#) indicates that the hardness number was 75% with the proportion of 0.5:0.5 (CMC:kaolin). This hardness number was relative moderate when compared with standard value where an appropriate level of hardness of the GAC should be over 70% (TIS. 900-2004).

Bulk density and yield

[Table 4.10](#) demonstrates that the bulk density of GAC product with this condition was 0.214 g cm^{-3} . It was observed that bulk density decreased with increasing proportion of kaolin. The bulk densities of CMC and kaolin were 0.725 and 0.606 g cm^{-3} , respectively, whereas that of the original PAC was relatively low at 0.251 g cm^{-3} . This might answer why the bulk density of the product was quite low. Nevertheless, the bulk density as stated above was still higher than the standard for the GAC at over 0.200 g cm^{-3} (TIS. 900-2004). The yield of the final granule product was found as only 62.7%. This was caused mainly by the loss during the production of granule in the laboratory extruder.

Ash content

The ash content of the GAC product increased with the amount of kaolin as it had high ash content of 88.5%. The ash content of the CMC was also quite low at 18.2% and that of original PAC was 4.88%. Therefore including kaolin in the GAC

structure significantly increased the ash content of the GAC product. [Table 4.10](#) illustrates that the ash content of the GAC product was 12.7%.

pH

[Table 4.10](#) illustrates that the pH of the GAC product was quite neutral at 6.67. This came from the multiple effects of the various constituents in the GAC where CMC had a pH of 7.28, kaolin of 5.69, and the original PAC of 6.50 ([see Section 4.1](#)).

4.4.2 with Carboxymethyl cellulose (CMC) as binder and Calcium carbonate as reinforcer

In this study, the final GAC product was obtained by using carboxymethyl cellulose as binder and calcium carbonate as reinforcer. The suitable weight proportion of binder and reinforcer (impregnation ratio) was 1:0 or no calcium carbonate was found to be the best or in other words, carbonate was not at all required for such synthesis. The weight proportion of mixture (CMC : calcium carbonate) to powdered activated carbon was 20:80. The properties of GAC obtained from this synthesis is summarized in [Table 4.10](#) and are explained as follows.

Iodine and methylene blue numbers

Iodine and methylene blue numbers obtained from the GAC product with carboxymethyl cellulose as binder and calcium carbonate as reinforcer were rather low (662 and 281 mg g⁻¹, respectively) when compared with that of the original PAC (917 and 427 mg g⁻¹, respectively). The adsorption capacity slightly decreased with increasing the proportion of binder (CMC) as CMC could deposit on the pore structure as reducing the active surface area. Hence, a reduction in iodine and methylene blue became apparent. SEM results are shown in [Figure 4.8\(b\)](#) and this demonstrates the characteristics in micropore structure and the CMC dispersed in porous the GAC. [Figure 4.9\(b\)](#) displays the XRD patterns of this product and shows dominant peaks at low diffraction angles 2θ at 25-28°, indicating the main functional groups of binder (CMC). The resulting FT-IR spectra as shown in [Figure 4.10\(b\)](#) identifies the functional groups as illustrated in [Table 4.11](#). It was observed that there were some broad band shifts from the original PAC. These were functional groups of amine and carboxylic acids groups whereas increases in the clear band in the wave number for dominant peaks indicated the functional groups of CMC. For N-H stretching in amine group, there was a shift in the wave number from 3390.59 cm⁻¹ of original PAC to 3410.56 cm⁻¹ of the GAC. For O-H stretching in carboxylic acids

group, there was a shift in the wave number from 2943.07 cm^{-1} of the original PAC to 2858.06 cm^{-1} of the GAC. Moreover, an increase the dominate peaks in this GAC indicated the functional groups of CMC representing O-H stretching of alcohol groups. This band overlapped with N-H stretching groups of amine at the wave number of 3410.56 cm^{-1} . Charges on CMC seemed to be responsible for an increase in the positively charged groups on the surface of GAC product.

Specific surface area

Table 4.10 shows that the surface area obtained by the BET method of this GAC product was $657\text{ m}^2\text{ g}^{-1}$ with 65.3% and 34.7% micropore and mesopore, respectively. This surface area was much lower than the original PAC of $1239\text{ m}^2\text{ g}^{-1}$ (in Section 4.1). It could be that there were a large amount of CMC being deposited in the pore structure, blocking the active surface, and reducing the adsorption capacity. **Figure 4.11** indicates that isotherm was classified as Type I.

Hardness number

Table 4.10 indicates that the hardness of the final granule was relatively high (92%), and that the hardness was slightly increased with an increasing proportion of CMC. Because of the molecule structural on CMC consists with a long chain of cellulose which helps strengthening the hardness of the GAC.

Bulk density and yield

Bulk density and yield of this GAC product obtained from this work are summarized in **Table 4.10**. The bulk density slightly increased with an increasing proportion of CMC and reached the highest of 0.725 g cm^{-3} . This was considered moderate when compared with the industrial standard of over 0.200 g cm^{-3} (TIS. 900-2004). The yield in this case was around 61.7% (**Table 4.10**) which seemed to be lower when compared with other conditions employed in this work. This could be due to the loss of carbon during the extruder (in the preparation of granular).

Ash content

Initially, the original powdered activated carbon contained the ash content of only 4.88%. This is considered good property as activated carbon should have low ash content. With this experiment, ash content increased with increasing the proportion of CMC as CMC had a relatively high ash at 18.2%. The CMC structure was consisted of a long chain of cellulose which led to a high ash after being carbonized. The results as summarized in **Table 4.10** demonstrates that the ash content was relatively moderate (6.16%) when compared with those prepared from other conditions.

However, the ash content are still quite low when compared with the standard value in TIS. 900-2004.

pH

Table 4.10 demonstrates that the GAC product had moderate pH at close to neutrality of 6.90. This was the results of the mixing between CMC with the pH of 7.28 and the original PAC of 6.50.

4.4.3 with Methyl cellulose (MC) as binder and Kaolin as reinforcer

Under this condition, using methyl cellulose (MC) as binder and kaolin as reinforcer. As results, we found that the optimal weight proportion of binder and reinforcer (impregnation ratio) was 0.5:0.5 and the optimal weight proportion of mixture (binder : reinforcer) to powdered activated carbon was still as 20:80. The important properties are shown in **Table 4.10** and are discussed below.

Iodine and methylene blue numbers

Table 4.10 illustrates that the GAC product from this condition had iodine and methylene blue numbers were 672 and 305 mg g⁻¹, respectively. This was relative moderate when compared with other conditions of this research. Similar explanation as in **Section 4.4.1** could be used in this case, i.e. the sorption capacities decreased with increasing the proportion of both MC and kaolin. **Figure 4.8(c)**, the image in pore structure of this GAC with received by SEM. From this could be illustrated the dispersion of MC and kaolin on the pore structure of the GAC. In **Figure 4.9(c)** illustrates the XRD pattern of product obtained from this condition. **Figure 4.10(c)**, which the results were analyzed by FT-IR method. Which is demonstrates characteristics for peaks obtained by this GAC with the mainly functional groups both of MC and kaolin. It was observed that the dominate peak on this GAC product were changes from original powdered activated carbon. For amine group, in N-H stretching there was a shift in the wave number from 3390.59 cm⁻¹ of original powdered activated carbon to 3426.78 cm⁻¹ of this GAC. In carboxylic acids group, for O-H stretching there was a shift in the wave number from 2943.07 cm⁻¹ of original powdered activated carbon to 2893.32-2833.19 cm⁻¹ of this GAC. In addition, an increase the dominate peaks in this GAC, there are the functional groups of MC as binder representing O-H stretching of alcohol groups. This band could be observed that overlapped with N-H stretching groups of amine in wave number 3694.90-3426.78 cm⁻¹. Other bands are representing the functional groups of MC in wave number 938.56 cm⁻¹ representing C-O-C stretching of ethers. While, the functional

groups are refer to kaolin as reinforcer consists of silicon and peroxide groups. For silicon group, in wave numbers 1102.26-1008.74 cm^{-1} representing Si-O stretching. And peroxide groups, in wave number 912.41 cm^{-1} representing O-O stretching vibration. The others functional groups for this GAC product using MC as binder and kaolin as reinforcer are summarized in [Table 4.11](#).

Specific surface area

[Table 4.10](#) illustrate that the BET surface area was 769 $\text{m}^2 \text{g}^{-1}$. It was observed that the surface area decreased when compared with the original powdered activated carbon (up to 1239 $\text{m}^2 \text{g}^{-1}$) in [Section 4.1](#). The reduction in the surface area could occur as the porous structure of the carbon was being filled by the addition of MC and kaolin. The resulting in [Figure 4.11](#) illustrates N_2 adsorption-desorption isotherms at -196 °C on the GAC product. The isotherm shape was classifying with Type I, Which is still can say the well development in porosity on this GAC product with the porous volume were 69.0 and 31.0% micro- and mesopore, respectively.

Hardness number

[Table 4.10](#), indicates that the hardness number on final product was 80% with the weight proportion of MC:kaolin as 0.5:0.5. From the results, demonstrates the hardness increased with increasing proportion of MC close to 0.5 (by weight). In this experiment, the hardness number was relative moderate when compared with the prepared various binders and reinforcers. While, the hardness number for standard of the GAC is over 70% (TIS. 900-2004).

Bulk density and yield

For bulk density on this GAC product was 0.221 g cm^{-3} that shown in [Table 4.10](#), illustrates that decreased with increasing proportion of MC. The bulk density of MC and kaolin obtained from analyses were 0.345 g cm^{-3} and 0.606 g cm^{-3} , respectively. Also, the results in this GAC were considered the decreased when compared with the original powdered activated carbon (0.251 g cm^{-3}). For the standard of the GAC is over 0.200 g cm^{-3} (TIS. 900-2004). The yield of the final product was found that rather higher (up to 81.8%) which caused by the appropriate for proportion of MC:kaolin (0.5:0.5). This mean that well sticky in mixture and powdered activated carbon.

Ash content

As the results shown in [Table 4.10](#), it was illustrated the ash content increased with the amount of kaolin used as reinforcer. The ash content was the rather high

(10.1%) with the GAC product. While, the ash content were 0.50 and 88.5% for MC and kaolin, respectively. For kaolin, it was observed that their structural consists the mostly of metal salts and metal oxides caused by the highest ash content and this also affect to the high ash content in this GAC product.

pH

The result in [Table 4.10](#), illustrate that high pH of 8.52 with this GAC product. This reason could explained by the effect on MC (pH 10.6). With this condition, the pH of the product was increased with increasing the weight proportion of MC.

4.4.4 with Methyl cellulose (MC) as binder and Calcium carbonate as reinforcer

Finally, the GAC product was obtained using methyl cellulose (MC) as binder and calcium carbonate as reinforcer. The optimal weight proportion of binder and reinforcer (impregnation ratio) was 1:0 which, in fact, meant that calcium carbonate was not needed at all. The weight proportion of mixture (binder : reinforcer) to powdered activated carbon was, again, found at 20:80. Details of the properties of the GAC obtained in this case are described below.

Iodine and methylene blue numbers

The iodine and methylene blue numbers of the GAC were 655 and 276 mg g⁻¹, respectively as summarized in [Table 4.10](#). These were quite low when compared to the original powdered activated carbon of 917 and 427 mg g⁻¹ for iodine and methylene blue numbers. Similar explanation as in [Section 4.4.2](#) could be used in this case, i.e. the sorption capacities decreased with increasing the proportion of binder. In this case, MC as a binder exhibited the lowest adsorption capacity and still could block in the pore structure the GAC, reducing the adsorption efficiency. The morphology obtained by SEM as shown in [Figure 4.8\(d\)](#) illustrated that there existed a large amount of MC in the pore structure. [Figures 4.9\(d\)](#) and [4.10\(d\)](#) demonstrate the results analyzed by XRD and FT-IR which indicated the functional groups on surface of the GAC with this condition. The FT-IR spectra demonstrates that there were band shifts from the original PAC which were functional groups of amine and carboxylic acid groups. The clear band increased in the wave number for dominant peaks which indicated the functional groups of MC as binder. For N-H stretching in the amine group, there was a shift in the wave number from 3390.59 cm⁻¹ of the original PAC to 3427.59 cm⁻¹ of GAC. In carboxylic acid group (O-H stretching), there was a shift in the wave number from 2943.07 cm⁻¹ of original PAC to 2897.12-

2834.21 cm^{-1} of this GAC. Moreover, there was an increase in the dominate peaks in this GAC, which was the functional groups of MC, i.e. O-H stretching of alcohol groups. This band overlapped with N-H stretching groups of amine at the wave number of 3427.59 cm^{-1} . Ethers group (also from MC) was also visible at the wave number of 946.20 cm^{-1} (representing C-O-C stretching vibration). As previously described, the surface of activated carbon were mostly negative charged. In this case, the positive charge on the binder (MC) could be deposited on the surface of the final GAC product. Others functional groups are identified as shown in [Table 4.11](#).

Specific surface area

[Table 4.10](#) shows the results of the surface area on this GAC obtained by BET method which was 652 $\text{m}^2 \text{g}^{-1}$ with 64.4 and 35.6% micropore and mesopore, respectively. This was lower than when compared with other GAC products, particularly when compared with the original PAC which had the surface area of as high as 1239 $\text{m}^2 \text{g}^{-1}$ with 88.5 and 11.5% micro- and mesopore volume, respectively. The same explanation as in [Section 4.4.2](#) can be applied here.

Hardness number

[Table 4.10](#) demonstrates that the hardness increased with an increasing proportion of MC. In this work, the highest hardness number could be as high as 97% which was far higher than the requirement in the TIS standard of over 70%.

Bulk density and yield

Density and yield with this GAC product were analyzed and the results are displayed in [Table 4.10](#). The density slightly increased with increasing weight proportion of MC. The resulting bulk density was quite moderate at 0.269 g cm^{-3} which still complied with the standard of over 0.200 g cm^{-3} (TIS. 900-2004). In addition, the yield of 70.4% was considered moderate when compared with the various binders and reinforcers used in this research.

Ash content

The results shown in [Table 4.10](#) illustrated that ash content decreased with increasing ratio of MC. This is because MC had only 0.50% ash content and when this was mixed with the original PAC with ash content of 4.88% at the condition as used in this case, the resulting GAC had the ash content of around 3.88%.

pH

GAC product from this synthetic condition had a rather high pH of 8.60. This was due to the basic effect of MC as MC alone could exhibit the pH of as high as 10.6. Hence, the pH of GAC increased with increasing proportion of MC.

4.5 Comparison of the properties of various GAC products

This section provides a comparison of the properties on various GAC products obtained from the various fabrication methods. It is reminded here that the ratios between different binders and reinforcers that yielded the four GACs can be summarized again as follows: CMC/Kaolin (0.5:0.5), CMC/Calcium carbonate (1:0), MC/Kaolin (0.5:0.5) and MC/Calcium carbonate (1:0). It was observed that the best properties on the GAC was obtained when CMC was used as binder and kaolin as reinforcer, and the results are summarized in [Table 4.12](#).

[Table 4.13](#) illustrates that the best GAC product with this chemical activation method in this work had an iodine number of 686 mg g⁻¹. This was relative moderate when compared with those prepared from other activation processes. On the other hand, this carbon product had a relatively high surface area (up to 1085 m² g⁻¹) which was relatively high when compared with reported works using the same raw material. The differences could be due to several reasons such as different preparing methods and conditions. However, the hardness of the GAC product was only 75% which was still rather low when compared with those prepared from other raw materials such as tar (99%), cork waste (>95%) and fly ash (95%). However, this drawback is not considered significant as the hardness of all samples still complies well with TIS.900-2004 Standard.

In short, when compared the properties of the carbon with those reported values, it was clear that the properties of the carbon from this work is relatively good with reasonable high properties in all indicators.

Table 4.1 Proximate and ultimate properties of powdered activated carbon

Parameter	Value (% by weight)
<i>Proximate</i>	
Fixed carbon	65.3
Moisture content	7
Volatile matter	22.8
Ash content	4.88
<i>Ultimate</i>	
C	62
H	4
Other-N, O, S	34

Table 4.2 Properties of powdered activated carbon

Properties	Value
<i>Physical properties</i>	
Yield (%)	30.5
Bulk density (g cm ⁻³)	0.251
BET surface area (m ² g ⁻¹)	1239
- Micropore (%)	88.5
- Mesopore (%)	11.5
<i>Chemical properties</i>	
pH	6.50
Ash content (%)	4.88
<i>Adsorption properties</i>	
Iodine number (mg g ⁻¹)	917
Methylene blue number (mg g ⁻¹)	427

Table 4.3 FT-IR spectra result from powdered activated carbon

Assignment	Frequency (cm^{-1})
<i>Alcohols</i>	
O-H (stretching)	3390.59
O-H (bending-in plane)	1417.04
O-H (bending-out of plane)	709.54
C-O (stretching)	1200.85
<i>Amine</i>	
N-H (stretching)	3390.59
N-H (bending-in plane)	1590.93
<i>Amide</i>	
N-H (stretching)	3390.59
C-O (stretching)	1693.14
<i>Carboxylic acids</i>	
O-H (stretching)	2943.07, 2866.90
O-H (bending-in plane)	1417.04
COO ⁻ (stretching-asymmetric)	1590.93

Table 4.4 Properties of binders (Carboxymethyl cellulose and Methyl cellulose) and reinforcers (Kaolin and Calcium carbonate)

Properties	Value			
	Binders		Reinforcers	
	Carboxymethyl cellulose	Methyl cellulose	Kaolin	Calcium carbonate
Iodine number (mg g^{-1})	53	23	206	10
Methylene blue number (mg g^{-1})	5	2	51	1
Bulk density (g cm^{-3})	0.725	0.345	0.606	0.850
Ash content (%)	18.2	0.50	88.5	95.4
pH	7.28	10.6	5.69	11.2

Table 4.5 FT-IR spectra results from binders (Carboxymethyl cellulose and Methyl cellulose) and reinforcers (Kaolin and Calcium carbonate)

Assignment	Frequency (cm ⁻¹)			
	Binders		Reinforcers	
	Carboxymethyl cellulose	Methyl cellulose	Kaolin	Calcium carbonate
<i>Alkanes</i>				
C-H (stretching)	2922.19	2837.18	-	-
<i>Alcohols</i>				
O-H (stretching)	3435.03	3465.75	3695.86, 3442.19	-
O-H (bending-in plane)	1418.19, 1327.18, 1267.68	1408.58, 1375.57	-	-
O-H (bending-out of plane)	595.81	567.48	696.98, 470.38	-
C-O (stretching)	1052.51	1064.00	1031.66	-
<i>Carboxylic acids</i>				
OC-OH (bending-out of plane)	897.38	-	-	-
COO ⁻ (stretching-asymmetric)	1606.55	-	-	-
<i>Amino acids</i>				
O-H (stretching)	2146.93	2399.21, 2059.96	-	-
COO ⁻ (stretching-asymmetric)	-	1633.52	-	-
<i>Ethers</i>				
C-O-C (stretching)	-	945.09	-	-

Table 4.5 (Continued)

Assignment	Frequency (cm ⁻¹)			
	Binders		Reinforcers	
	Carboxymethyl cellulose	Methyl cellulose	Kaolin	Calcium carbonate
<i>Aluminum compounds</i>				
Al-O (stretching)	-	-	1823.51, 1629.67	-
<i>Peroxides</i>				
O-O (stretching)	-	-	912.60	-
<i>Silicon compounds</i>				
Si-O (stretching)	-	-	1112.51, 1008.20	-
<i>Carbonyl compounds</i>				
C=O (stretching)	-	-	-	1797.29
<i>Inorganic compounds</i>				
Ca-O (stretching)	-	-	-	1462.81

Table 4.6 Properties of the GAC products obtained from the fabrication at various proportion of binder (CMC) and reinforcer (Kaolin)

Samples	Proportion	Properties							
	(binder : reinforcer)	Iodine	Methylene	BET	Hardness	Bulk	Ash	pH	Yield
	CMC : Kaolin	number	blue	surface	number	density	content		(%)
		(mg g ⁻¹)	number	area	(%)	(g cm ⁻³)	(%)		
			(mg g ⁻¹)	(m ² g ⁻¹)					
1	1 : 0	655	276	-	92	0.270	6.16	6.90	61.7
2	0.7 : 0.3	662	288	-	84	0.253	9.46	6.80	63.3
3	0.625 : 0.375	669	295	-	80	0.231	10.7	6.80	62.2
4	0.583 : 0.417	676	297	-	78	0.229	11.5	6.70	63.0
5	0.5 : 0.5	686	310	1,085	75	0.214	12.7	6.67	62.7
6	0.417 : 0.583	690	315	-	63	0.207	15.8	6.50	61.4
7	0.375 : 0.625	692	318	-	51	0.185	19.5	6.40	52.1
8	0.3 : 0.7	696	322	-	40	0.172	22.4	6.30	45.1
9	0 : 1	729	331	-	13	0.169	29.4	6.00	43.4

Table 4.7 Properties of the GAC products obtained from the fabrication at various proportion of binder (CMC) and reinforcer (Calcium carbonate)

Samples	Proportion	Properties							
	(binder : reinforcer)	Iodine number (mg g ⁻¹)	Methylene blue number (mg g ⁻¹)	BET surface area (m ² g ⁻¹)	Hardness number (%)	Bulk density (g cm ⁻³)	Ash content (%)	pH	Yield (%)
1	1 : 0	662	281	657	92	0.270	6.16	6.90	61.7
2	0.7 : 0.3	631	261	-	35	0.254	9.90	7.14	80.8
3	0.625 : 0.375	629	258	-	29	0.247	10.3	7.35	79.5
4	0.583 : 0.417	628	255	-	25	0.240	13.0	7.96	80.2
5	0.5 : 0.5	627	253	-	23	0.235	13.9	8.26	81.9
6	0.417 : 0.583	626	248	-	20	0.232	15.7	8.28	80.5
7	0.375 : 0.625	624	243	-	18	0.229	17.2	8.33	82.7
8	0.3 : 0.7	623	240	-	12	0.226	18.9	8.35	80.8
9	0 : 1	616	235	-	1	0.219	21.4	10.9	40.2

Table 4.8 Properties of the GAC products obtained from the fabrication at various proportion of binder (MC) and reinforcer (Kaolin)

Samples	Proportion (binder : reinforcer)	Properties							
	MC : Kaolin	Iodine number (mg g ⁻¹)	Methylene blue number (mg g ⁻¹)	BET surface area (m ² g ⁻¹)	Hardness number (%)	Bulk density (g cm ⁻³)	Ash content (%)	pH	Yield (%)
1	1 : 0	651	270	-	97	0.269	3.88	8.60	70.3
2	0.7 : 0.3	657	278	-	95	0.252	6.31	8.53	77.2
3	0.625 : 0.375	660	288	-	89	0.237	7.01	8.53	78.4
4	0.583 : 0.417	664	293	-	84	0.228	8.98	8.52	80.6
5	0.5 : 0.5	672	305	769	80	0.221	10.1	8.52	81.8
6	0.417 : 0.583	682	311	-	71	0.215	13.7	8.51	81.5
7	0.375 : 0.625	693	317	-	63	0.211	15.5	8.51	80.9
8	0.3 : 0.7	713	320	-	52	0.201	19.8	8.50	80.8
9	0 : 1	720	322	-	13	0.169	20.8	6.00	43.4

Table 4.9 Properties of the GAC products obtained from the fabrication at various proportion of binder (MC) and reinforcer (Calcium carbonate)

Samples	Proportion (binder : reinforcer)	Properties							
	MC : CaCO ₃	Iodine number (mg g ⁻¹)	Methylene blue number (mg g ⁻¹)	BET surface area (m ² g ⁻¹)	Hardness number (%)	Bulk density (g cm ⁻³)	Ash content (%)	pH	Yield (%)
1	1 : 0	655	276	652	97	0.269	3.88	8.60	70.4
2	0.7 : 0.3	647	268	-	47	0.256	7.78	9.80	70.7
3	0.625 : 0.375	643	261	-	34	0.256	10.0	10.1	70.9
4	0.583 : 0.417	639	254	-	32	0.255	11.3	10.2	71.0
5	0.5 : 0.5	631	249	-	20	0.252	14.6	10.5	72.0
6	0.417 : 0.583	627	243	-	13	0.245	15.3	10.6	73.7
7	0.375 : 0.625	623	240	-	12	0.238	16.0	10.7	73.7
8	0.3 : 0.7	619	238	-	1	0.237	17.7	10.8	73.8
9	0 : 1	615	235	-	1	0.219	21.4	10.9	40.2

Table 4.10 Properties of the best GAC products at various binders and reinforcers

Properties	Value			
	CMC:Kaolin (0.5:0.5)	CMC:Calcium carbonate (1:0)	MC:Kaolin (0.5:0.5)	MC:Calcium carbonate (1:0)
<i>Physical properties</i>				
Yield (%)	62.7	61.7	81.8	70.4
Bulk density (g cm ⁻³)	0.214	0.270	0.221	0.269
BET surface area (m ² g ⁻¹)	1085	657	769	652
- Micropore (%)	80.9	65.3	69.0	64.4
- Mesopore (%)	19.1	34.7	31.0	35.6
Hardness number (%)	75	92	80	97
<i>Chemical properties</i>				
pH	6.67	6.90	8.52	8.60
Ash content (%)	12.7	6.16	10.1	3.88
<i>Adsorption properties</i>				
Iodine number (mg g ⁻¹)	686	662	672	655
Methylene blue number (mg g ⁻¹)	310	281	305	276

Table 4.11 FT-IR spectra results from the best GAC products at various binders and reinforcers

Assignment	Frequency (cm ⁻¹)			
	CMC:Kaolin (0.5:0.5)	CMC:Calcium carbonate (1:0)	MC:Kaolin (0.5:0.5)	MC:Calcium carbonate (1:0)
<i>Alkanes</i>				
C-H (stretching)	2915.51, 2851.80	2856.06	2893.32, 2833.19	2897.12, 2834.21
<i>Alcohols</i>				
O-H (stretching)	3418.56	3410.56	3694.90, 3426.78	3427.59
O-H (bending-in plane)	1406.76	1407.12	-	-
O-H (bending-out of plane)	537.13, 695.68	-	696.56, 537.20	-
C-O (stretching)	1031.70	1052.60	1031.80	1062.79
<i>Amine</i>				
N-H (stretching)	3418.56	3410.56	3426.78	3427.59
N-H (bending-in plane)	1586.53	1587.46	1587.11	1590.66
<i>Amide</i>				
N-H (stretching)	3418.56	3410.56	3426.78	3427.59
C-O (stretching)	1700.52	1690.73	1697.40	1700.40
<i>Ethers</i>				
C-O-C (stretching)	-	-	938.56	946.20

Table 4.11 (Continued)

Assignment	Frequency (cm ⁻¹)			
	CMC:Kaolin (0.5:0.5)	CMC:Calcium carbonate (1:0)	MC:Kaolin (0.5:0.5)	MC:Calcium carbonate (1:0)
<i>Carboxylic acids</i>				
O-H (stretching)	2915.54, 2851.80	2858.06	2893.32, 2833.19	2897.12, 2834.21
O-H (bending-in plane)	-	1407.12	1447.26	1447.90
COO ⁻ (stretching-asymmetric)	1586.53	1587.46	-	-
<i>Peroxides</i>				
O-O (stretching)	912.07	-	912.41	-
<i>Silicon compounds</i>				
Si-O (stretching)	1100.13, 1008.59	-	1102.26, 1008.74	-

Table 4.12 Comparison for the properties of the best GAC products at various binders and reinforcers obtained from this work with Thai Industrial Standard (TIS.900-2004) and commercial grade GAC (Carbokarn Co., Ltd.)

Granular activated carbon	Properties						
	Iodine number (mg g ⁻¹)	Methylene blue number (mg g ⁻¹)	BET surface area (m ² g ⁻¹)	Hardness number (%)	Bulk density (g cm ⁻³)	Ash content (%)	pH
CMC:Kaolin (0.5:0.5)	686	310	1085	75	0.214	12.7	6.67
CMC:Calcium carbonate (1:0)	662	281	657	92	0.270	6.16	6.90
MC:Kaolin (0.5:0.5)	672	305	769	80	0.221	10.1	8.52
MC:Calcium carbonate (1:0)	655	276	652	97	0.269	3.88	8.60
Commercial grade (Carbokarn Co., Ltd.)	≥ 950	-	≥ 1000	≥ 98	0.500	≤ 3.50	9-11
Thai Industrial Standard (TIS.900-2004)	≥ 600	-	900-1100	≥ 70	≥ 0.200	-	-

Table 4.13 Comparison for the properties of the best GAC products at various binders and reinforcers obtained from this work with the other recent works

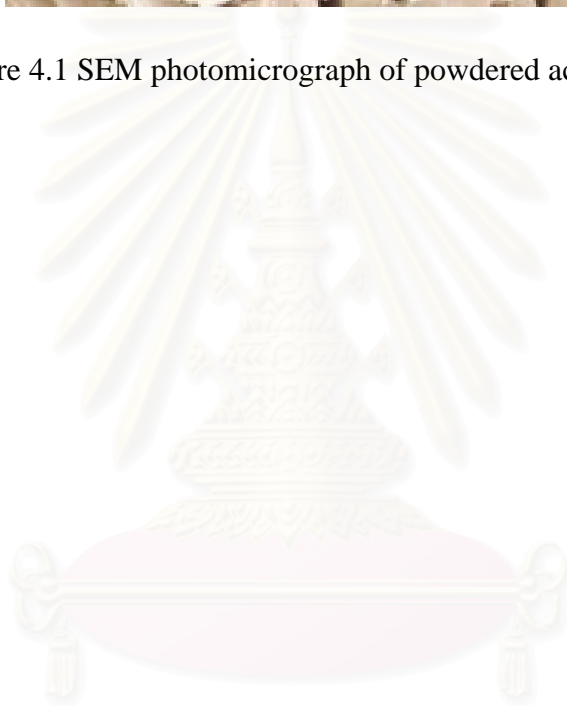
Raw materials	Binders	Reinforcers	Method of activation	Properties of granular activated carbon				References
				Iodine number	Methylene blue number	BET surface area	Hardness number	
				(mg g ⁻¹)	(mg g ⁻¹)	(m ² g ⁻¹)	(%)	
Rice husk	water	-	Chemical	1232	-	1136	>95	Usmani et al., 1994
Sugarcane bagasse	coal tar	-	Physical	-	-	165	65	Pendyal et al., 1999
Sugarcane bagasse	corn syrup	-	Physical	-	-	337	80	Ahmedna et al., 2000
Tar	polyvinyl butyral (PVB)	dibutyl phthalate (DBP)	Physical	-	-	1052	99	Qiao et al., 2001
Eucalyptus grandis sawdust	CMC	kaolin	Physical	-	-	450	-	Trancredi et al., 2004
Cork waste	clays	-	Chemical	903	-	-	>95	Carvalho et al., 2006
Fly ash	water	coal tar	Chemical	835	-	744	95	Li et al., 2006

Table 4.13 (Continued)

Raw materials	Binders	Reinforcers	Method of activation	Properties of granular activated carbon				References
				Iodine number	Methylene blue number	BET surface area	Hardness number	
				(mg g ⁻¹)	(mg g ⁻¹)	(m ² g ⁻¹)	(%)	
Eucalyptus bark	CMC	kaolin	Chemical	686	310	1085	75	This work
Eucalyptus bark	CMC	calcium carbonate	Chemical	662	281	657	92	This work
Eucalyptus bark	MC	kaolin	Chemical	672	305	769	80	This work
Eucalyptus bark	MC	calcium carbonate	Chemical	655	276	652	97	This work



Figure 4.1 SEM photomicrograph of powdered activated carbon



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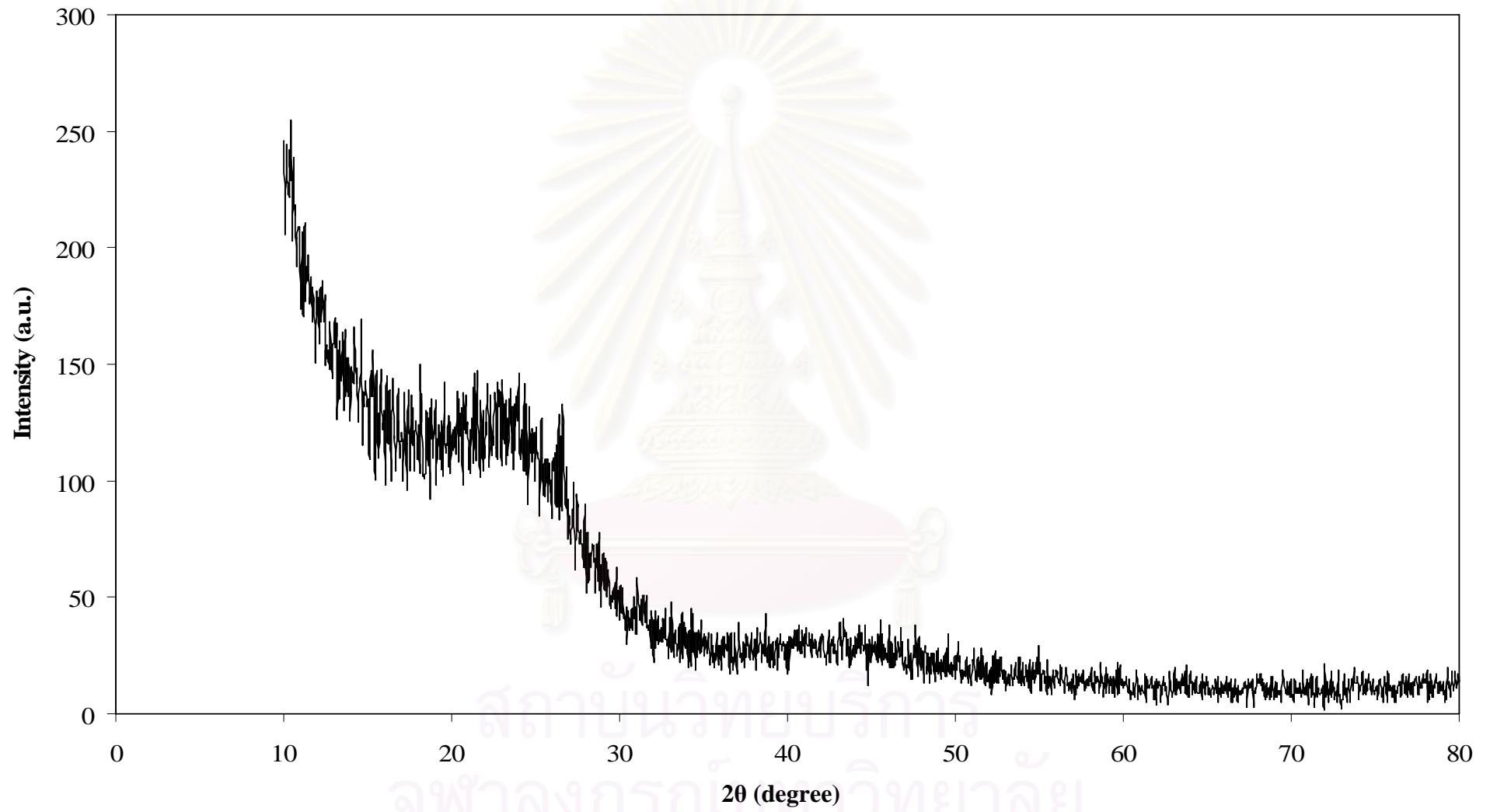


Figure 4.2 XRD pattern of powdered activated carbon

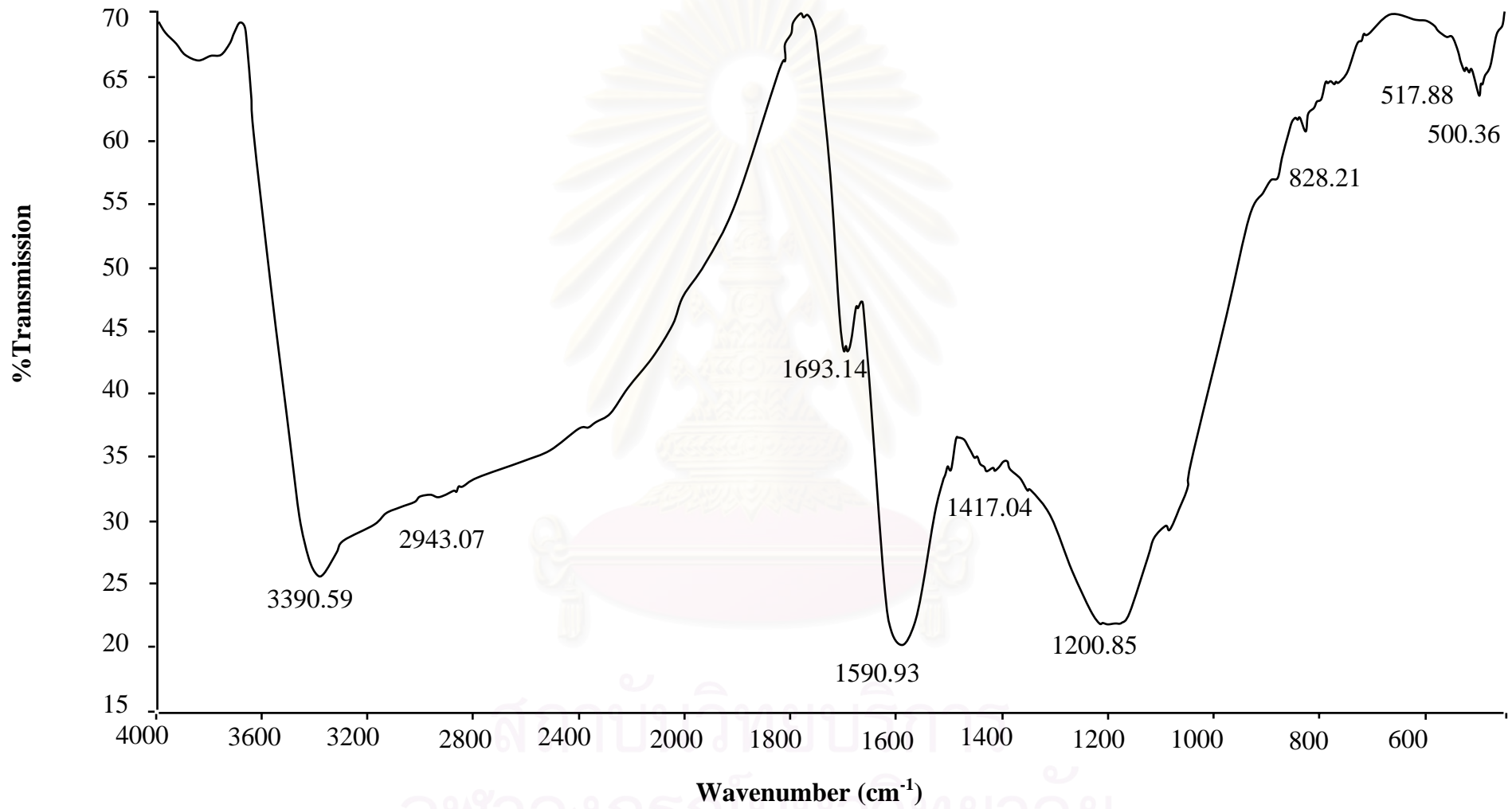


Figure 4.3 FT-IR transmission spectra of powdered activated carbon

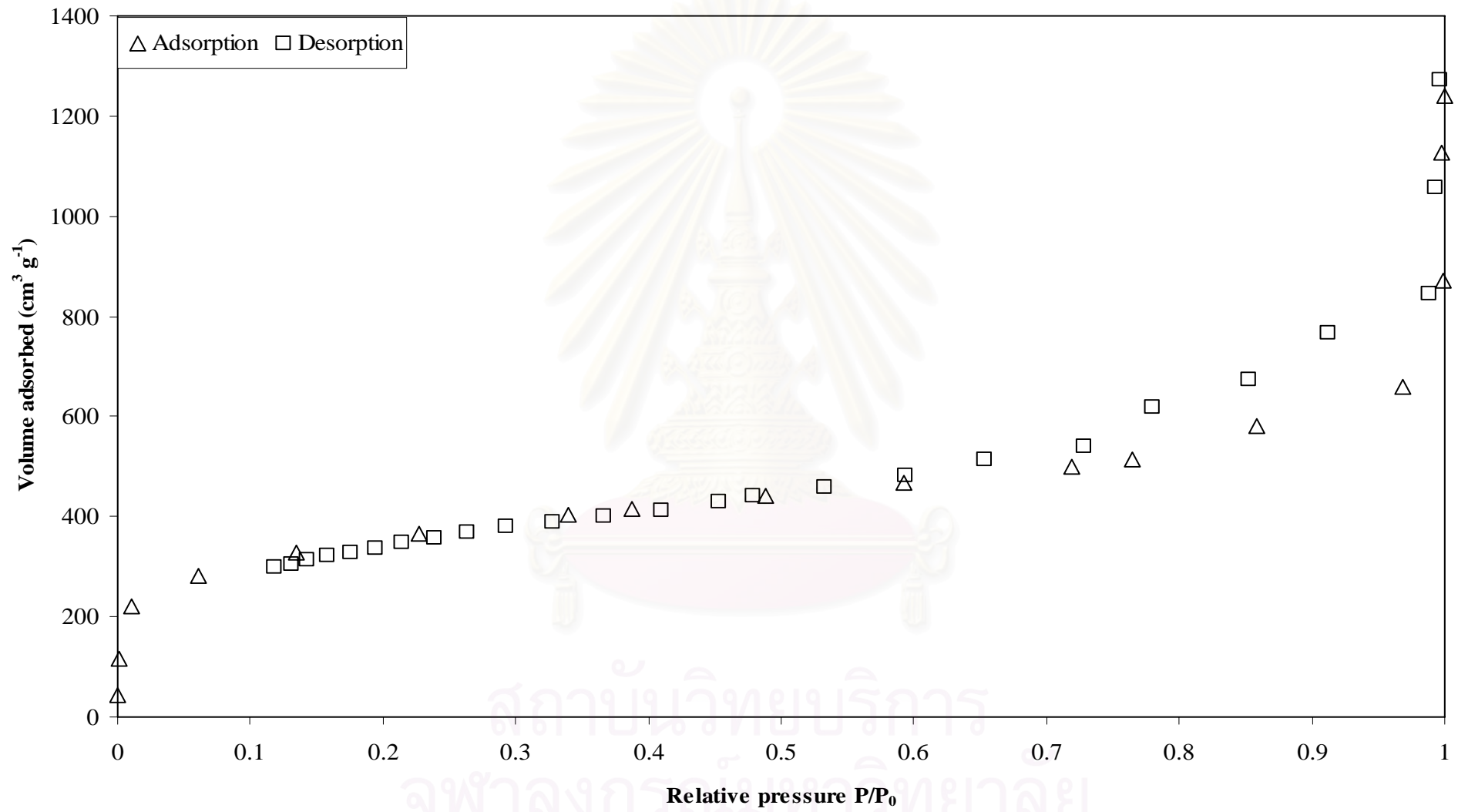
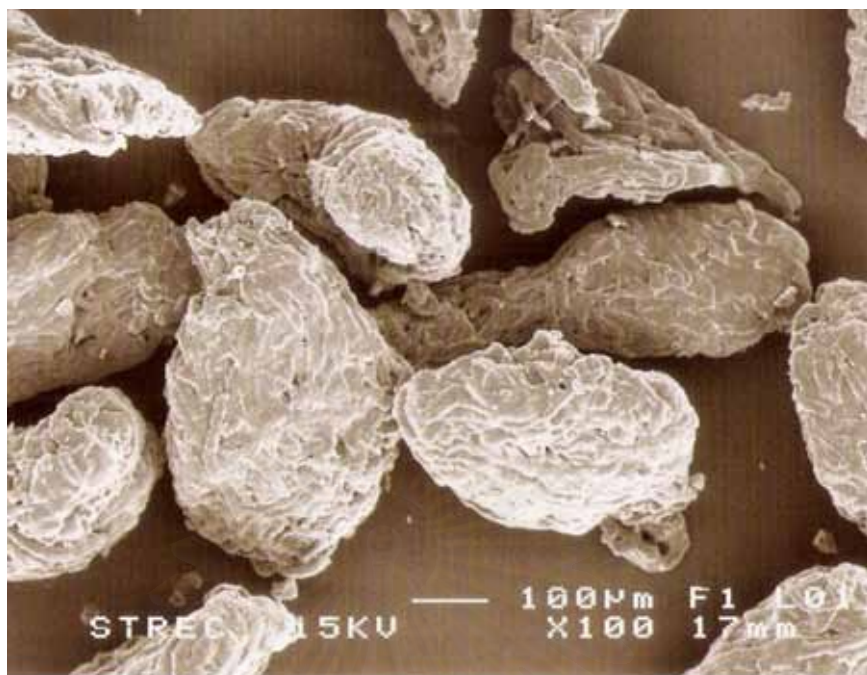
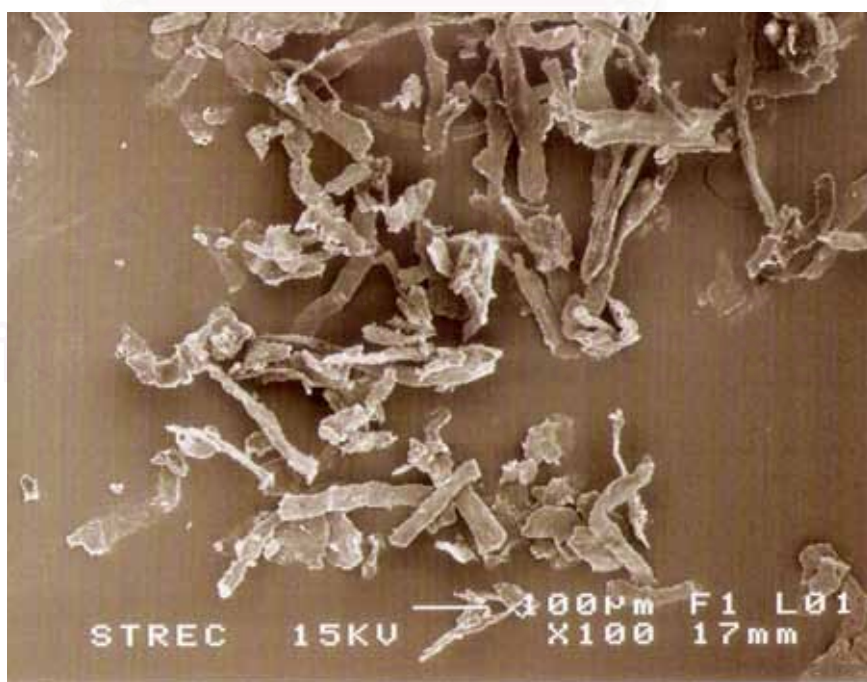


Figure 4.4 N₂ adsorption and desorption isotherms at -196 °C on powdered activated carbon



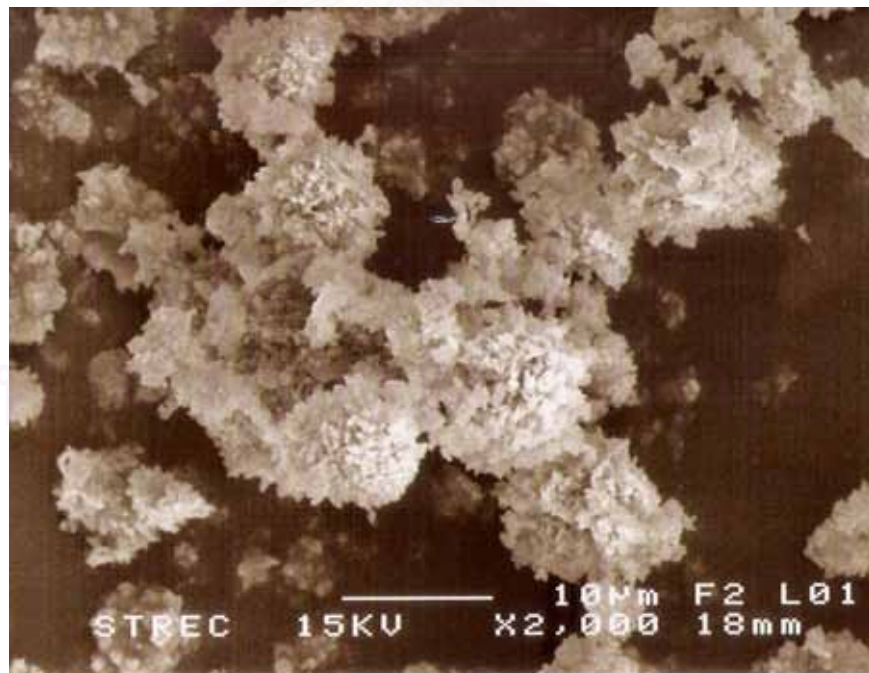
(a) Carboxymethyl cellulose



(b) Methyl cellulose

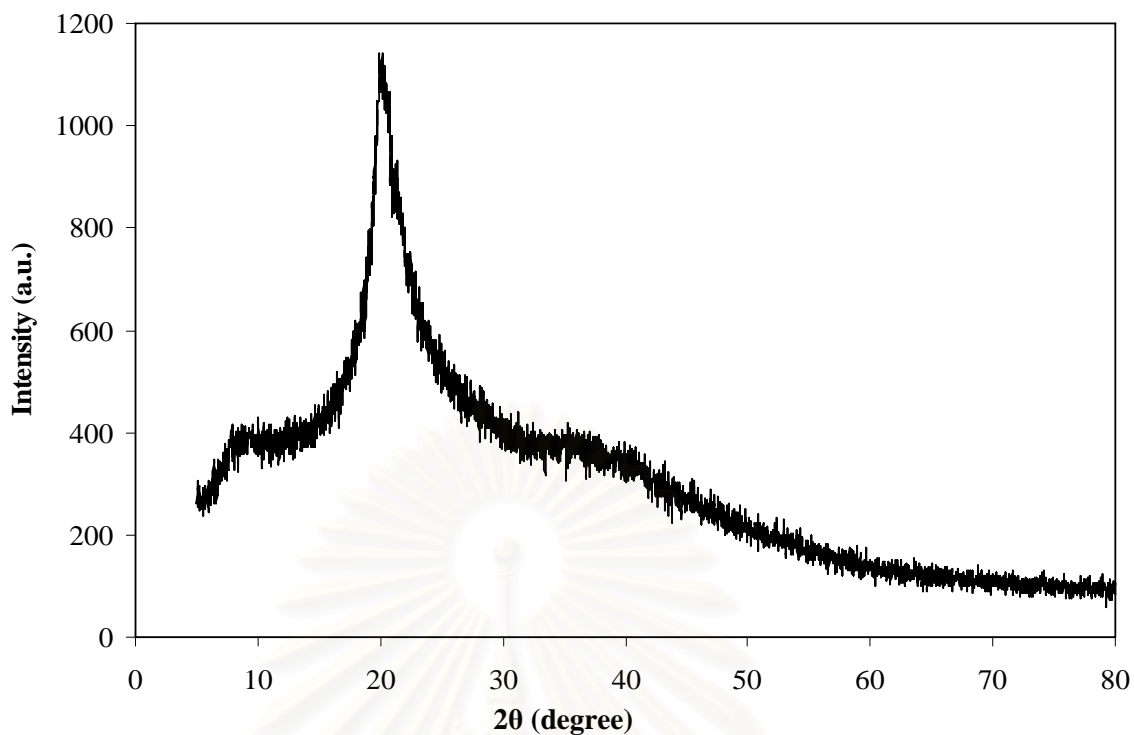


(c) Kaolin

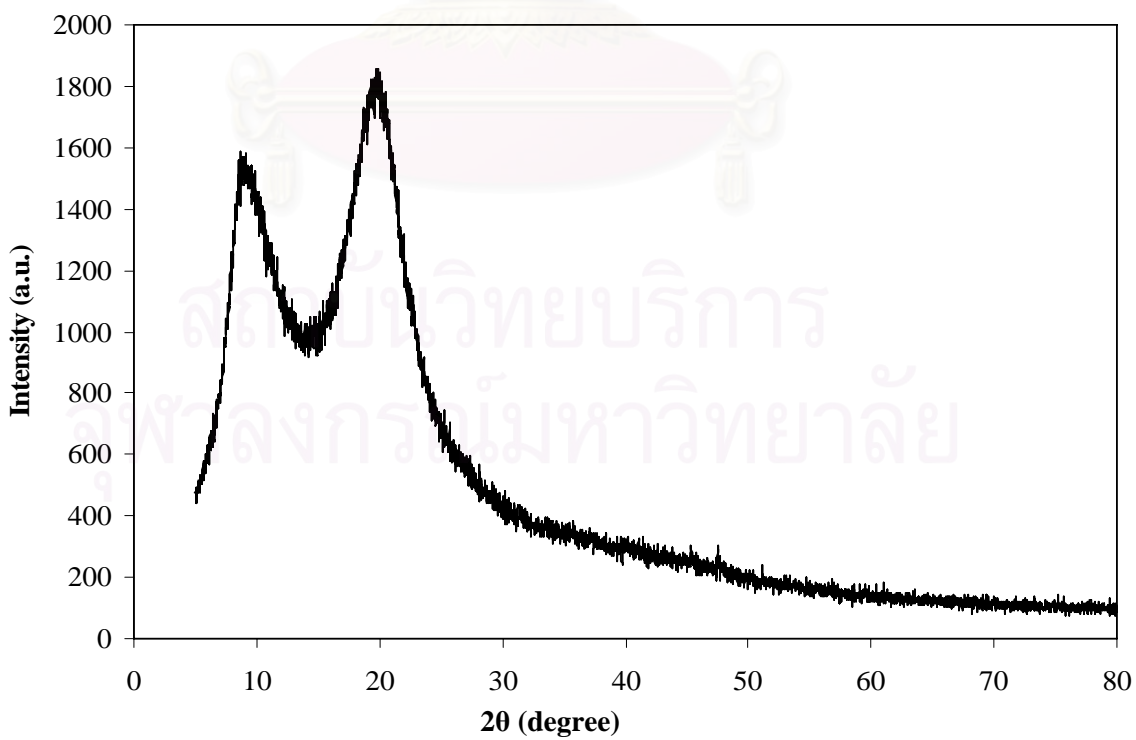


(d) Calcium carbonate

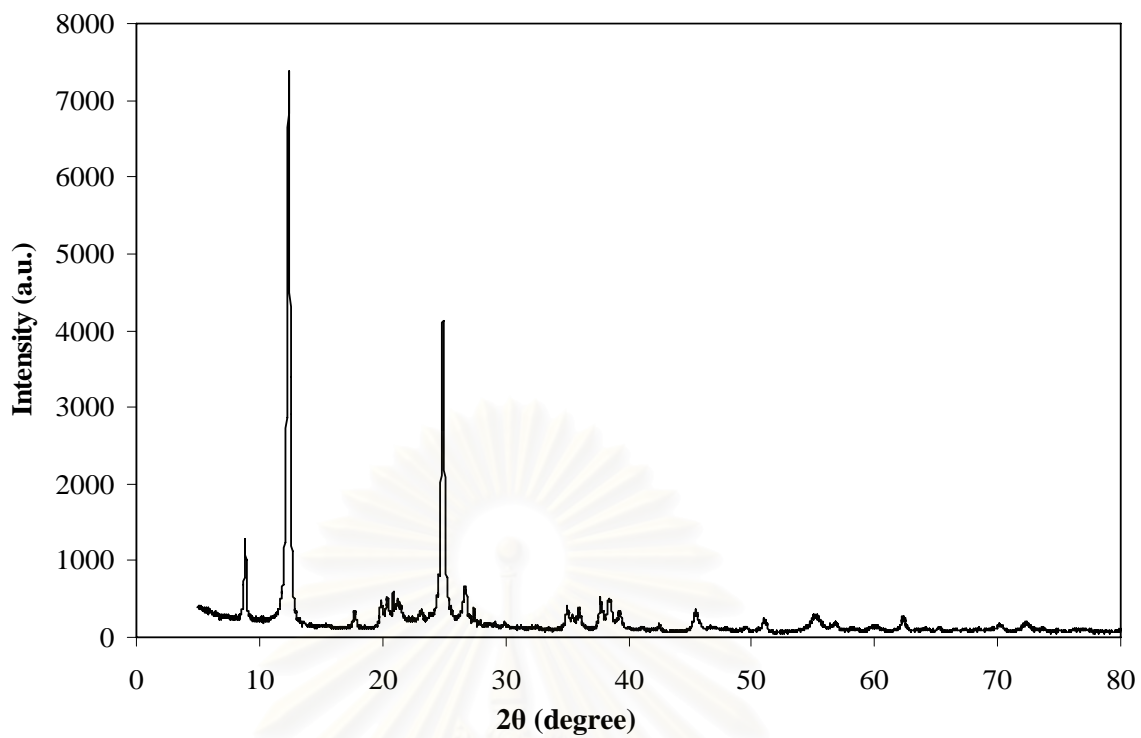
Figure 4.5 SEM photomicrographs for binders and reinforcers



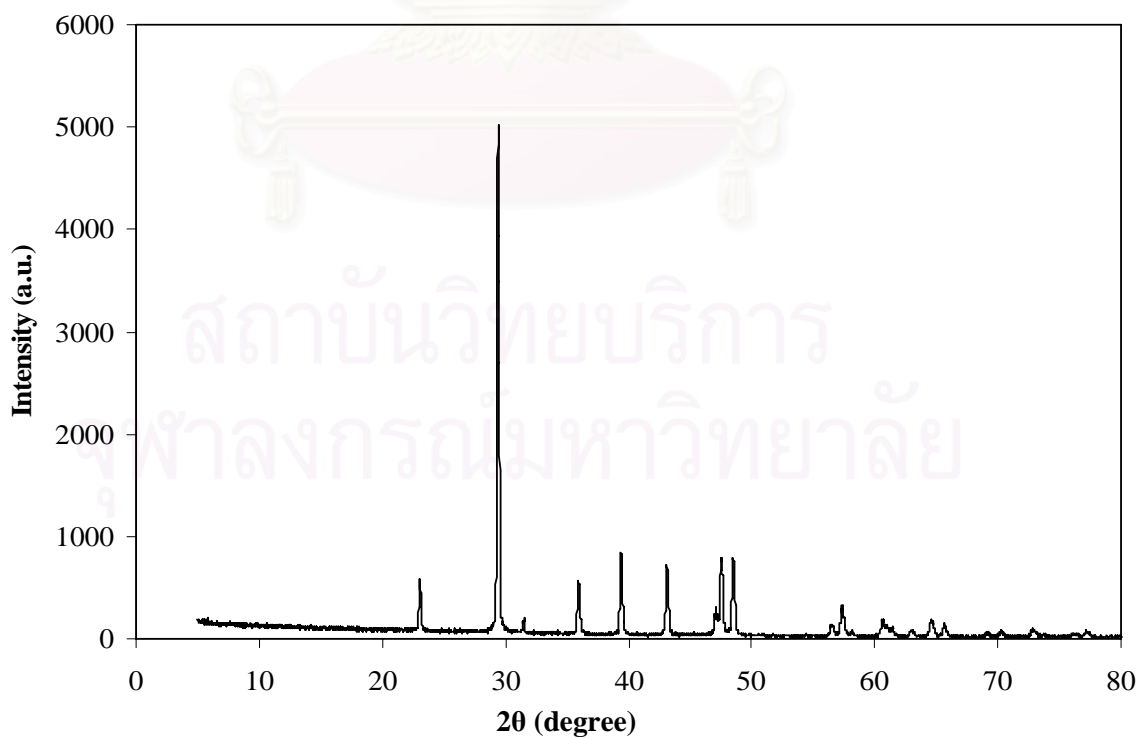
(a) Carboxymethyl cellulose



(b) Methyl cellulose

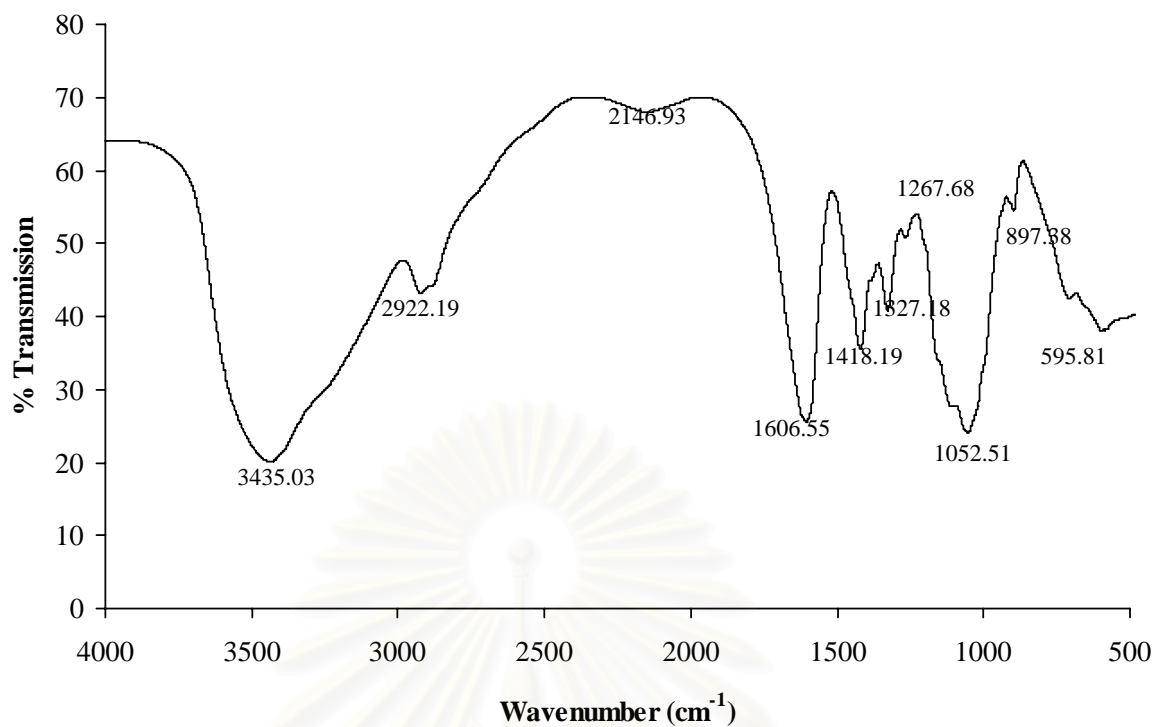


(c) Kaolin

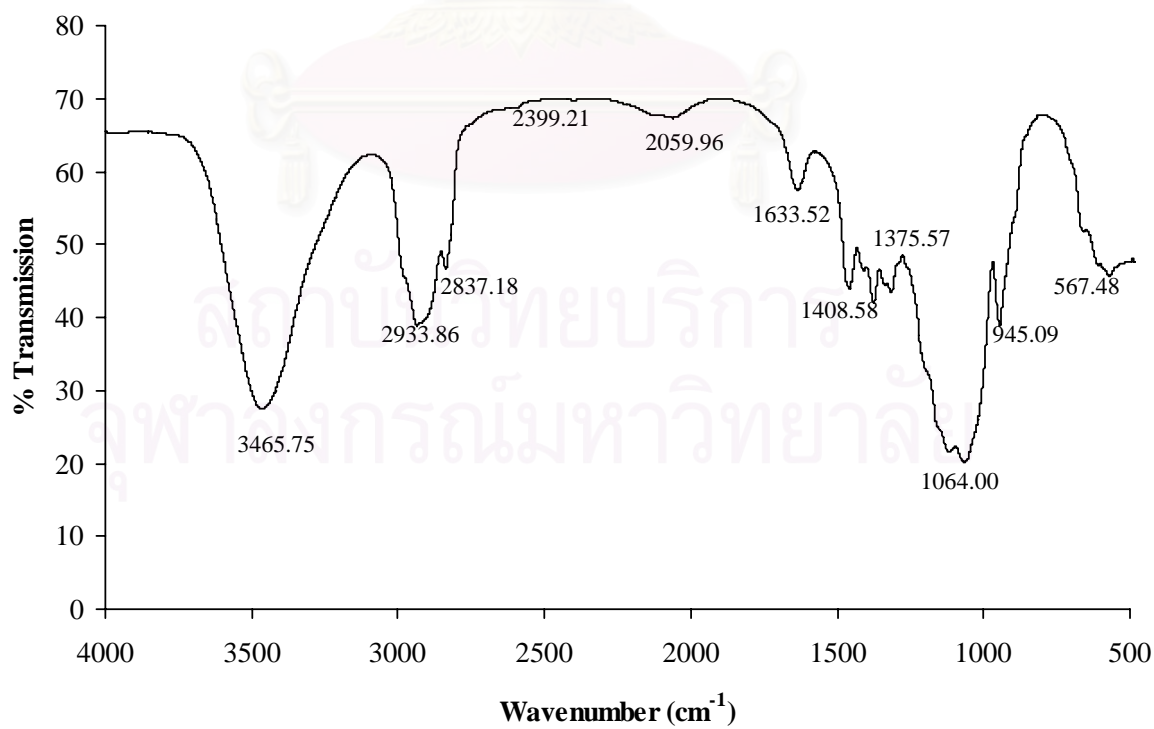


(d) Calcium carbonate

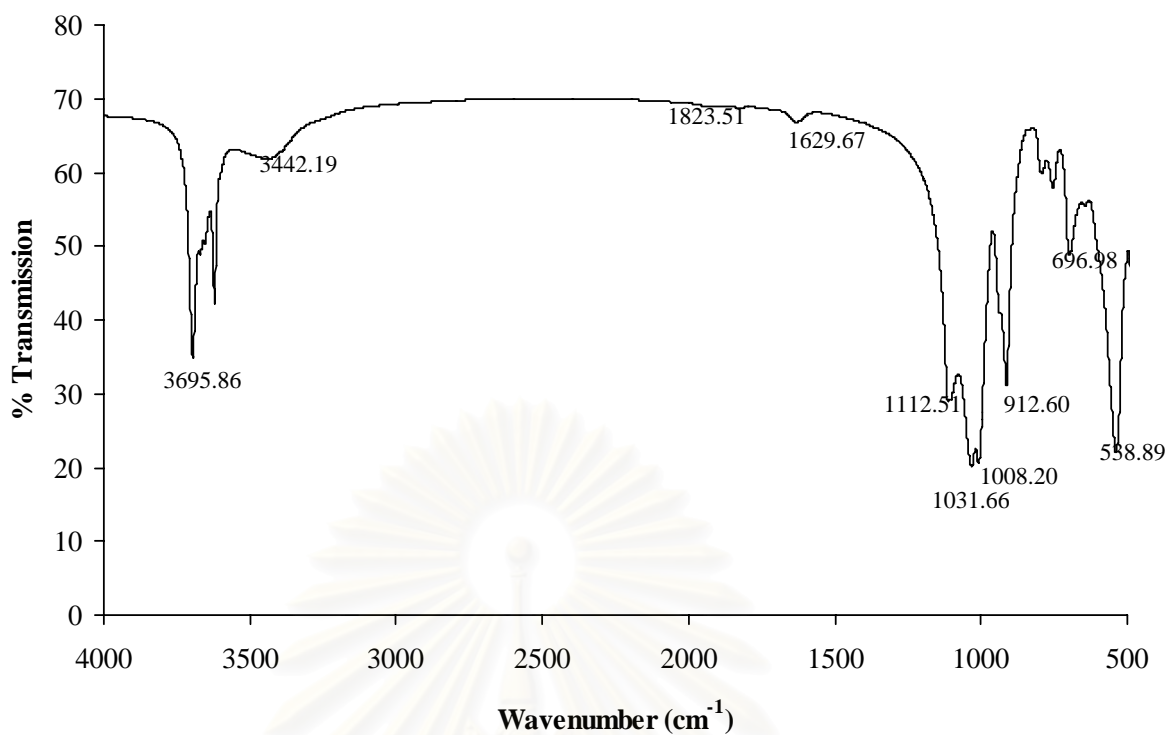
Figure 4.6 XRD patterns for binders and reinforcers



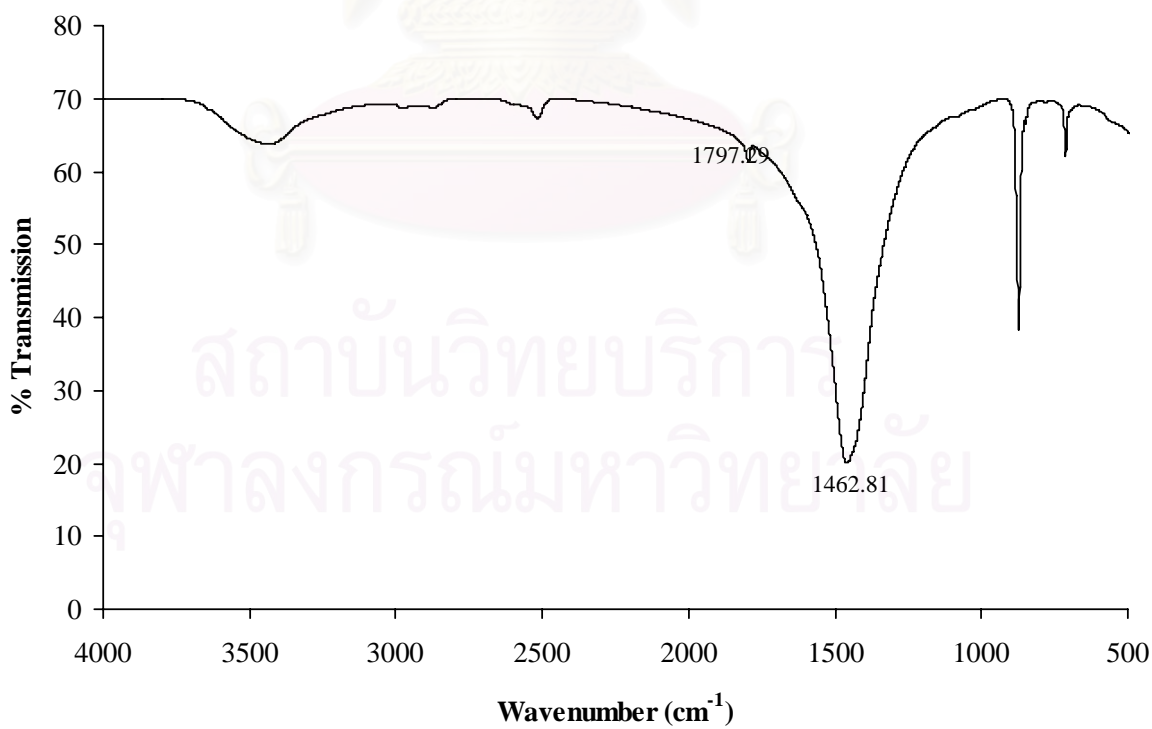
(a) Carboxymethyl cellulose



(b) Methyl cellulose

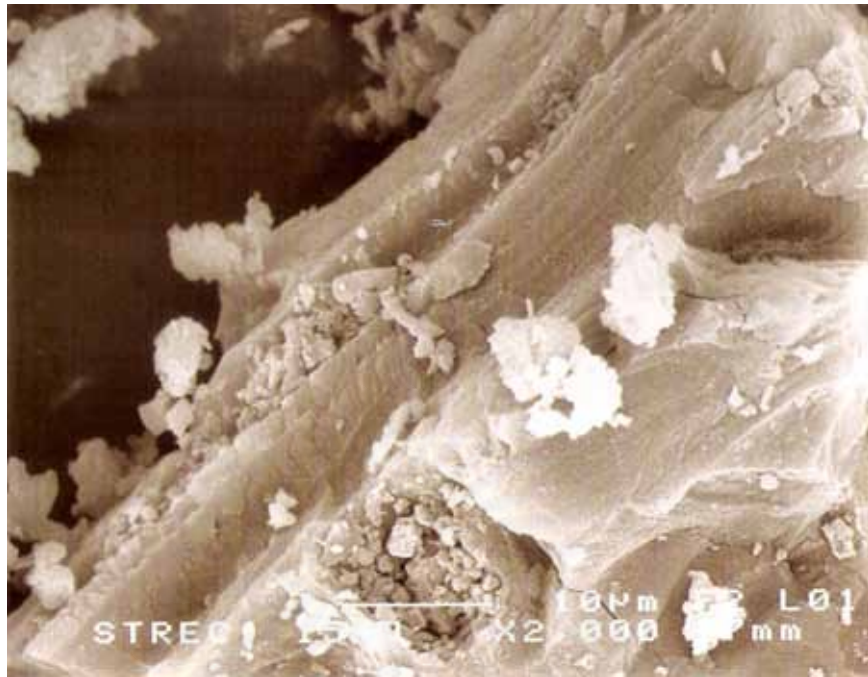


(c) Kaolin

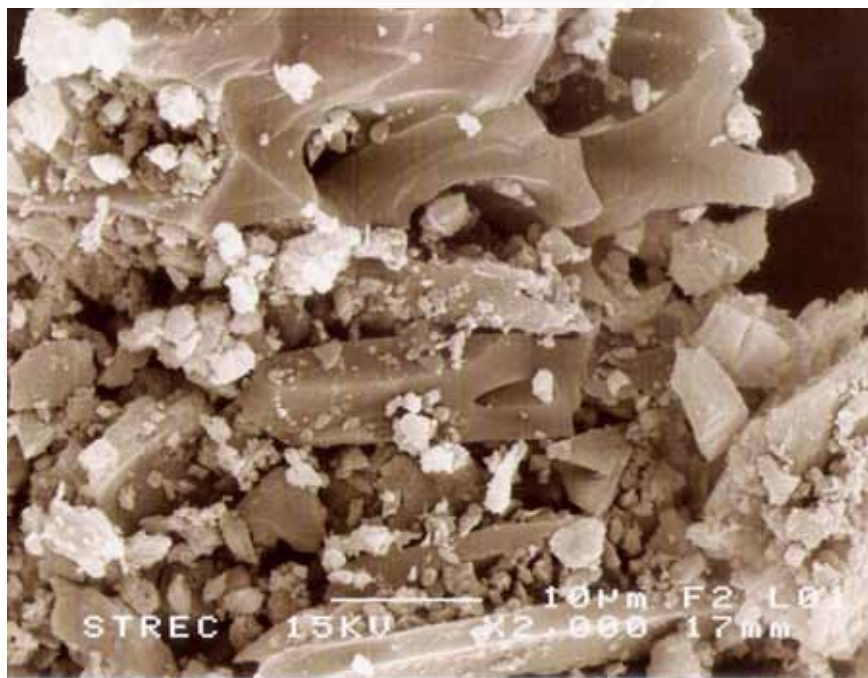


(d) Calcium carbonate

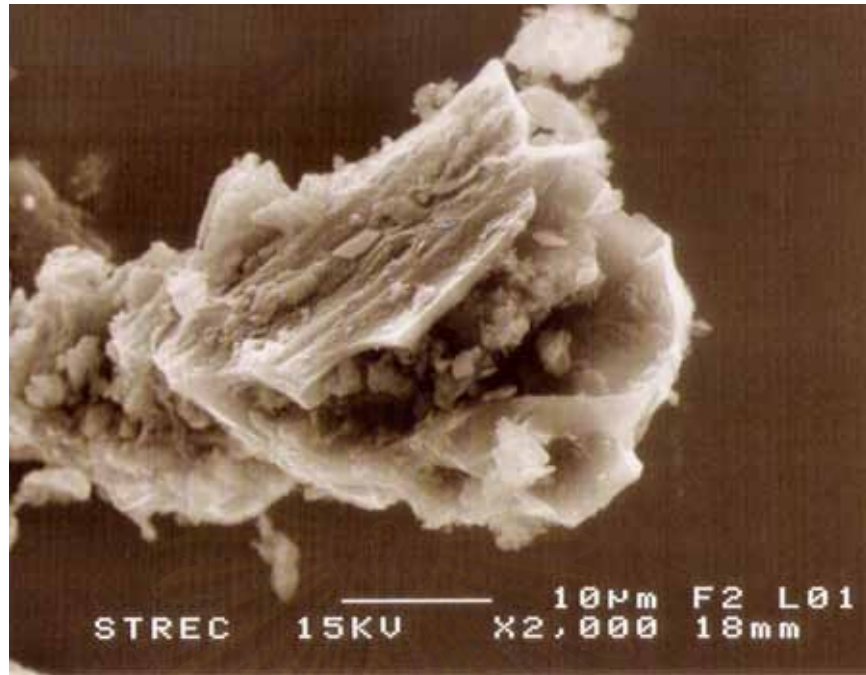
Figure 4.7 FT-IR transmission spectra for binders and reinforcers



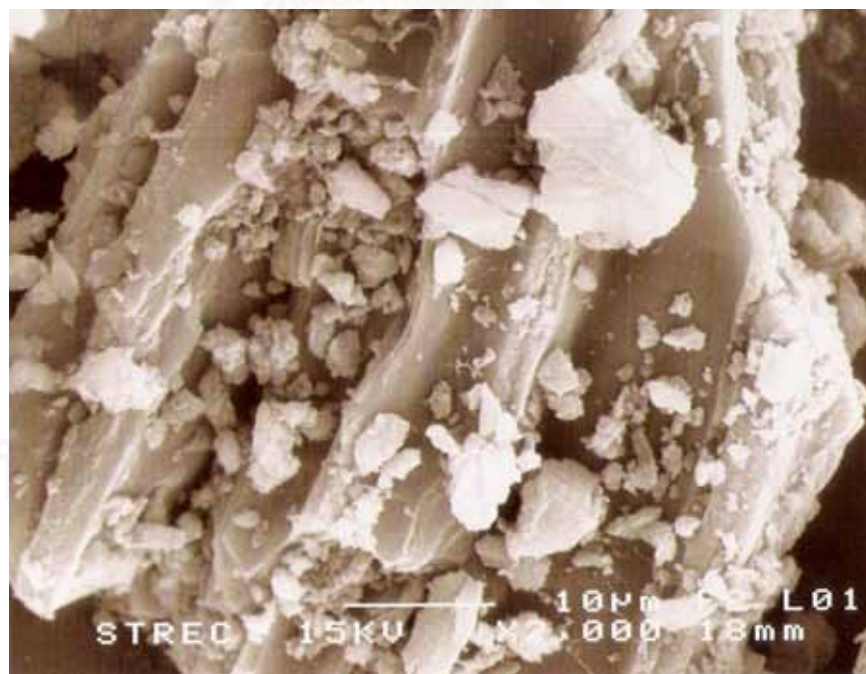
(a) Carboxymethyl cellulose : Kaolin



(b) Carboxymethyl cellulose : Calcium carbonate

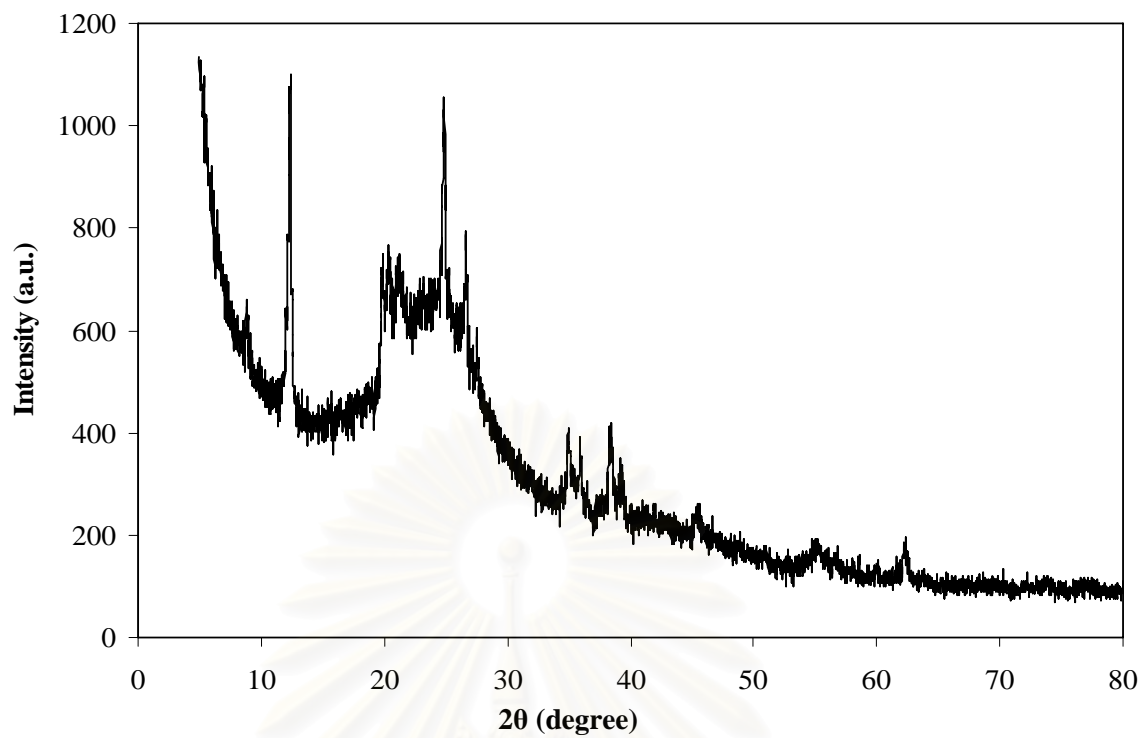


(c) Methyl cellulose : Kaolin

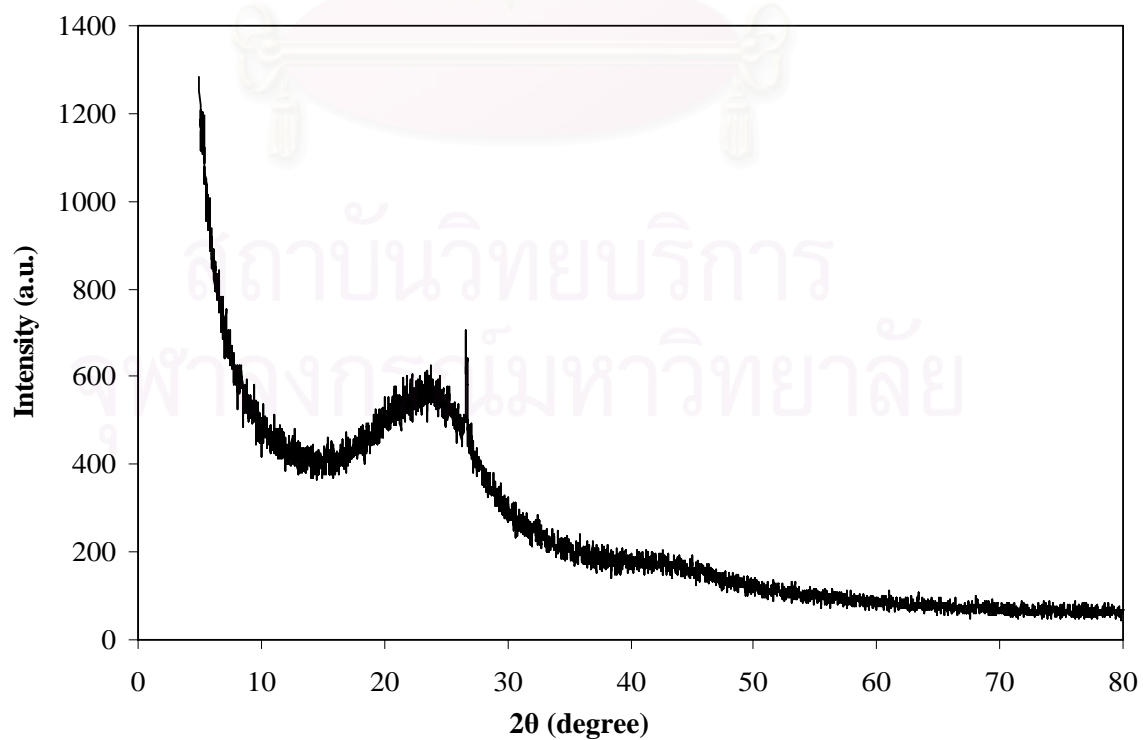


(d) Methyl cellulose : Calcium carbonate

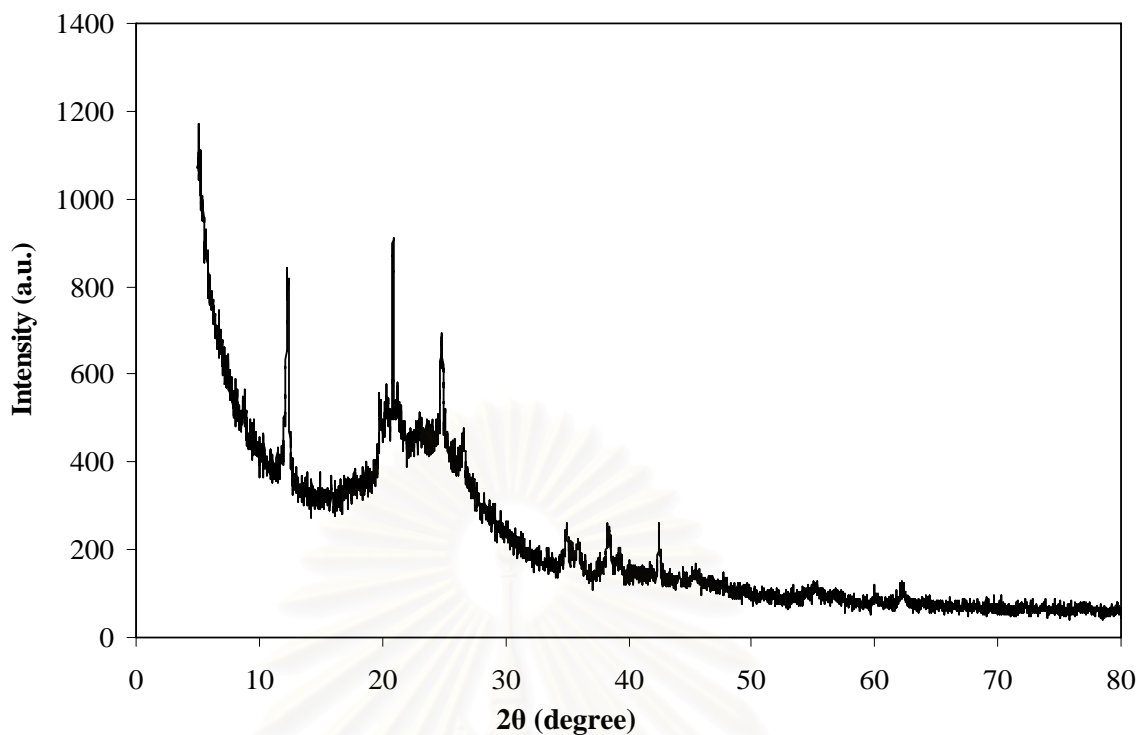
Figure 4.8 SEM photomicrographs for the GAC products with various binders and reinforcers



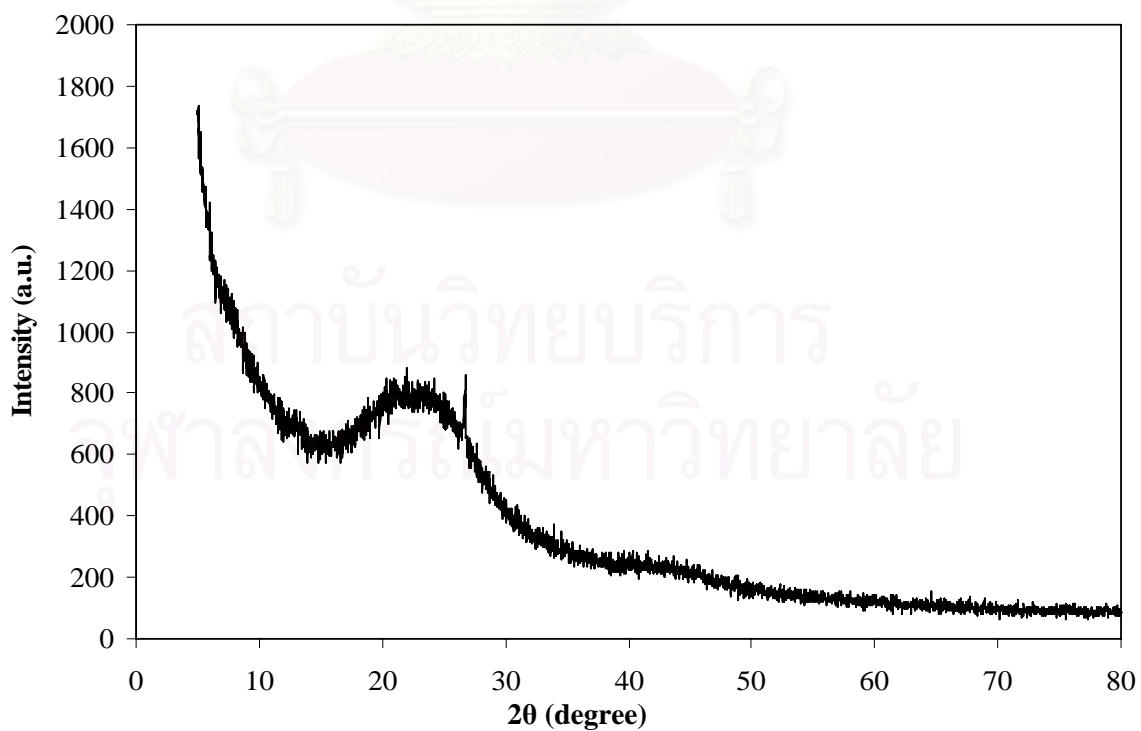
(a) Carboxymethyl cellulose : Kaolin



(b) Carboxymethyl cellulose : Calcium carbonate

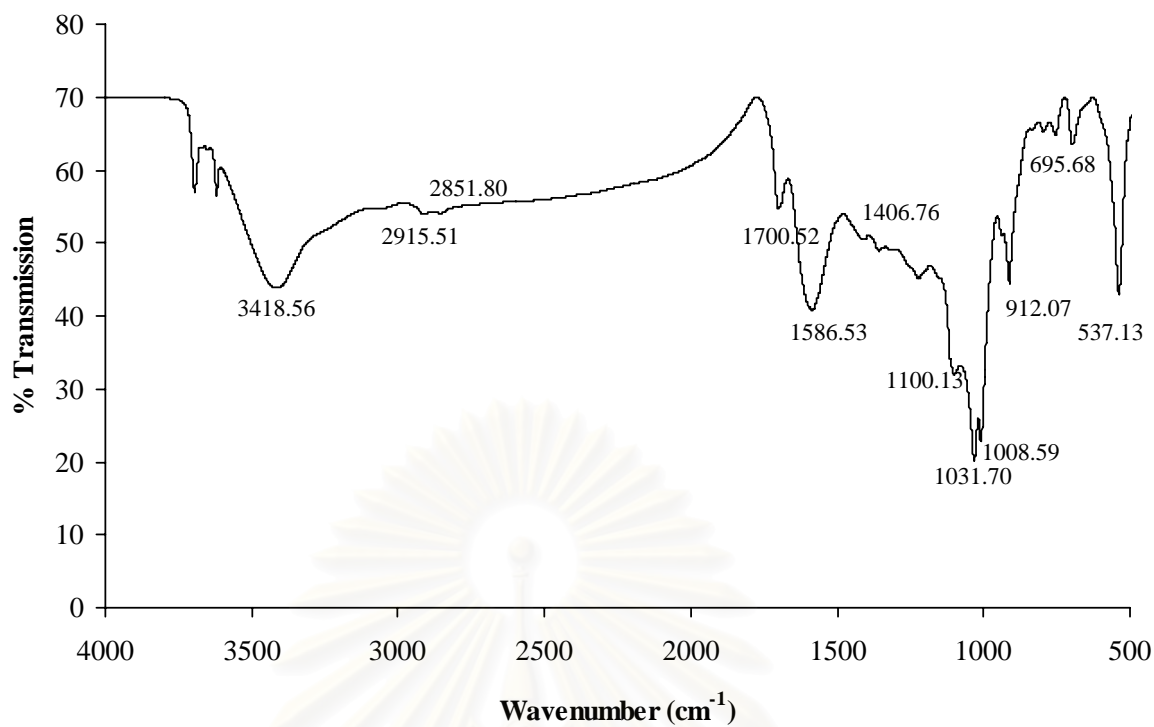


(c) Methyl cellulose : Kaolin

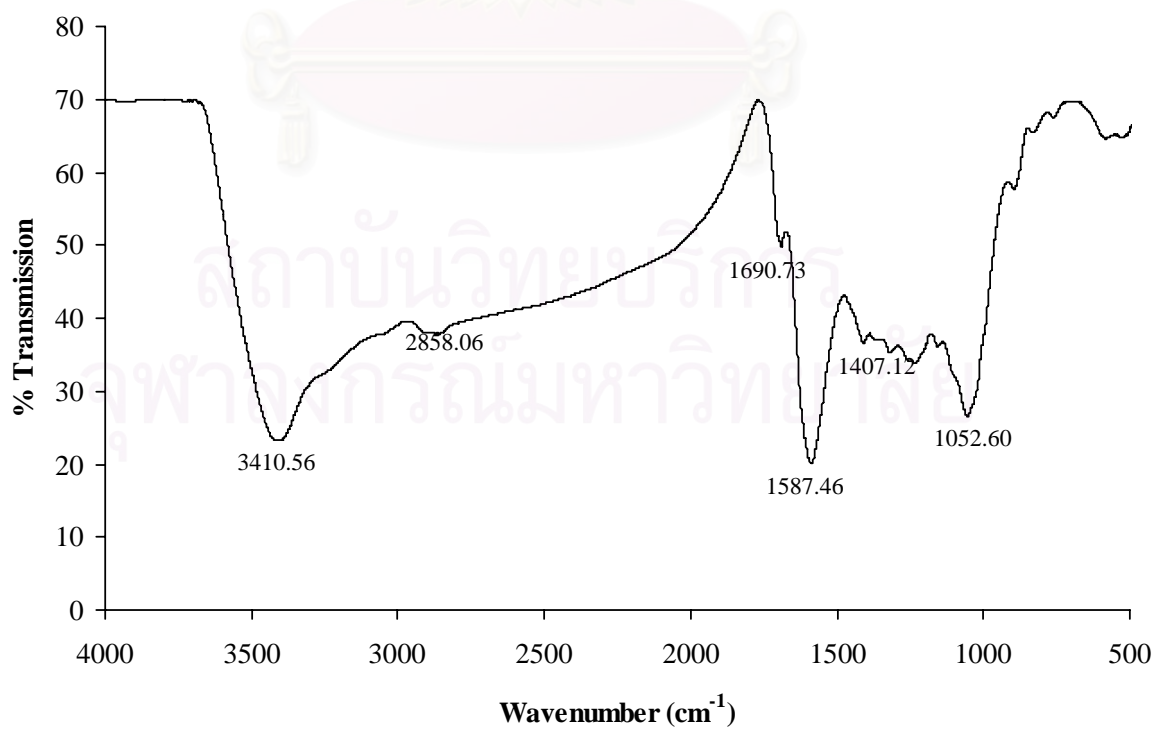


(d) Methyl cellulose : Calcium carbonate

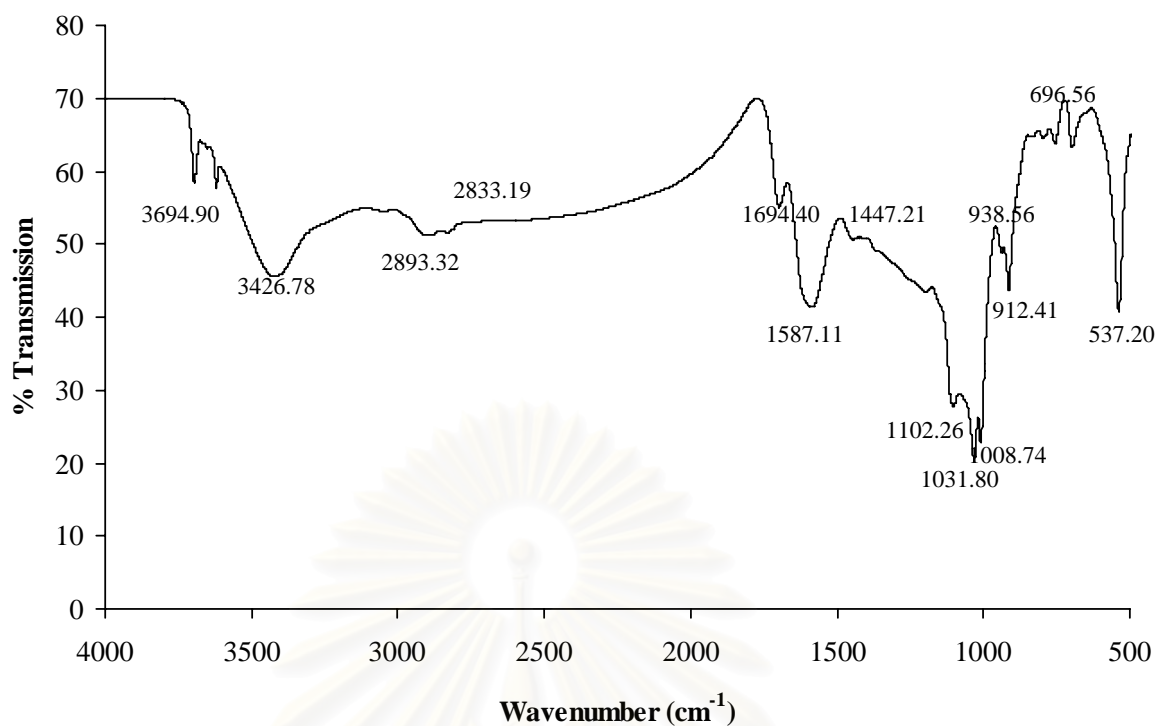
Figure 4.9 XRD patterns for the GAC products with various binders and reinforcers



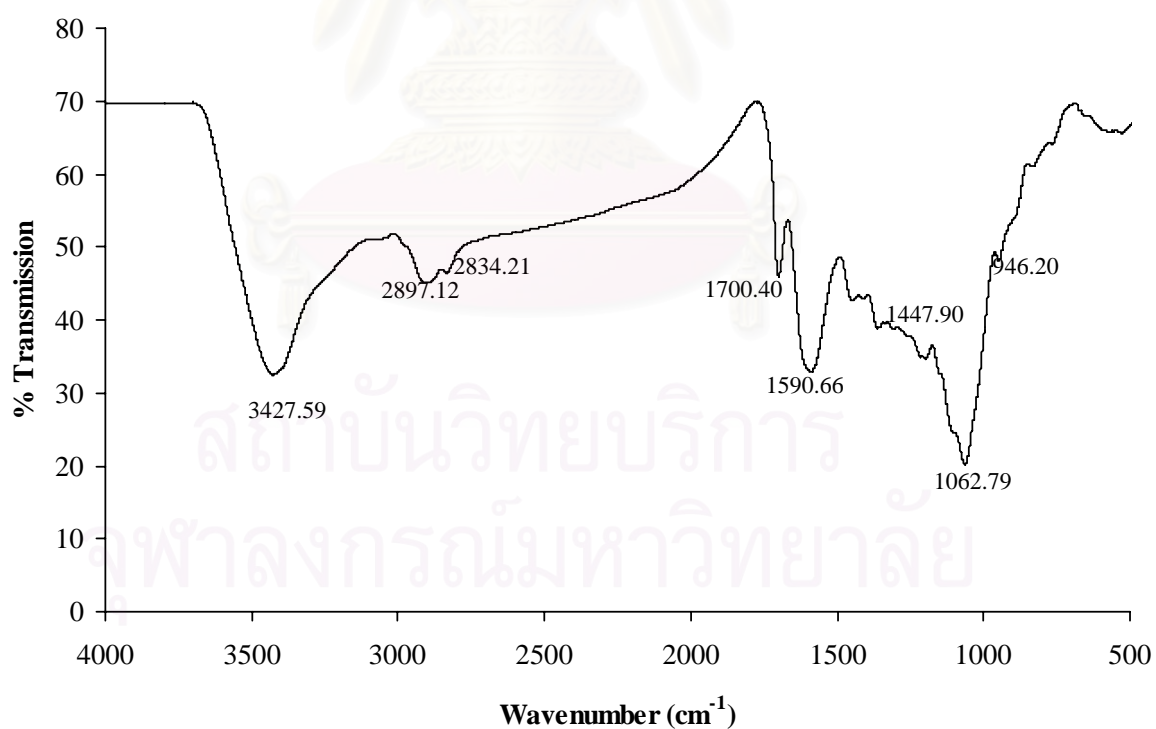
(a) Carboxymethyl cellulose : Kaolin



(b) Carboxymethyl cellulose : Calcium carbonate



(c) Methyl cellulose : Kaolin



(d) Methyl cellulose : Calcium carbonate

Figure 4.10 FT-IR transmission spectra for the GAC products with various binders and reinforcers

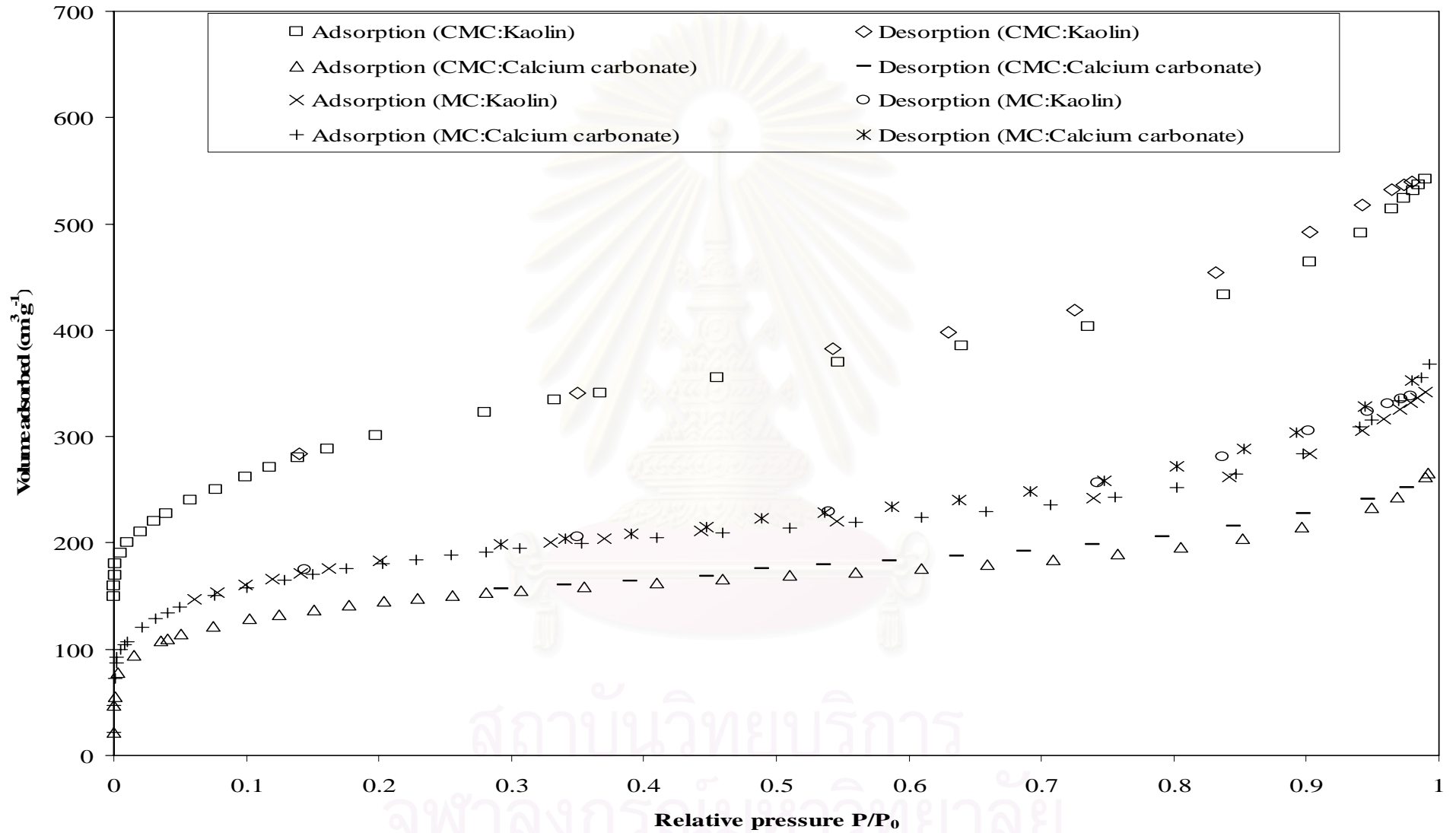


Figure 4.11 N₂ adsorption isotherms at -196°C on the GAC products with various binders and reinforcers

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The investigation in this work leads to the following conclusions:

1. Eucalyptus bark could provide effective original powdered activated carbon by phosphoric acid activation and this gave relatively high properties involved iodine number, methylene blue number, and BET surface area.
2. Original powdered activated carbon could provide effective granular activated carbon by using suitable binder and reinforcer agents.
3. Carboxymethyl cellulose (CMC) and Kaolin were suitable binder and reinforcer, respectively. The most appropriate weight proportion of CMC and Kaolin was 0.5:0.5.
4. The optimal weight proportion of the mixture of CMC and Kaolin, and the original powdered activated carbon was 20:80.
5. From this work, the best GAC product could be complied with all of the standard properties of Thai Industrial Standard (TIS.900-2004). However, these properties were still lower than those obtained from the commercial reference grade.

5.2 Contributions

This study utilizes eucalyptus bark as a source material for the GAC production and optimizes condition for their production. Powdered activated carbon is ordinarily prepared from the eucalyptus bark with great quality but with limitation in the use due to handling difficulties. Suitable binders and reinforcers were proposed to enhance the handling while sacrificing the quality of the final product. The GAC product passed the standard activated carbon requirement but still the comparison with commercial grade GAC indicates that there is still room for further improvement. Nevertheless, although experimental results demonstrated the potential applicability of such GAC product, it was learnt through the course of research that this chemical synthesis could end up with a large amount of wastewater being produced and required further treatment.

5.3 Recommendations/Future works

Based on the results of this study, some recommendations for future studies can be proposed.

1. The chemical used in our case was phosphoric acid which is impregnated into the raw material to influence the quality of the wastewater effluent. Therefore, the use of this phosphoric acid should be minimized. Alternative methods particularly physical methods are also encouraged.
2. The washing produced the loss of a great amount of chars, and so alternative washing methods should be exercised, e.g. using overflow packed columns.



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REFERENCES

- Abe, I., Fukuhara, T., Iwasaki, S., Yasuda, K., Nakagawa, K., Iwata, Y., Kominami, H., and Kera, Y. 2001. Development of a high density carbonaceous adsorbent from compressed wood. Carbon 39: 1485-1490.
- Activated Carbon Markets. 1994. Report No. 612. The Freedonia Group Inc., Cleveland. OH, pp.161.
- Agullo, J.A., Moore, B.C., Amoros, D.C., and Solano, A.L. 2004. Activation of coal tar pitch carbon fibres: Physical activation vs. chemical activation. Carbon 42: 1367–1370.
- Ahmedna, M., Marshall, W.E., and Rao, R.M. 2000. Production of granular activated carbons from select agricultural by-products and evaluation of their physical, chemical and adsorption properties. Bioresource Technology 71: 113-123.
- Ahmedna, M., Marshall, W.E., and Rao, R.M. 2000. Surface properties of granular activated carbons from agricultural by-products and their effects on raw sugar decolorization. Bioresource Technology 71: 103-112.
- Amen-Chen, C., Pakdel, H., and Rout, C. 1997. Separation of phenols from eucalyptus wood. Biomass and Bioenergy 13: 25-37.
- Arriagada, R., Gercia, R., and Reyes, P. 1994. Steam and carbon dioxide activation of *Eucalyptus globulus* charcoal. Journal of Chemical Technology and Biotechnology 60: 427-345.
- AWWA (American Water Works Association). 1991. AWWA standard for granular activated carbon. AWSI/AWWA, B604-90. American Water Works Association, Denver, CO.
- Aygün, A., Yenisoy-Karakas, S., and Duman, I. 2003. Production of granular activated carbon from fruit stones and nutshells and evaluation of their physical, chemical and adsorption properties. Microporous and Mesoporous Materials 66: 189-195.
- Bansal, R.C., and Goyal, M. 2005. Removal of copper from aqueous solutions by adsorption on activated carbons. Colloids and Surfaces A: Physicochemical and Engineering Aspects 190: 229–238.

- Bansode, R.R., Losso, J.N., Marshall, W.E., Rao, R.M., and Portier, R.J. 1998. Adsorption of metal ions by pecan shell-based granular activated carbons. Bioresource Technology 89: 115–119.
- Baquero, M.C., Giraldo, L., Moreno, J.C., Suárez-García, F., Martínez-Alonso, A., and Tascón, J.M.D. 2003. Activated carbons by pyrolysis of coffee bean husks in presence of phosphoric acid. Journal of Analytical and Applied Pyrolysis 70: 779-784.
- Boudou, J.P. 1996. Surface chemistry of a viscose-based activated carbon cloth modified by treatment with ammonia and steam. Carbon 41: 1955–1963.
- Boudou, J.P., Gérard, I., Bégin, D., Marêché, J.F., Furdin, G., Albiniak, A., and Siemieniowska, T. 2003. Effect of MoCl addition on the carbonization and the subsequent steam activation of pitch and coking coals. Carbon 38: 525–534.
- Bourke, M.J., and Mazzoni, A.F. 1989. Activated carbon for mercury removal. Gas Separation & Purification 52: 201-202.
- Cartro, J.B., Bonelli, P.R., Cerrella, E.G., and Cukierman, A.L. 2000. Phosphoric acid activation of agricultural residues and bagasse from sugar cane: Influence of the experimental conditions on adsorption characteristics of activated carbons. Industrial and Engineering Chemical Research 39: 4166-4172.
- Carvalho, A.P., Mestre, A.S., Pires, J., Pinto, M.L., and Rosa, M.E. 2006. Granular activated carbons from powdered samples using clays as binders for the adsorption of organic vapours. Microporous and Mesoporous Materials: 226-231.
- Chuang, C.L., Fan, M., Xu, M., Brown, R.C., Sung, S., Saha, B., and Huang, C.P. 2005. Adsorption of arsenic(V) by activated carbon prepared from oat hulls. Chemosphere (In press).
- Clarke, D.E., and Marsh, H. 1989. Factors influencing properties of coal briquettes. Fuel 68: 1031-1038.
- Daifullah, A.A.M., Girgis, B.S., and Gada, H.M.H. 2004. A study of the factors affecting the removal of humic acid by activated carbon prepared from biomass material. Colloids and Surfaces A: Physicochemical and Engineering Aspects 235: 1–10.

- Darmstadt, H., Garcia-Perez, M., Chaala, A., Nai-Zhen, C., and Roy, C. 2001. Co-pyrolysis under vacuum of sugar cane bagasse and petroleum residue properties of the char and activated char products. Carbon 39: 815–825.
- Degel, J., Henning, K.D., Keldenicht, K., and Knoblauch, K. 1990. Impregnated activated carbon for mercury removal. Gas Separation & Purification 2: 20–22.
- Diao, Y., Walawender, W.P., and Fan, L.T. 2002. Activated carbons prepared from phosphoric acid activation of grain sorghum. Bioresource Technology 81: 45–52.
- DiPanfilo, R., and Egiebor, N.O. 1996. Activated carbon production from synthetic crude coke. Fuel Processing Technology 46: 157–169.
- El-Hendawy, A.A., Samra, S.E., and Girgis, B.S. 2001. Adsorption characteristics of activated carbons obtained from corncobs. Colloids and Surfaces A: Physicochemical and Engineering Aspects 180: 209–221.
- Fuertes, A.B., Marbán, G., and Nevskaia, D.M. 2003. Adsorption of volatile organic compounds by means of activated carbon fibre-based monoliths. Carbon 41: 87–96.
- Galiatsatou, P., Metaxas, M., and Kasselouri-Rigopoulou, V. 2002. Adsorption of zinc by activated carbons prepared from solvent extracted olive pulp. Journal of Hazardous Materials B91: 187–203.
- Gan, Q., Allen, S.J., and Matthews, R. 2004. Activation of waste MDF sawdust charcoal and its reactive dye adsorption characteristics. Waste Management 24: 841–848.
- García, F.S., Martínez-Alonso, A., and Tascón, M.D. 2004. Nomex polyaramid as a precursor for activated carbon fibres by phosphoric acid activation. Temperature and time effects. Microporous and Mesoporous Materials 75: 73–80.
- Gergova, K., Petrov, N., and Eser, S. 1994. Adsorption properties and microstructure of activated carbons produced from agricultural by-products by steam pyrolysis. Carbon 32: 693–702.
- Girgis, B.S., and Ishak, M.F. 1999. Activated carbon from cotton stalks by impregnation with phosphoric acid. Materials Letters 39: 107–114.

- Girgis, B.S., Yunis, S.S., and Soliman, A.M. 2002. Characteristics of activated carbon from peanut hulls in relation to conditions of preparation. Materials Letters 57: 164–172.
- Gómez-Serrano, V., Cuerda-Correa, E.M., Fernández-González, M.C., Alexandre-Franco, M.F., and Macías-García, A. 2005. Preparation of activated carbons from chestnut wood by phosphoric acid-chemical activation. Study of microporosity and fractal dimension. Materials Letters 59: 846– 853.
- Guo, J., Xu, W.S., Chena, Y.L., Lua, A.C. 2005. Adsorption of NH₃ onto activated carbon prepared from palm shells impregnated with H₂SO₄. Journal of Colloid and Interface Science 281: 285–290.
- Hayashi, J., Horikawa, T., Muroyama, K., and Gomes, V.G. 2002. Activated carbon from chickpea husk by chemical activation with K₂CO₃: preparation and characterization. Microporous and Mesoporous Materials 55: 63–68.
- Helleur, R., Popovic, N., Ikura, M., Stanculescu, M., and Liu, D. 2001. Characterization and potential applications of pyrolytic char from ablative pyrolysis of used tires. Journal of Analytical and Applied Pyrolysis 58–59: 813–824.
- Ismadji, S., Sudaryanto, Y., Hartono, S.B., Setiawan, L.E.K., and Ayucitra, A. 2005. Activated carbon from char obtained from vacuum pyrolysis of teak sawdust: pore structure development and characterization. Bioresource Technology 96: 1364–1369.
- IUPAC Recommendations. 1985. Pure Apply Chemical 57(4): 603.
- Jagtoyen, M., and Derbyshire, F. 1998. Activated carbons from yellow poplar and white oak by H₃PO₄ activation. Carbon 36(7): 1085–1097.
- Jindaphunphairoth, V. 2000. Preparation of activated carbon from *Eucalyptus camaldulensis* Dehnh. by activation with carbon dioxide and superheated steam. Master's thesis. Program of Chemical Technology. Faculty of Science. Chulalongkorn University.
- Johns, M.M., Marshall, W.E., and Toles, C.A. 1998. Agricultural by-products as granular activated carbons for adsorbing dissolved metals and organics. Journal of Chemical Technology and Biotechnology 71: 131-140.

- Juang, R.S., Wu, F.C., and Tseng, R.L. 2002. Characterization and use of activated carbons prepared from bagasses for liquid-phase adsorption. Colloids and Surfaces A: Physicochemical and Engineering Aspects 201: 191–199.
- Kadirvelu, K., and Namasivayam, C. 2003. Activated carbon from coconut coirpith as metal adsorbent: adsorption of Cd(II) from aqueous solution. Advanced Environment Resource 7: 471–478.
- Karthikeyan, T., Rajgopal, S., and Miranda, L.R. 2005. Chromium(VI) adsorption from aqueous solution by *Hevea Brasiliensis* sawdust activated carbon. Journal of Hazardous Materials B124: 192–199.
- Khalid, T.T. 1998. Production of activated carbon from olive expression residues jift. using a fluidized-bed reactor. Master's thesis. University of Jordan.
- Khalili, N.R., Campbell, M., Sandi, G., and Golas, J. 2000. Production of micro- and mesoporous activated carbon from paper mill sludge. I. Effect of zinc chloride activation. Carbon 38: 1905-1915.
- Khuysangaaïn, S. 2001. Lead and mercury removal from textile wastewater by activated carbon from plam shell and coconut shell. Master's thesis. Program of Inter-Department of Environmental Science. Graduate school. Chulalongkorn University.
- Kobyas, M., Demirbas E., Senturk, E., and Ince, M. 2005. Adsorption of heavy metal ions from aqueous solutions by activated carbon prepared from apricot stone. Bioresource Technology 96: 1518-1521.
- Kumar, R., Garg, V.K., and Gupta, R.K. 2004. Adsorption of chromium from aqueous solution on treated sawdust. Bioresource Technology 92: 79-81.
- Laine, J., and Yunes, S. 1992. Effect of the preparation method on the pore size distribution of activated carbon from coconut shell. Carbon 30: 601-604.
- Laszlo, K., Bota, A., Nagy, L.G., and Cabasso, I. 1998. Porous carbon from polymer waste materials. Colloid Surface A151: 311–320.
- Li, J.J., Cui, J., Zhao, N.Q., Shi, C.S., and Du, X.W. 2006. The properties of granular activated carbons prepared from fly ash using different method. Carbon 44: 1298-1352.
- Maciá-Agulló, J.A., Moore, B.C., and Cazorla-Amorós, D., and Linares-Solano, A. 2004. Activation of coal tar pitch carbon fibres: Physical activation vs. chemical activation. Carbon 42: 1367–1370.

- Martin-Gullon, I. M, Marco-Lozar, J.P., Cazorla-Amoós, D., and Linares-Solano, A. 2004. Analysis of the microporosity shrinkage upon thermal post-treatment of H_3PO_4 activated carbons. Carbon 42: 1339–1343.
- Miguel, S.G., Fowler, G.D., Dall, O.M., and Sollars, C.J. 2001. Porosity and surface area characteristics of activated carbons produced from waste tyre rubber. Journal of Chemical Technology Biotechnology 77: 1-8.
- Montané, D., Torné-Fernández, V., and Fierro, V. 2005. Activated carbons from lignin: kinetic modeling of the pyrolysis of Kraft lignin activated with phosphoric acid. Chemical Engineering Journal 106: 1–12.
- Mozammel, H.M., Masahiroa, O., and Bhattacharya, S.C. 2002. Activated charcoal from coconut shell using $ZnCl_2$ activation. Biomass and Bioenergy 22: 397-400.
- Nabais, J.M.V., Carrott, P.J.M., Ribeiro-Carrott, M.M.L., and Menendez, J.A. 2004. Preparation and modification of activated carbon fibres by microwave heating. Carbon 42: 1315–1320.
- Nakagawa, K., Namba, A., Mukai, S.A., Tamon, H., Ariyadejwanich, P., and Tanthapanichakoon, W. 2004. Adsorption of phenol and reactive dye from aqueous solution on activated carbons derived from solid wastes. Water Research 38: 1791–1798.
- Namane, A., Mekarzia, A., Benrachedi, K., Belhaneche-Bensemraa, N., and Hellala, A. 2005. Determination of the adsorption capacity of activated carbon made from coffee grounds by chemical activation with $ZnCl_2$ and H_3PO_4 . Journal of Hazardous Materials B119: 189–194.
- Namasivayan, C., and Kadirvelu, K. 1997. Activated carbons prepared from coir pith by physical and chemical activation methods. Bioresource Technology 62: 123–127.
- Nasser, A.A., El-Hendawy, Samra, S.E., and Girgis, B.S. 2001. Adsorption characteristics of activated carbons obtained from corncobs. Colloids and Surfaces A: Physicochemical and Engineering Aspects 180: 209-221.
- Ng, C., Losso, J.N., Marshall, W.E., and Rao, R.M. 2002. Physical and chemical properties of selected agricultural byproduct-based activated carbons and their ability to adsorb geosmin. Bioresource Technology 84: 177-185.

- Patnukao, P., and Pavasant, P. 2008. Activated carbon from *Eucalyptus camaldulensis* Dehn bark using phosphoric acid activation. Bioresource Technology 99: 8540-8543.
- Pendyal, B., Johns, M.M., Marshall, W.E., Ahmedna, M., and Rao., R.M. 1999. Activated carbons. Bioresource Technology 68: 247-254.
- Pendyal, B., Johns, M.M., Marshall, W.E., Ahmedna, M., and Rao, R.M. 1999. Removal of sugar colorants by granular activated carbons made from binders and agricultural by-products. Bioresource Technology 69: 45-51.
- Philip, C.A., and Giegis, B.S. 1996. Adsorption characteristic of microporous carbons from apricot stone activated by phosphoric acid. Journal of Chemical Technology Biotechnology 67: 248-254.
- Qiao, W., Korai, Y., Mochida, I., Hori, Y., and Maeda, T. 2001. Preparation of an activated carbon artifact : influencing strength when using a thermoplastic polymer as binder. Carbon 39: 2355-2368.
- Rahman, M.K., Isa, M.H., Ibrahim, N., Aziz, H.A., Adlan, M.N., Sabiani, N.H., and Lorestani Zinatizadeh, A.A. 2008. Removal of chromium (VI) from aqueous solution using treated oil palm fibre. Journal of Hazardous Materials 152: 662–668.
- Redriguez-Reinoso, F, 1997. Activated carbon: Structure characterization preparation and applications. Carbon Technology: 35-36.
- Rubio, B., Izquierdo, M.T., and Segura, E. 1999. Effect of binder addition on the mechanical and physicochemical properties of low rank coal char briquettes. Carbon 37: 1833-1841.
- Shawwa, A.R., Smith, W.D., and Sego, D.C. 2001. Color and chlorinated organics removal from pulp mills wastewater using activated petroleum coke. Water Resources 35: 745-749.
- Sheikh, A.H., Newman, A.P., Daffae, H.A., Phull, S., Cresswell, N., and York, S. 2004. Deposition of anatase on the surface of activated carbon. Surface & Coatings Technology 187: 284– 292.
- Sing, K.S.W. 1998. Adsorption methods for the characterization of porous materials. Advances in Colloid and Interface Science 76-77: 3-11.

- Sirichote, O., Innajitara, W., Chuenchom, L., Chunchit, D., and Naweekan, K. 2002. Adsorption of iron (III) ion on activated carbons obtained from bagasse, pericarp of rubber fruit and coconut shell. Songklanakarin Journal Science Technology 24(2): 235-242.
- Solano, A.L., Salinas-Martínez, L.C., Cazorla-Amorós, D., and Martín- Gullón, I. 2000. Porosity development during CO₂ and steam activation in a fluidized bed reactor. Energy Fuels 14: 142–149.
- Sun, J., Hippo, E.J., Marsh, H.H., OBrien, W.S., and Crelling, J.C. 1997. Activated carbon produced from an Illinois Basin Coal. Carbon 35: 341-352.
- Tamon, H., Nakagawa, K., Suzuki, T., and Nagano, S. 1999. Improvement of mesoporosity of activated carbons from PET by novel pre-treatment for steam activation. Carbon 37: 1643–1645.
- Tancredi, N., Cordero, T., Mirasol, J.R., and Rodríguez, J.J. 1996. Activated carbons from Uruguayan eucalyptus wood. Fuel 75(15): 1701-1706.
- Tancredi, N., Medero, N., Möller, F., Píriz, J., Plada, C., and Cordero, T. 2004. Phenol adsorption onto powdered and granular activated carbon, prepared from *Eucalyptus wood*. Journal of Colloid and Interface Science 279: 357-363.
- Taylor, J.W., and Hennah, L. 1991. The effect of binder displacements during briquetting on the strength of formed coke. Fuel 70: 873-876.
- Teng, H., and Lin, Y. 2002. Mesoporous carbons from waste tire char and their application in wastewater discoloration. Microporous and Mesoporous Materials 54: 167–174.
- Thailand Industrial Standard Institute. Industry Ministry Activated carbon. 2004. Standard of commercial activated carbon. TIS. 900-2004: 1-10.
- Toles, C.A., Marshall, W.E., and Johns, M.M. 1997. Granular activated carbons from nutshells for the uptake of metals and organic compounds. Carbon 35 (9): 1407–1411.
- Usmani, T.H., Ahmad, T.W., and Yousufzai, A.H.K. 1994. Preparation liquid-phase characterization of granular activated-carbon from rice husk. Bioresource Technology 48: 31-35.

Vitidsant, T., Suravattanasakul, T., and Damronglerd, S. 1999. Production of Activated Carbon from Palm-oil Shell by Pyrolysis and Steam Activation in a Fixed Bed Reactor. Science Asia 25: 211-222.

Williams, P.T., and Reed, A.R. 2004. High grade activated carbon matting derived from the chemical activation and pyrolysis of natural fibre textile waste. Journal of Analytical and Applied Pyrolysis 71: 971–986.



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APPENDICES

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APPENDIX A.1

Determination for Iodine Number (ASTM D4607)

Procedure

1. Crush and sieve the activated carbon in the size ranged between mesh number 325 (0.045 mm) and 100 (0.150 mm)
2. Dry in an oven at 105°C for 4 h and cool to room temperature
3. Determine of iodine number requires an estimation of three carbon dosages
4. Weigh three appropriate amounts of activated carbon
5. Transfer to 250 ml Erlenmeyer flask equipped with a ground glass stopper
6. Pipet 10.0 mL of 5 wt % hydrochloric acid solution into each flask containing carbon
7. Stopper each flask and swirl gently until the carbon is completely wetted
8. Loose the stoppers to vent the flasks
9. Place on a hot plate in a fume hood
10. Boil gently for 30 ± 2 s
11. Remove the flasks from the hot plate and cool to room temperature
12. Pipet 100.0 mL of 0.100 N iodine solutions into each flask
13. Stopper the flasks, and shake vigorously for 30 ± 1 s
14. Filter each mixture through filter paper (Whatman No. 42) into a beaker
15. Pipet 50 mL of each filtrate into a clean 250 mL Erlenmeyer flask
16. Titrate each with standardized 0.100 N sodium thiosulfate solutions until the solution is a pale yellow
17. Add 2 mL of the starch indicator solution
18. Continue the filtration with sodium thiosulfate until one drop produces a colorless solution
19. Record the volume of sodium thiosulfate used

Calculation of iodine number (X/M) (mg/g)

$$X / M = \frac{[A - (DF)(B)(S)]}{M} \quad (\text{A.1-1})$$

where S is sodium thiosulfate volume (mL), M the weight of carbon (g).

To calculate the value of X/M, first device the following value:

$$A = (N_2)(12693.0) \quad (\text{A.1-2})$$

where N_2 is iodine concentration (N).

$$B = (N_1)(126.93) \quad (\text{A.1-3})$$

where N_1 is sodium thiosulfate concentration (N).

$$DF = \frac{[I + H]}{F} \quad (\text{A.1-4})$$

where DF is dilution factor, I iodine volume (mL), H hydrochloric acid volume (mL) and F filtrate volume (mL).

- Calculation of carbon dosage (M) (g) for calculation iodine number, Eq. (A.1-1)

$$M = \frac{[A - (DF)(C)(126.93)(50)]}{E} \quad (\text{A.1-5})$$

where C is residual filtrate (N) and E estimated iodine number of the carbon.

for approximation carbon dosage (M) may be use Table A.1-1

Table A.1-1 Approximation carbon dosage (M)

M				M			
E	C=0.01	C=0.02	C=0.03	E	C=0.01	C=0.02	C=0.03
300	3.766	3.300	2,835	1550	0.729	0.639	0.549
350	3.228	2.829	2.430	1600	0.706	0.619	0.531
400	2.824	2.475	2.126	1650	0.684	0.600	0.515
450	2.510	2.200	1.890	1700	0.664	0.582	0.500
500	2.259	1.980	1.701	1750	0.645	0.566	0.486
550	2.054	1.800	1.546	1800	0.628	0.550	0.472
600	1.883	1.650	1.417	1850	0.610	0.535	0.460
650	1.738	1.523	1.308	1900	0.594	0.521	0.447
700	1.614	1.414	1.215	1950	0.579	0.508	0.436
750	1.506	1.320	1.134	2000	0.565	0.495	0.425
800	1.412	1.237	1.063	2050	0.551	0.483	0.415

M				M			
E	C=0.01	C=0.02	C=0.03	E	C=0.01	C=0.02	C=0.03
850	1.329	1.164	1.000	2100	0.538	0.471	0.405
900	1.255	1.100	0.945	2150	0.525	0.460	0.396
950	1.189	1.042	0.895	2200	0.513	0.450	0.388
1000	1.130	0.990	0.850	2250	0.502	0.440	0.378
1050	1.076	0.943	0.810	2300	0.491	0.430	0.370
1100	1.027	0.900	0.773	2350	0.481	0.421	0.362
1150	0.982	0.861	0.739	2400	0.471	0.412	0.354
1200	0.941	0.792	0.680	2450	0.461	0.404	0.347
1250	0.904	0.792	0.680	2500	0.452	0.396	0.340
1300	0.869	0.761	0.654	2550	0.443	0.388	0.333
1350	0.837	0.733	0.630	2600	0.434	0.381	0.327
1400	0.807	0.707	0.607	2650	0.426	0.374	0.321
1450	0.799	0.683	0.586	2700	0.418	0.367	0.315
1500	0.753	0.666	0.567	2750	0.411	0.360	0.309

- Calculation of residual filtrate (C) (N) for calculation iodine number, Eq. (A.1-5)

$$C = \frac{(N_1 \cdot S)}{F} \quad (\text{A.1-6})$$

Using logarithmic paper, plot X/M versus C 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 greater than 0.995.

APPENDIX A.2

Determination for Methylene Blue Number

Preparation of solutions

- Potassium dihydrogen phosphate solution

1. Dry of potassium dihydrogen phosphate (KH_2PO_4) in the oven at 110-120 °C for 2 h
2. Cool to room temperature in a desiccator
3. Dissolve 9.07 g of KH_2PO_4 with distilled water
4. Transfer to a 1 L volumetric flask and fill to the mark with distilled water

- Disodium hydrogen phosphate solution

1. Dry of disodium hydrogen phosphate (Na_2HPO_4) in the oven at 110-120 °C for 2 h
2. Cool to room temperature in a desiccator
3. Dissolve 23.88 g of dry Na_2HPO_4 with distilled water
4. Transfer to a 1 L volumetric flask and fill to the mark with distilled water

- Buffer solution

Mix 400 mL of potassium dihydrogen phosphate solution and 600 mL of disodium hydrogen phosphate solution

- Standard methylene blue solution

1. Dry of methylene blue in the oven at 105 ± 5 °C For 4 h
2. Cool to room temperature in a desiccator
3. Dissolve 1.2 g of dry methylene blue with buffer solution
4. Transfer to a 1 L volumetric flask and fill to the mark with buffer solution

Procedure

1. Add 0.05 g of activated carbon to 25 mL of a solution of methylene blue (1,200 mg/L)
2. Stir for 30 min at room temperature
3. Remove activated carbon by centrifuge at 10,000 rpm for 30 min.
4. Determine the dye concentration using light absorbance at 665 nm (UV-vis spectrophotometer, JIS K 1470-1991).

Calculation of methylene blue

- Preparation of calibration curve

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.

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

Plot the remaining concentration of methylene blue solution on the abscissa and the adsorption amount of methylene blue obtained using the calculation method (Eq. 9) 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.

Using the remaining concentration of methylene blue, the methylene blue amount (mg/g) shall be calculated using the following formula.

$$Q = \frac{(1200 - C)(25/1000)}{S} \quad (\text{A.2-1})$$

where Q is methylene blue adsorption amount (mg/g), C remaining concentration of methylene blue (mg/L), S mass of activated carbon (g) and 1200 concentration of methylene blue solution (mg/L).

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APPENDIX A.3

Determination for Specific Surface Area (ASTM C 819-77)

Apparatus

- Micromeritics, ASAP 2000
- Computer and Program
- Sample tubing

Procedure

1. Weigh activated carbon sample size 8×30 mesh
2. Dry the activated carbon sample in oven at 150 °C
3. Weigh sample tubing and record
4. Weigh 0.3-0.5 g of activated carbon sample in sample tubing
5. Wash the contaminant molecule on surface area of activated carbon at 150 °C under vacuum pressure
6. Weigh activated carbon sample and sample tubing after outgas

Specific surface area analysis

1. Fix 10 point of relative pressure at equilibrium (P/Po)
2. Pass 99.5% N₂ (free oxygen) until equal to the relative pressure at equilibrium

Calculation

- *Determination for specific surface area of activated carbon*

Plot graph between relative pressure (P/Po) and quantities of N₂ that adsorped at the relative pressure $[W (P/Po) - 1] - 1$, we can calculated the specific surface area by Eq. (A.3-1)

$$S_{BET} (m^2 / g) = \frac{NA_{CS}}{[(S + I)(MW)]} \quad (A.3-1)$$

where : N = Avogadro number (6.02×10^{23} molecule/mole)

A_{CS} = Cross section area of N₂ molecule

MW = Molecular weight of N₂

APPENDIX A.4

Determination for Ash Content (ASTM D 2866-94)

Apparatus

- *Muffle Furnace*, having air circulation, capable of temperature regulation of $\pm 25^{\circ}\text{C}$ at 650°C
- *High-Temperature Crucible*, high-form
- *Analytical Balance*, having a sensitivity of 0.1 mg
- *Desiccator*
- *Oven*, forced-air circulation, capable of temperature regulation between 145 and 155°C

Procedure

1. Ignite the crucible in the muffle furnace at $650 \pm 25^{\circ}\text{C}$ for 1 h. Place the crucible in the desiccator. Cool to room temperature and weigh to the nearest 0.1 mg.
2. Dry an adequate sample of activated carbon to constant weight at $150 \pm 5^{\circ}\text{C}$ (3 h 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 $650 \pm 25^{\circ}\text{C}$. Ashing will require from 3 to 16 h, 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. Weight to the nearest 0.1 mg.

Calculation

- Calculate the ash content as follows:

$$\text{Total ash, \%} = \frac{(D - B)}{(C - B)} \times 100 \quad (\text{A.4-1})$$

- where :
- B = weight of crucible, g
 - C = weight of crucible plus original sample, g
 - D = weight of crucible plus ashed sample, g

APPENDIX A.5

Determination for Apparent Density (ASTM D 2854-89)

Apparatus

- *Reservoir Funnel*, fabricated of glass or metal
- *Feed Funnel*, also of glass or metal
- *Metal Vibrator*, 26-gage galvanized sheet metal
- *Cylinder*, graduated, 100 mL capacity
- *Balance*, having a sensitivity of 0.1 g

Procedure

1. Dry an adequate sample of the carbon to be tested to constant weight at $150 \pm 5^\circ\text{C}$.
2. Carefully place a representative sample of the activated carbon into the reservoir funnel so that the material does not prematurely flow into the graduated cylinder. If this occurs, return the material to the reservoir funnel.
3. Add the sample to the cylinder using to vibrator feeder through the feed funnel having a stem 23.8 mm (15/16 in.) in inside diameter.
4. Fill the cylinder at a uniform rate not less than 0.75 or exceeding 1.0 mL/s, up to the 100 mL mark. The rate can be adjusted by changing the slope of the metal vibrator or raising or lowering the reservoir funnel, or both.
5. Transfer the contents from the cylinder to a balance pan and weigh to the nearest 0.1 g.

Calculation

- For predried samples, calculate the apparent density as follows:

$$\text{Apparent density, g/mL} = \frac{\text{weight of activated carbon}}{100} \quad (\text{A.5-1})$$

- For samples that have not been predried, calculated the apparent density on the dry basis as follows:

$$\text{Apparent density, g/mL} = 10^{-4} (\text{weight of activated carbon, g}) \times (100 - \% \text{ moisture}) \quad (\text{A.5-2})$$

APPENDIX A.6

Determination for Moisture Content (ASTM D 2867-95)

1). Oven-Drying Method

Apparatus

- *Moisture Oven*-Most commercial, electrically heated, forced-circulation drying ovens capable of temperature regulation between 145 °C and 155 °C may be used
- *Capsules with Covers*-Low form glass weighing bottles with ground-glass stoppers or seamless metal boxes with covers may be used. They should be as shallow as possible, consistent with convenient handling
- *Desiccator*

Materials

- *Desiccant*-Anhydrous calcium chloride or other suitable desiccant

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 representative sample. Put this into a predried tared capsule with lid, close and weigh 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 °C to 155 °C). Close the oven and dry to constant weight (3 h normally sufficient). Open the oven and cover the capsule quickly. Cool in a desiccator to ambient temperature and weigh.

Procedure for Activated Carbon Larger than A No. 50 Sieve

- Use a 5 to 10 g representative sample and weigh to the nearest 2 mg. Complete the determination as described in above.

Calculation

- Calculate the moisture content as follows:

$$\text{Moisture, weight\%} = \frac{(C - D)}{(C - B)} \times 100 \quad (\text{A.6-1})$$

- where :
- B = weight of capsule with cover, g
 - C = weight of capsule with cover plus original sample, g
 - D = weight of capsule with cover plus dried sample, g

2). Xylene-Extraction Method

Apparatus

- *Boiling Flask*-A 300 mL flat-bottom Erlenmeyer flask with ground-glass joints
- *Condenser*-A 300 mL water-cooled condenser of the Allihn type with ground-glass joints
- *Drying Tube*, containing a suitable desiccant with fiber-glass filter
- *Water Trap*-A Bidwell and Sterling 10 mL or a Dean and Stark receiver with ground-glass joints. The water trap should be clean so that the shape of the meniscus at the end of the test is the same as at the beginning
- *Hot Plate*-An electrically heated hot plate with enclosed elements and temperature control

Reagent

- Xylene-Reagent grade in accordance with the specifications of the Committee on Analytical Reagents of the American Chemical Society

Preparation of Apparatus

- Clean the condenser, flask, and trap and carefully dry to ensure that it is free of water. Assemble the condenser and water trap

Procedure

1. Weigh the sample bottle. Dip out with a spoon from the sample bottle 25 to 50 g of the sample. Put this into the boiling flask and reweigh the sample bottle to the nearest 0.1 g. Add 100 mL of xylene and connect the boiling flask to the water trap. For carbons having density less than 0.30 g/cm³, 200 mL of xylene should be used for a 25 g sample.
2. Place the hot plate under the boiling flask and heat to boiling. Adjust the temperature control so as to reflux the xylene at the rate of about 1 drop/s from the tip of the condenser. Continue to reflux until there is no further increase in the water layer in the trap over a 30 min period (from 2 to 8 h may be required).

Calculation

- Calculate the moisture content as follows:

$$\text{Moisture, weight\%} = \frac{V}{(C - E)} \times 100 \quad (\text{A.6-2})$$

where :
 V = water collected, mL
 C = initial weight of sample bottle, g
 E = weight of sample bottle after removing moisture sample, g



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APPENDIX A.7

Determination for Chemical Analysis (ASTM D 1762-84)

Apparatus

- *Mill*, for grinding samples
- *Oven*, with automatic temperature control at 105 ± 1 °C
- *Muffle Furnace*, to control temperature at 750 ± 5 °C and 950 ± 5 °C
- *Analytical balance*, with a capacity of at least 100 g and a sensitivity of 0.1 mg
- *Containers*, airtight, such as screw-top bottles for storage of ground samples
- *Sieves*, as specified in Method D 410
- *Crucibles*, porcelain, 41 by 37 mm with porcelain lids
- *Desiccator*, containing calcium chloride as drying agent

Sample

1. *Sample Selection*-The sample shall be selected so as to be representative of all of the material contained in a lot. Sample selection shall be carried out in accordance with Practices D 346, D 3176, and D 3180.

2. *Sample Preparation*-Samples will normally be air-dry charcoal lumps or briquets. Rainsoaked or wet samples shall be spread out to air-dry before carrying out the analysis. For purchase specification, the moisture content of the charcoal, as received, shall be determined on samples ground to pass No.20 (850- μ m) sieve, since excessive grinding will result in loss of moisture due to the generation of heat. For laboratory evaluation, moisture, ash, and volatile matter shall be determined on a sample ground as follows:

2.1 All of the selected sample shall be ground; no part of the sample shall be rejected. The sample shall be pulverized rapidly in a mill. Long grinding time shall be avoided because of generated heat which will cause loss of volatile material. Excessive grinding will produce a large amount of fine particles smaller than a No. 100 (150- μ m) sieve. These fine particles contribute to errors of being swept out of the crucible during the rapid evolution of gases in the determination of volatile matter. Particles that will be retained on a No. 20 (850- μ m) sieve shall not be used.

The ground sample shall be well mixed and stored in an airtight container.

Procedure

1. Make duplicate determinations.
2. *Moisture*-Heat the muffle furnace to 750 °C and place previously ignited porcelain crucibles and covers in the furnace for 10 min. Cool the crucibles in a desiccator for 1 h. 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 °C for 2 h. Place the dried samples in a desiccator for 1 h.
3. *Volatile Matter*-Heat the muffle furnace to 950 °C. Preheat the crucibles used for the moisture determination, with lids in place and containing the sample, as follows: with the furnace door open, for 2 min on the outer ledge of the furnace (300 °C) and then for 3 min on the edge of the furnace (500 °C). Then move the samples to the rear 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. Cool the samples in a desiccator for 1 h and weigh.
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 h. Cool the crucibles with lids in place in a desiccator for 1 h and weigh. Repeat burning of the sample until a succeeding 1 h period of heating results in a loss of less than 0.0005 g.

Calculation and Report

- Calculate the percentage of moisture in the sample as follows:

$$\text{Moisture, \%} = \frac{(A - B)}{A} \times 100 \quad (\text{A.7-1})$$

where : A = grams of air-dry sample used

B = grams of sample after drying at 105 °C

- Calculate the percentage of volatile matter in the sample as follows:

$$\text{Volatile - matter, \%} = \frac{(B - C)}{B} \times 100 \quad (\text{A.7-2})$$

where : C = grams of sample after drying at 950 °C

- Calculate the percentage of ash in the sample as follows:

$$\text{Ash, \%} = \frac{D}{B} \times 100 \quad (\text{A.7-3})$$

where : D = grams of residue

- Report all results to the first decimal place. Values for duplicate determinations should agree within the following:

Constituent Determined	Permissible Differences Between Duplicates, %
Moisture	0.1
Volatile matter	0.5
Ash	0.1



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APPENDIX A.8

Determination for Ball-Pan Hardness (ASTM D 3802-79)

Apparatus

- *Mechanical Sieve Shaker*, designed to produce from 140 to 160 taps and from 280 to 320 rotating motions per minute in a stack of standard Specification E11 sieves. Adjust the sieve shaker to accommodate the desired number of sieve, receiver pan, and sieve cover. Adjust the bottom stops to give a clearance of approximately 1.6 mm between the bottom plate and the sieves so that the sieves will be free to rotate. Fit the cover plate with a cork stopper which extends from 3.2 to 9.5 mm above the metal recess.

- *Wire Cloth Sieves*, in accordance with Specification E 11; six required, at least four of which bracket the expected nominal particle size distribution of the sample, and one of which, designated the hardness test sieve, has an opening as close as possible to one half the opening of the sieve that defines the smaller nominal particle size of the original sample.

- *Bottom Receiver Pan and Top Sieve Cover*

- *Hardness Test Pan*

- *Adjustable Interval Timer*, with a precision of at least ± 5 s, duration at least 600 s (10 min)

- *Sample Splitter*, single-stage riffle type

- *Balance*, with sensitivity and accuracy of at least 0.1 g

- *Soft Brass-Wire Brush*

- *Steel Balls*, fifteen 12.7 ± 0.1 mm (1/2 in.) in diameter and fifteen 9.5 ± 0.1 mm (3/8 in.) in diameter

Procedure

1. Determine the nominal particle size of the sample in accordance with Test Method D 2862, and its moisture content in accordance with Test Method D 2867.
2. Obtain an additional representative sample of approximately 125 mL of the carbon in accordance with Practice E 300.
3. Screen this sample to its nominal particle size distribution using Test Method D 2862. Discard the fractions above the larger and below the smaller nominal

particle size. Obtain at least 100 mL of material within the nominal mesh size range.

4. Measure out 100 mL of the screened sample into a tared, graduated cylinder in accordance with Test Method D 2854, and weigh to the nearest 0.1 g.
5. Place the hardness pan on the standard bottom receiver pan. Pour the screened and weighed sample into the hardness pan and add the steel balls.
6. Complete the sieve stack by attaching five full-height sieves and the sieve cover on top of the hardness pan. The extra sieves, in this case, serve only to form a stack which fills the shaker, thus avoiding changes in tapping action and readjustment of the sieve stack retainer.
7. Place sieve stack in the sieve shaker and shake for 30 ± 0.5 min, with tapping hammer operating.
8. At the end of the shaker period, remove the sieve stack from the sieve shaker and remove the hardness pan from the sieve stack. Place the hardness test sieve on top of the receiving pan.
9. Remove the steel balls from the hardness pan and transfer sample to the hardness test sieve, brushing adhering particle into the sieve. Stack the five full-height sieves and sieve cover on top of the hardness test sieve and receiving pan, and replace the stack in the sieve shaker. Shake with the hammer operating for $10 \text{ min} \pm 10 \text{ s}$.
10. At the end of the shaking period, remove the sieve stack from the sieve shaker and transfer the remainder of the sample on the hardness test sieve to a tared weighing pan. Weigh to the nearest 0.1 g.

Calculation

- Calculate the ball-pan hardness number from the equation:

$$H = 100 \frac{B}{A} \quad (\text{A.8-1})$$

where :

- H = ball-pan hardness number
- B = weight of sample retained on hardness test sieve,g
- A = weight of sample loaded onto hardness pan,g

- As a check on the accuracy of the test, calculate ball-pan hardness from the pan catch as follows:

$$H_2 = 100\left(1 - \frac{C}{A}\right) \quad (\text{A.8-2})$$

where : C = pan catch,g

If H_2 differs from H by more than 2%, one may assume that significant amounts of carbon are not accounted for, and the run must be rejected.



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APPENDIX A.9

Determination for pH (ASTM D 3838-80)

Apparatus

- *Analytical Balance*, capacity 100 g, precision ± 0.01 g
- *Hot Plate*
- *Glassware for Boiler-Reflux Condenser Apparatus*
- *Thermometer*, glass, approximately 0 to 120°C, long enough to be read at 100°C when inserted to bottom of Erlenmeyer flask
- *Thermometer*, glass, approximately 20 to 55°C
- *Graduated Cylinder*, 100 mL
- *Beaker*, 200 mL
- *Filter Funnel*
- *Filter Paper*, qualitative, medium flow rate, 12.5 cm or larger in diameter
- *Timer*
- *pH Meter*
- *Reagent Water*,

Procedure

1. Determine the moisture content of the carbon in accordance with Test Method D 2867. Calculate the weight of moist carbon equivalent to 10 g on a dry basis
2. Weigh out a sample of carbon equivalent to 10.00 ± 0.01 g on a dry basis. Remove boiler flask from apparatus and add carbon sample.
3. Bring approximately 110 mL of reagent water to a gentle boil. Measure 100.0 ± 0.1 mL in graduate cylinder while water is hot. Immediately add this water to the carbon in the flask. Reconnect joints to flask seated on hot plate.
4. Bring water in flask to a boil, using thermometer reading to assure that no false boiling, due to gasses trapped in carbon, occurs.
5. Boil gently for 900 ± 10 s
6. Remove the flask from the hot plate and filter its contents immediately through the filter paper premoistened with the distilled water used for the test. Catch the filtrate in a 500 mL vacuum filter flask, being careful to prevent carbon fines from overrunning into the flask.

7. Cool the filtrate to $50 \pm 5^{\circ}\text{C}$
8. Measure pH as described in Test Methods D 1293

Calculation

- If the pH meter is calibrated in pH units, read value from pH meter. If the meter reading is in voltage units, use the equation from the Terminology section of Test Methods D 1293.



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จุฬาลงกรณ์มหาวิทยาลัย

APPENDIX B**Paper Publications (Conference Articles)**

Thipawan Thong ton, Phussadee Patnukao, Prasert Pavasant. **Effects of binders and reinforcers on physical and chemical properties of granular activated carbon from eucalyptus bark.** 2008. The 18th Thailand Chemical Engineering and Applied Chemistry Conference October 20-21, 2008, Pattaya Thailand.



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จุฬาลงกรณ์มหาวิทยาลัย

Effects of binders and reinforcers on physical and chemical properties of granular activated carbon from eucalyptus bark

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Abstract Eucalyptus bark was employed as a raw material for the preparation of granular activated carbon (GAC). Firstly, eucalyptus bark was converted to powdered activated carbon (PAC) using the chemical method with H_3PO_4 as carbonizing/activating agent. The GAC was prepared by mixing PAC with carboxymethyl cellulose (CMC) as binders and kaolin as reinforcer. The results illustrated that adsorption capacity was best obtained from the mixture with the weight proportion of carboxymethyl cellulose and kaolin of 50:50, and with the weight proportion of the mixture and PAC of 20:80. With this formula, 62.7% yield was obtained with the properties of the resulting GAC of: BET surface area $1,085 \text{ m}^2 \text{ g}^{-1}$, bulk density 0.214 g cm^{-3} , hardness number 75%, pH 6.7 and ash content 12.65 %.

1. Introduction

Granular activated carbon (GAC) is generally considered more versatile than the powdered activated carbon (PAC) and command a large percentage of the carbon market (Activated Carbon Markets, 1994). Type of raw material is important in determining its suitability for GAC product. In the production of GAC from soft, low density bark, binder and reinforcer are also required to produce a hard, higher density granule product. Typically carboxymethyl cellulose was used as binder as it can act as a viscosity modifier or thickener and kaolin as reinforcer has good plasticity and strength properties such as hardness.

In the present work, the production of PAC by chemical activation technique has been attempted using eucalyptus bark as the raw material. The GAC was obtained from mixing PAC with the mixture of carboxymethyl cellulose as binder and kaolin as reinforcer. The GAC product was examined for its properties and compared with commercial GAC grade reference.

2. Methods

2.1 Preparation of PAC

Raw material (eucalyptus bark) was prepared by impregnation into phosphoric acid (85% by weight) using the weight ratio of raw material and phosphoric acid at 1:1. The mixture was stirred thoroughly until well mixed at room temperature and then carbonized in a muffle furnace at 500°C for 1 h. The char was washed by hot distilled water until the final pH of the leachate was 6 and dried in an oven at 105°C for 4 h. Finally, the activated carbon was crushed and sieved in the size ranged between mesh number 100 (0.150 mm) and 325 (0.045 mm) [1].

2.2 Preparation of granular activated carbon

Granular activated carbon was made by mixing PAC with a mixture of carboxymethyl cellulose and kaolin of 50:50, in a weight proportion of the mixture and powdered activated carbon of 20:80. Water was added 2 ml/g, and the wet mixture was stirred thoroughly until well mixed and passed through a laboratory extruder with a 3-mm-diameter hole. The extruded product was dried at 105°C for 2 h [2].

2.3 Granular activated carbon characteristics

The surface morphology of GAC was visualized via scanning electron microscopy (SEM, XL 30 ESEM FEG). Surface areas were calculated from adsorption isotherms using the method of Brunauer, Emmet and Teller (BET method). The BET surface area was determined by nitrogen adsorption (-196°C) on surface area analyzer (Thermo Finnigan, Sorptomatic 1990). The ash content of the GAC was determined using a standard method according to ASTM D 2866-94 [3]. This method involved pre-drying the sample at 150°C , followed by burning in a muffle furnace at 650°C for 4 h in the presence of air. The ash content was calculated from the combustion residue. This test was repeated until constant ash content was obtained.

Apparent (bulk) density of all samples was calculated as the ratio between weight and volume of packed dry material. The yield of GAC was defined as the ratio of the weight of the GAC product to that of the

original mixture (PAC, binders, and reinforcers), both weights were on a dry basis, i.e.

$$\% \text{Yield} = \frac{W_1}{W_0} \times 100 \quad (1)$$

where W_0 is the weight of original mixture (powder activated carbon, binders, and reinforcers) and W_1 is the weight of GAC product.

X-ray diffraction (XRD) patterns were obtained in SIEMENS D5000 using $\text{CuK}\alpha$ radiation ($\lambda = 0.154056 \text{ nm}$), with Ni filter.

Adsorption tests for the final granular activated carbon product were performed using iodine and methylene blue solutions as adsorbate. The iodine and methylene blue numbers were determined following the ASTM D4607-94 [4] and JIS K 1470-1991 [5], respectively.

pH measurement of the GAC was suspended in 100 ml of distilled water at pH 7.0 and the suspension was heated to 90°C with continuous stirring for 20 min. Evaporation was minimized by placing watch glasses on top of the beakers. The suspension was cooled to 25°C and the pH measured with pH meter [6].

3. Results and discussion

3.1 Characterization of granular activated carbon

XRD patterns and isotherms of the granular activated carbon product shown in Fig. 1 and 2, respectively. The results

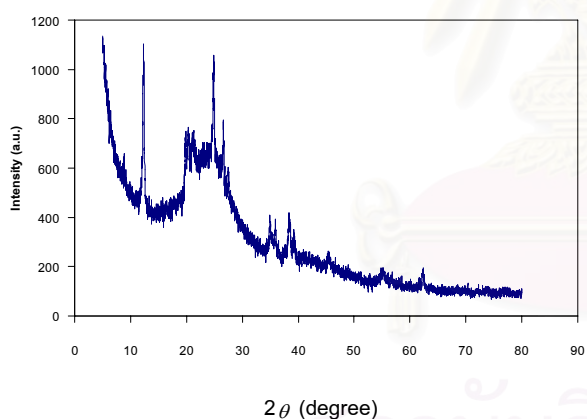


Fig. 1 XRD patterns of granular activated carbon product at the weight proportion of binder (carboxymethyl cellulose) and reinforcer (kaolin) of 50:50

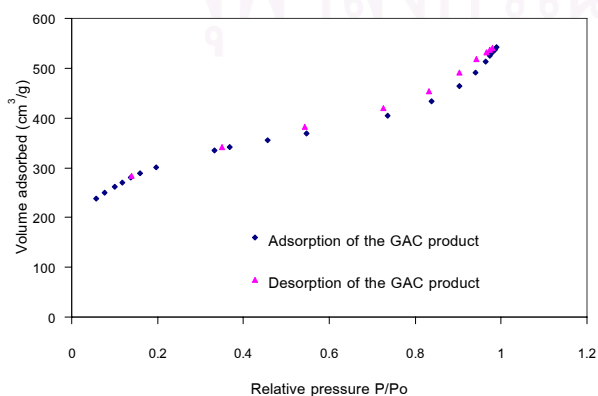


Fig. 2 Nitrogen adsorption-desorption isotherms at -196° of granular activated carbon product obtained from the weight proportion of binder (carboxymethyl cellulose) and reinforcer (kaolin) of 50:50 and XRD patterns are implied that more amorphous characteristics.

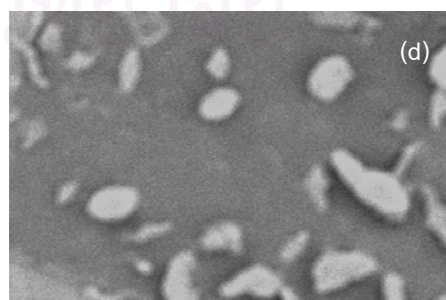
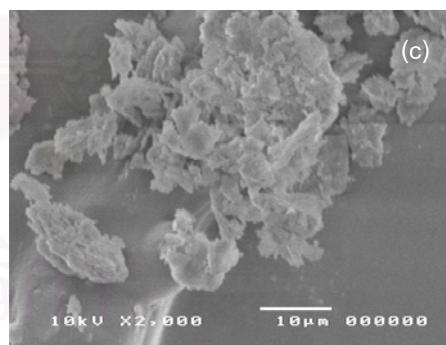
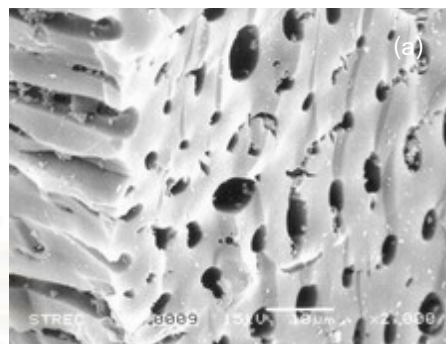


Fig. 3 SEM photomicrographs of samples: (a) powder activated carbon ; (b) granular activated carbon product at the weight proportion of binder (carboxymethyl

cellulose) and reinforcer (kaolin) of 50:50 ; (c) carboxymethyl cellulose and (d) kaolin

The results in Table 1 indicate that the pH values of the GAC product correlated with the proportion of binder and reinforcer, which in the selected proportion was 6.7. The pH value is lower than the commercial grade GAC

Table 1

Comparison of the properties of PAC and GAC obtained from this work and the commercial grade GAC

Properties	Powdered activated carbon	Granular activated carbon Binder/reinforcer (50:50)	Commercial GAC grade
<i>Physical properties</i>			
Bulk density (g cm^{-3})	0.251	0.214	0.500
BET surface area ($\text{m}^2 \text{g}^{-1}$)	1239	1085	>1000
- Micropore (%)	88.5	80.9	- ^a
- Mesopore (%)	11.48	19.1	- ^a
Hardness number (%)	- ^a	75	>98
Yield (%)	30.5	62.7	- ^a
<i>Chemical properties</i>			
pH	6.5	6.7	9-11
Ash content (%)	4.88±0.09	12.65±0.02	<3.5
<i>Adsorption properties</i>			
Iodine number (mg g^{-1})	916.7±5	685±7	>950
Methylene blue number (mg g^{-1})	427±2	310±3	- ^a

^a Not analyzed.

3.2 Physical properties of GAC: Bulk density, surface area, and hardness

Table 1 shows the comparison of the physical properties of PAC and the GAC obtained from this work with the commercial grade GAC. The best bulk density of 0.214 g cm^{-3} was obtained in the sample with the proportion of binder (carboxymethyl cellulose) and reinforcer (kaolin) of 50:50.

The surface area generally reflects the activated carbon adsorptive capacity, which is then related to methylene blue and iodine numbers. Table 1 demonstrates that a higher BET surface area ($1,085 \text{ m}^2 \text{g}^{-1}$) could be obtained from the same GAC product with the proportion of binder (carboxymethyl cellulose) and reinforcer (kaolin) of 50:50.

Hardness number (75%) was best obtained from the sample with the weight proportion of binder (carboxymethyl cellulose) and reinforcer (kaolin) of 50:50, which is lower than of the commercial grade GAC.

3.3 Chemical properties of GAC: Ash content and pH

Ash content of the GAC product increased with increasing proportion of binder and reinforcer, but it is noted that ash can be found in both binder (carboxymethyl cellulose) and reinforcer (kaolin). Table 1 shows that ash content was 12.65 % with the proportion of binder (carboxymethyl cellulose) and reinforcer (kaolin) of 50:50.

and a neutral pH range of 6-8 is recommended for the best properties of GAC product.

3.4 Adsorption capacity

Iodine and methylene blue numbers are indicators of the adsorption capacity in micropores and mesopores, respectively, and therefore, are often employed to examine the adsorption capacity of the GAC product. Table 1 demonstrates that these parameters decreased with an increase in the weight of binder (carboxymethyl cellulose). With the proportion of carboxymethyl cellulose and kaolin of 50:50, it was found that iodine number 685 mg g^{-1} and methylene blue number 310 mg g^{-1} .

4. Conclusions

Type of binders and reinforcers considerably influenced the physical and chemical properties of GAC. Carboxymethyl cellulose was used as binder as it can act as a viscosity modifier/thickener and kaolin has good hardness and give a porous structure. Both binder (carboxymethyl cellulose) and reinforcer (kaolin) were best substances and they do not liquefy when carbonized. The physical properties (bulk density, surface area and hardness) and chemical properties (ash content and pH) of the GAC product in this work, were ranked in relation

to the reference carbons as potential commercial grade GAC.

5. Acknowledgements

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6. References

- [1] P. Patnukao, P. Pavasant, Activated carbon from Eucalyptus camaldulensis Dehn bark using phosphoric acid activation, *Bioresource Technology*. 99, 2008, 8540-8543.
- [2] N. Tancredi, M. Medero, F. Möller, F. Piriz, C. Plada, T. Cordero, Phenol adsorption onto powdered and granular activated carbon, prepared from *Eucalyptus* wood, *J. Colloid Interf. Sci.* 279, 2004, 357–363.
- [3] American Standard of Testing Material, Standard test method for total ash content of activated carbon, *Annual book of ASTM standards* D 2866-94, 498-499.
- [4] American Standard of Testing Material, Standard test method for determination of iodine number of activated carbon, *Annual book of ASTM standards*, D 4607-94, 542-545.
- [5] 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.
- [6] American Standard of Testing Material, Standard test method for pH of activated carbon, *Annual book of ASTM standards*, D 3838-80, 531-532.
- [7] M. Ahmedna, W.E. Marshall, R.M. Rao, Production of granular activated carbons from select agricultural by-products and evaluation of their physical, chemical and adsorption properties, *Bioresource Technology* 71, 2000, 113-123.
- [8] A. Aygün, S. Yenisoy-Karakas, I. Duman, Production of granular activated carbon from fruit stones and nutshells and evaluation of their physical, chemical and adsorption properties, *Microporous and Mesoporous Materials* 66, 2003, 189-195.
- [9] A.P. Carvalho, A.S. Mestre, J. Pires, M.L. Pinto, M.E. Rosa, Granular activated carbons from powdered samples using clays as binders for the adsorption of organic vapours, *Microporous and Mesoporous Materials*, 2006, 226-231.
- [10] J.B. Castro, P.R. Bonelli, E.G. Cerrella, A.L. Cukierman, Phosphoric acid activation of agricultural residues and bagasse from sugar cane: Influence of the experimental conditions on adsorption characteristics of activated carbons, *Industrial and Engineering Chemical Research* 39, 2000, 4166-4172.
- [11] D.E. Clarke, H. Marsh, Factors influencing properties of coal briquettes, *Fuel* 68, 1989, 1031-1038.
- [12] A.C. Deiana, D.L. Granados, L.M. Petkovic, M.F. Sardella, H.S. Silva, Use of grape must as a binder to obtain activated carbon briquettes, *Brazilian Journal of Chemical Engineering* 21(04), 2004, 585-591.
- [13] Y. Diao, W.P. Walawender, L.T. Fan, Activated carbons prepared from phosphoric acid activation of grain sorghum, *Bioresource Technology* 81, 2002, 45-52.
- [14] V. Gómez-Serrano, E.M. Cuerda-Correa, M.C. Fernández-González, M.F. Alexandre-Franco, A. Macías-García, Preparation of activated carbons from chestnut wood by phosphoric acid-chemical activation, Study of microporosity and fractal dimension, *Materials Letters* 59, 2005, 846– 853.
- [15] A. Gürses, Ç. Dogar, S. Karaca, M. Açıkyıldız, R. Bayrak, Production of granular activated carbon from waste *Rosa canina* sp. Seeds and its adsorption characteristics for dye, *Journal of Hazardous Materials* 131, 2006, 254-259.
- [16] W. Heschel, E. Klose, On the suitability of agricultural by-products for the manufacture of granular activated carbon, *Fuel* 74 (12), 1995, 1786-1791.
- [17] V. Jindaphunphairoth, Preparation of activated carbon from *Eucalyptus camaldulensis* Dehn. by activation with carbon dioxide and superheated steam, Master's thesis, Program of Chemical Technology, Faculty of Science, Chulalongkorn University, Thailand 2000.
- [18] R.S. Juang, F.C. Wu, R.L. Tseng, Characterization and use of activated carbons prepared from bagasses for liquid-phase adsorption, *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 201, 2002, 191–199.
- [19] J.W. Kim, M.H. Sohn, D.S. Kim, S.M. Sohn, Y. S. Kwon, Production of granular activated carbon from waste walnut shell and its adsorption characteristics for Cu^{2+} ion, *Journal of Hazardous Materials* 85, 2001, 301–315.

- [20] J.J. Li, J. Cui, N.Q. Zhao, C.S. Shi, X.W. Du, The properties of granular activated carbons prepared from fly ash using different method, *Carbon* 44, 2006, 1298-1352.



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