

**ADSORPTION OF METHYLENE BLUE AND 2,4-DICHLOROPHENOL  
ONTO MODIFIED ACTIVATED CARBONS PREPARED FROM  
AGRICULTURAL WASTE**

**by**

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**Thesis submitted in fulfilment of the  
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## LIST OF ABBREVIATIONS

AC	Activated carbon
ASTM	American Society for Testing and Materials Standard
BET	Brunauer-Emmet-Teller
BJH	Barrett-Joyner-Halenda
BS	British Standard
CA	Citric acid
DCP	Dichlorophenol
EFBAC	Empty fruit bunch based activated carbon
FAC	Fibre based activated carbon
FTIR	Fourier Transform Infrared
I.R	Impregnation ratio (acid:precursor)
IUPAC	International Union of Pure and Applied Chemistry
JIS	Japanese Industrial Standard
MB	Methylene blue
NH <sub>3</sub>	Ammonia
OPEFB	Oil palm empty fruit bunch
OPF	Oil palm fibre
rpm	Rotation per minute
SEM	Scanning Electron Microscopy
TGA	Thermogravimetric Analyzer
USA	United States of America
UV-Vis	Ultraviolet-visible

## LIST OF SYMBOLS

<i>Symbol</i>	<b>Description</b>	<b>Unit</b>
<i>A</i>	Arrhenius factor	-
<i>C<sub>e</sub></i>	Equilibrium concentration of adsorbate	mg/L
<i>C<sub>o</sub></i>	The highest initial adsorbate concentration	mg/L
<i>E<sub>a</sub></i>	Arrhenius activation energy	kJ/kmol
<i>K<sub>F</sub></i>	Freundlich isotherm constant	(mg/g)(L/mg) <sup>1/n</sup>
<i>K<sub>L</sub></i>	Langmuir isotherm constant	L/mg
<i>k<sub>diff</sub></i>	Intraparticle diffusion rate constant	mg/g.h <sup>1/2</sup>
<i>k<sub>1</sub></i>	Rate constant of pseudo-first-order sorption	1/h
<i>k<sub>2</sub></i>	Rate constant of pseudo-second-order sorption	g/h.mg
<i>N</i>	Total number of data points	-
<i>n</i>	Constant for Freundlich isotherm	-
<i>Q<sub>o</sub></i>	Adsorption capacity for Langmuir isotherm	mg/g
<i>q<sub>e</sub></i>	Amount adsorbate adsorbed at equilibrium	mg/g
<i>q<sub>t</sub></i>	Amount of the adsorbate adsorbed at time <i>t</i>	mg/g
<i>R</i>	Universal gas constant, 8.314	J/ mol. K
<i>R<sub>L</sub></i>	Separation factor	-
<i>R<sup>2</sup></i>	Correlation coefficient	-
<i>T</i>	Transmittance	%
<i>T</i>	Absolute temperature	K
<i>t</i>	Time	h
<i>V</i>	Solution volume	L
<i>W</i>	Dry weight of adsorbent	g



$w_c$	Dry weight of activated carbon	g
$w_o$	Dry weight of precursor	g
$\Delta G^\circ$	Changes in standard free energy	kJ/mol
$\Delta H^\circ$	Changes in standard enthalpy	kJ/mol
$\Delta q_e$	Normalized standard deviation	%
$\Delta S^\circ$	Changes in standard entropy	J/mol K

**PENJERAPAN METILENA BIRU DAN 2,4-DIKLOROFENOL KE ATAS  
KARBON TERAKTIF YANG DIUBAH SUAI DISEDIAKAN DARIPADA  
BAHAN BUANGAN PERTANIAN**

**ABSTRAK**

Kos bahan mentah yang tinggi dalam penghasilan karbon teraktif komersil dan kesukaran dalam penjanaaan semula karbon teraktif yang telah digunakan menghadkan penggunaan karbon teraktif dalam industri rawatan air sisa. Oleh itu, penyelidikan ini bertujuan untuk menghasilkan karbon teraktif daripada sisa buangan pertanian yang banyak terdapat di Malaysia, iaitu gentian (OPF) dan tandan kosong buah kelapa sawit (OPEFB). Karbon teraktif disediakan melalui pengaktifan kimia menggunakan asid fosforik ( $H_3PO_4$ ) dan pengubahsuaian karbon teraktif dilakukan melalui rawatan kimia menggunakan larutan asid sitrik (CA) dan amonia ( $NH_3$ ). Kemungkinan kebolegunaan karbon teraktif yang dihasilkan diuji dalam penyingkiran metilena biru (MB) dan 2,4-diklorofenol (2,4-DCP). Kesemua karbon teraktif yang dihasilkan mempunyai luas permukaan dan isipadu liang yang tinggi manakala diameter liang purata lebih besar daripada 2.2 nm. Analisa imbasan electron mikroskopi (SEM) mengesahkan pembentukan liang yang homogen pada permukaan karbon teraktif sementara analisa infra-merah pengubahan Fourier (FTIR) membuktikan kehadiran pelbagai kumpulan berfungsi pada permukaan karbon teraktif. Kajian penjerapan berkelompok telah dijalankan pada kepekatan awal bahan jerap yang berbeza (MB: 50-500 mg/L, 2,4-DCP: 25-250 mg/L), masa sentuh, suhu larutan (30-50 °C) dan pH larutan (2-12). Penjerapan MB dan 2,4-DCP oleh karbon teraktif menunjukkan aturan yang sama di mana apabila kepekatan awal

meningkat kadar jerapan akan meningkat. Penyingkiran MB adalah maksimum pada pH 12 manakala penyingkiran 2,4-DCP tertinggi pada pH 2. Kesemua sistem bahan jerap-penjerap menunjukkan aturan yang sama dimana kesemua sistem adalah terbaik dihuraikan oleh model garis sesuhu Langmuir dan data juga sepadan dengan model kinetik pseudo tertib kedua. Karbon teraktif yang diubah suai melalui rawatan kimia membuktikan penambahbaikan kadar jerap. Penyelidikan ini memaparkan pengubahsuaian karbon teraktif melalui rawatan berasid menaikkan kadar jerapan MB antara 26.32 ke 46.43% sementara rawatan beralkali yang dijalankan ke atas karbon teraktif meningkatkan kadar jerapan 2,4-DCP antara 22.86 ke 39.13%. Parameter termodinamik seperti tenaga pengaktifan ( $E_a$ ), entalpi ( $\Delta H^\circ$ ), entropi ( $\Delta S^\circ$ ) dan tenaga bebas ( $\Delta G^\circ$ ) juga telah dianalisa. Kesemua karbon teraktif yang dihasilkan menunjukkan kecekapan dan kebolegunaan dalam penjerapan MB dan 2,4-DCP.

**ADSORPTION OF METHYLENE BLUE AND 2,4-DICHLOROPHENOL  
ONTO MODIFIED ACTIVATED CARBONS PREPARED FROM  
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**ABSTRACT**

The expensive cost of starting materials used to prepare commercial activated carbon and the difficulties in regenerating the used activated carbon restricted the activated carbon usage in wastewater treatment industries. Therefore, the objectives of this study are to prepare and modified activated carbons from agricultural wastes abundantly available in Malaysia, namely oil palm fibre (OPF) and oil palm empty fruit bunch (OPEFB). Activated carbons were prepared via chemical activation by using phosphoric acid ( $H_3PO_4$ ) and modification of prepared activated carbons were made via chemical treatment by using citric acid (CA) and ammonia ( $NH_3$ ) solution. The potential feasibility of prepared activated carbons were tested for the removal of methylene blue (MB) and 2,4-dichlorophenol (2,4-DCP). All prepared activated carbons possess high surface areas and total pores volumes whereas the average pore diameters for all samples were greater than 2.2 nm. Scanning Electron Microscopy (SEM) analyses confirmed that homogeneous pores were well developed on the surface of activated carbons while Fourier Transform Infrared (FTIR) analyses verified the presence of various functional groups on the surface of activated carbons. The batch adsorption study was carried out at different initial concentrations of adsorbate (MB: 50-500 mg/L, 2,4-DCP: 25-250 mg/L), contact time, solution temperature (30-50 °C) and solution pH (2-12). The adsorption uptakes of MB and 2,4-DCP showed the same trend where with the increasing of initial concentration

the adsorption uptake will increase. MB removal were maximum at pH 12 while 2,4-DCP removal were the highest at pH 2. All adsorbate-adsorbent systems were showing the same trend where they were well described by Langmuir adsorption isotherm model and the data fitted well pseudo-second-order kinetic model. Modified activated carbons via chemical treatment were proven to enhance the uptake of adsorbate. This work revealed that modification of activated carbons via acidic treatment enhanced the adsorption uptake of MB between 26.32 to 46.43% while basic treatment applied on activated carbons improved adsorption uptake of 2,4-DCP between 22.86 to 39.13%. Thermodynamic parameters such as activation energy ( $E_a$ ), enthalpy ( $\Delta H^\circ$ ), entropy ( $\Delta S^\circ$ ) and free energy ( $\Delta G^\circ$ ) were also evaluated. All prepared activated carbons demonstrate the effectiveness and feasibility for the removal of MB and 2,4-DCP.

## **CHAPTER ONE**

### **INTRODUCTION**

#### **1.0 Research Overview**

A brief introduction on wastewater problems and an overview on the current technologies available for wastewater treatment are presented in this chapter. The application of activated carbon as the adsorbent in wastewater treatment and the need to find alternative to replace the existing commercial activated carbon are incorporated as well. Later in this chapter, the problem statement, research objectives as well as the organization of this thesis are presented.

#### **1.1 Water Pollution**

As a developing country, Malaysia is no exception from facing a numbers of environmental problems. Among those, the most acute problem is the uncontrollable of water pollutions caused by untreated wastewater being discharged into common water sources such as rivers, water reservoirs, lakes, sea and underground water.

Generally wastewater contains various pollutants both organic and inorganic in nature. These pollutants are hazardous and may cause an impairment of water quality which greatly reduces the usability of the water for ordinary purposes or in a worst case scenario creates a hazard to public health through poisoning or the spread of diseases. Apart from causing a public health problem, water pollution also may affect countries' economic growth. Activities such as agriculture, manufacturing, animals herding as well as tourism are affected by water pollution. Thus this reduces the productivity of a nation and causes economics instability in the long run.

## 1.2 Dyes

Dyes are colored materials which exist naturally or synthetically. They may be classified in several ways, according to their chemical structure (anthraquinone, azo, etc.) or according to the way they are fixed to the textile fiber. Typical dyes used in textile dyeing operations are given in Table 1 (Demirbas, 2008). Currently it is estimated about 10,000 of different commercial dyes and pigments exist and over  $7 \times 10^5$  tonnes are produced annually worldwide (Grag *et al.*, 2004). It is estimated that 10-15% of the dye is lost in the effluent during the dyeing process (Lian *et al.*, 2009).

Table 1: Typical dyes used in textile dyeing operations (Demirbas, 2008)

Dye class	Description
Acid	Water-soluble anionic compounds
Basic	Water-soluble, applied in weakly acidic dyebaths; very bright dyes
Direct	Water-soluble, anionic compounds; can be applied directly to cellulose without mordants (or metals like chromium and copper)
Disperse	Not water-soluble
Reactive	Water-soluble, anionic compounds; largest dye class
Sulfur	Organic compounds containing sulfur or sodium sulfide
Vat	Water-insoluble; oldest dyes; more chemically complex

Most of the dyes are toxic, carcinogenic and can cause allergic dermatitis, skin irritation, mutation, etc (Royer *et al.*, 2008). Beside these they impart intense color to wastewater streams causing reduced photosynthesis of aquatic plants due to inhibition of the sunlight penetration (Attia *et al.*, 2008). Thus endanger aquatic life. Therefore the removal of these dyes from water bodies is extremely important from an environmental point of view.

### **1.3 Phenolic Compounds**

Phenols are pollutants of high priority concerns because of their toxicity and possible accumulation in the environment. Phenols are introduced into surface water from industrial effluents such as those from the coal tar, gasoline, plastic, rubber proofing, disinfectant, pharmaceutical, steel industries, domestic wastewaters, agricultural run-off and chemical spills (Lin and Juang, 2008).

Phenols and its derivatives are known or suspected to be human carcinogens (Abburi, 2003). According to the Environmental Protection Agency in USA, phenols and its derivatives are considered to constitute the 11<sup>th</sup> of the 126 chemicals which have been designated as priority pollutants (Caturla *et al.*, 1998), whereas referring to the Environmental Quality Act of Malaysia, the permissible limits for phenolic compounds in industrial effluents before discharging into municipal sewers and surface water is 0.001 mg/L.

### **1.4 Adsorption**

These days, highly developed technologies for the removal of industrial effluents containing dyes and phenolic compounds have been introduced. These include physical and chemical processes such as adsorption, membrane separation, oxidation, removal by ion exchange resins and aerobic or anaerobic biodegradation. Each technique possesses the advantages and disadvantages of its own. However many of these technologies are extremely expensive and their efficiencies in removing dyes are relatively low. Table 1.2 summarizes the advantages and disadvantages of the principal existing emerging process for dyes removal (Crini, 2006).



Table 1.2 Principal existing and emerging processes for dyes removal (Crini, 2006)

	<b>Technology</b>	<b>Advantages</b>	<b>Disadvantages</b>
Conventional treatment processes	Coagulation	Simple, economically feasible	High sludge production, handling and disposal problems
	Flocculation		
	Biodegradation	Economically attractive, publicly acceptable treatment	Slow process, necessary to create an optimal favorable environment, maintenance and nutrition requirements
	Adsorption on activated carbons	The most effective adsorbent, great capacity, produce a high-quality treated effluent	Ineffective against disperse and vat dyes, the regeneration is expensive and results in loss of the adsorbent, non-destructive process
Established recovery processes	Membrane separations	Removes all dye types, produce a high-quality treated effluent	High pressures, expensive, incapable of treating large volumes
	Ion-exchange	No loss of sorbent on regeneration, effective	Economic constraints, not effective for disperse dyes
	Oxidation	Rapid and efficient process	High energy cost, chemicals required
Emerging removal processes	Advanced oxidation process	No sludge production, little or no consumption of chemicals, efficiency for recalcitrant dyes	Economically unfeasible, formation of by-products, technical constraints
	Selective bioadsorbents	Economically attractive, regeneration is not necessary, high selectivity	Requires chemical modification, non-destructive process
	Biomass	Low operating cost, good efficiency and selectivity, no toxic effect on microorganisms	Slow process, performance depends on some external factors (pH, salts)

Adsorption technique employing activated carbon however has been found to be reasonably effective in the removal of dyes and phenolic compounds in wastewater. Adsorption is a process, which involves the contact of a free aqueous phase with a rigid particulate phase, which has the propensity to remove or store one or more solutes present in the solution selectively (Wong *et al.*, 2004). Due to economic considerations, adsorption process may require the use of inexpensive adsorbents which are either naturally available or available as waste products from agricultural activities. Due to this factor, amongst other consideration such as simplicity of design, ease of operation and insensitivity to toxic substances; adsorption is rapidly becoming a prominent technique of treating dyes and phenolic effluents in industrial processes.

### **1.5 Activated Carbon as an Adsorbent**

According to Banat *et al.* (2003), activated carbons have always been used as adsorbents for dye removal from wastewater due to its high surface area and adsorption capacity, microporous structure and special surface reactivity. These factors made adsorption process very favorable.

However the use of commercial activated carbon as adsorbent in adsorption process is becoming more restricted as a consequence of the expensive cost of starting materials used to produce the activated carbon such as bituminous coal, lignite and petroleum coke as well as the difficulties in regenerating the used activated carbon. On the other hand, in wastewater treatment industry the demand for adsorption processes is increasing. According to Polat *et al.* (2006) in year 2006, the average cost of activated carbon from the major producers was close to \$2500 per

ton, with a world demand expected to expand 5.2% per year through 2012 to 1.2 millions tons. These numbers provide compelling enough reasons for numerous researchers to manufacture activated carbon from alternative precursors including industrial wastes and agricultural by-products as a substitute to the existing commercial activated carbon.

Many studies on the use of agricultural by-products as precursors in activated carbon production have been published such as olive stones (Silvestre-Albero *et al.*, 2009), pecan shells (Klasson *et al.*, 2009), rice straw (Basta *et al.*, 2009), vetiver roots (Altenor *et al.*, 2009), coffee husks (Oliveira *et al.*, 2008), date stones (Hameed *et al.*, 2009), maize cob (Sathishkumar *et al.*, 2009), wood particleboard (Girods *et al.*, 2008) and kraft lignin (Fierro *et al.*, 2008). Agricultural by-products have become primary choice by researchers to be used as precursors in the production of activated carbon because they are economic and ecofriendly due to their unique chemical composition, availability in abundance, renewable, low in cost and more efficient.

#### **1.5.1 Precursors for Activated Carbons Production - Oil Palm Fibre and Oil Palm Empty Fruit Bunch**

Malaysia is well known as an agricultural country. One of the largest crops planted is the oil palm tree (*Elaeis guineensis*). This tropical plant tree is used in the production of palm oil and palm kernel oil, which are widely used in food and other industries such as detergents and cosmetics.

The oil palm tree which is also known as the golden crop, has positioned Malaysia as the leading nation in oil palm production in addition being the largest producer and exporter of palm oil in the world with a market share of about 50 and 58 percent, respectively (Mohd Nasir, 2003). With the increasing trend of world's demand for oils and fats, the oil palm industry in Malaysia has an important role to play in fulfilling the growing global needs for oils and fats. This has led to the rapid growth of oil palm plantation area in the country, which correspondingly saw growth in oil palm biomass residues being generated throughout harvesting and processing activities as well as during replanting.

Although oil from the oil palm tree is a beneficial product from the economic point of view, residues from palm oil have not been used sufficiently. Palm oil mills produce a large amount of solid wastes, such as extracted oil palm fibres, palm shells, palm stones and empty fruit bunches. For instance in Malaysia, 10.7 million tons (dry weight) of extracted oil palm fibre are estimated to be generated in the year 2006, whereas the empty fruit bunches (EFB) which been discharged from refinery regularly, amounting to 17.4 million tons per annum in the same year (Yacob, 2007).

The mounting amount of the oil palm tree by-products resulted from the milling activities only create a solid disposal problem. Most of these by-products are either burnt in open air or dumped in areas adjacent to the mill. These wastes if not served properly will only caused severe problem in the community.

Therefore, in this research the oil palm fibre and oil palm empty fruit bunch have been chosen as precursors in the production of activated carbons. They were

selected since they are easily and abundantly available, low cost and renewable. Furthermore these agricultural by products were known to have high carbon content and low inorganic component which make them suitable to be used as the activated carbon precursors.

## **1.6 Problem Statement**

Environmental concerns in the palm oil industry are also becoming more serious issues that need stern consideration by the community. By utilizing the oil palm tree by-products as precursors in activated carbon production, it will help to minimize the solid disposal problem arising from the palm oil industry as well as accomplish the need to preserve a clean environment through application in liquid phase adsorption for removal of pollutants from wastewater, mainly methylene blue and 2,4-dichlorophenol. Additionally, converting these unwanted wastes into useful, value added products may reduce the cost of activated carbon production.

## **1.7 Research Objectives**

The research objectives are:

- i. To produce activated carbons from oil palm fibres (OPF) and oil palm empty fruit bunch (OPEFB) by chemical activation using phosphoric acid.
- ii. To modify the surface of prepared activated carbons by chemical treatment.
- iii. To characterize the prepared activated carbons for their physical and chemical properties.
- iv. To study the adsorption isotherms, kinetics and mechanism of each pollutant on the prepared activated carbons.

## **1.8 Organization of the Thesis**

The thesis consists of five chapters, where each chapter represents five different topics which cover the whole picture of the present study.

Chapter one gives brief introduction on wastewater problems and an overview on the current technologies available to treat the wastewater problems. This chapter also enclosed the application of activated carbon as the adsorbent in wastewater treatment and the need to find alternative to replace the existing commercial activated carbon. The objectives of present study were also stated in the first chapter as well as thesis organization.

Chapter two presents the literature review which portrays the information on activated carbon as the adsorbent and adsorption process itself. The information on diverse precursors and activation methods used by previous researchers to manufacture activated carbons are too incorporated. Last but not least in this chapter is knowledge on adsorption isotherms, kinetics and thermodynamics which later will be useful in analyzing data obtained in this present work.

Chapter three describes the material and methods used to accomplish this study. All chemicals, equipments and methods involve in preparation of the activated carbons, batch experiments and characterization of samples are properly depict in order to give a clear picture on the whole processes involve in this present study.

Chapter four represents the results obtained from the experiments in preparation of activated carbons, batch experiments and characterization of samples.

All acquired results are summarized in the form of tables and graphs and supported with discussions which are elaborated in details the findings in this present study.

Chapter five concludes the findings from the present research and finally some recommendations are given for future studies.

## CHAPTER TWO

### LITERATURE REVIEW

#### 2.0 Introduction

This chapter presents the literature review which portrays the information on adsorption process and activated carbon as the adsorbent. The information on diverse precursors and activation methods used by previous researchers to manufacture activated carbons are incorporated as well. Last but not least in this chapter, knowledge on adsorption isotherms, kinetics and thermodynamics which later will be useful in analyzing data obtained is presented.

#### 2.1 Adsorption

When there is a natural tendency for components of liquid or a gas to collect often as a monolayer but sometimes as a multilayer at the surface of a solid material, this phenomenon is known as adsorption (Humphrey and Keller II, 1997). In an adsorption process, molecules, atoms or ions in a gas or liquid diffuse to the surface of a solid, where they bond with the solid surface or are held there by weak intermolecular forces. The components being adsorbed are referred to as adsorbate, whereas the solid material is the adsorbent (Seader and Henley, 1998). Figure 2.1 illustrates the adsorption process with solid-particle sorbent (Seader and Henley, 1998).

Adsorption is effective for purifications and bulk separations. For example, it is practical for water decontamination application, decolourization of liquid solutions, recovery of certain constituents (solvents from air) and to remove



objectionable odours and impurities from industrial gases such as carbon dioxide. Adsorption technique has been found to be prominent method for treating pollutants due to their efficiency, simplicity of design, ease of operation and also cost effective (Crini, 2006).

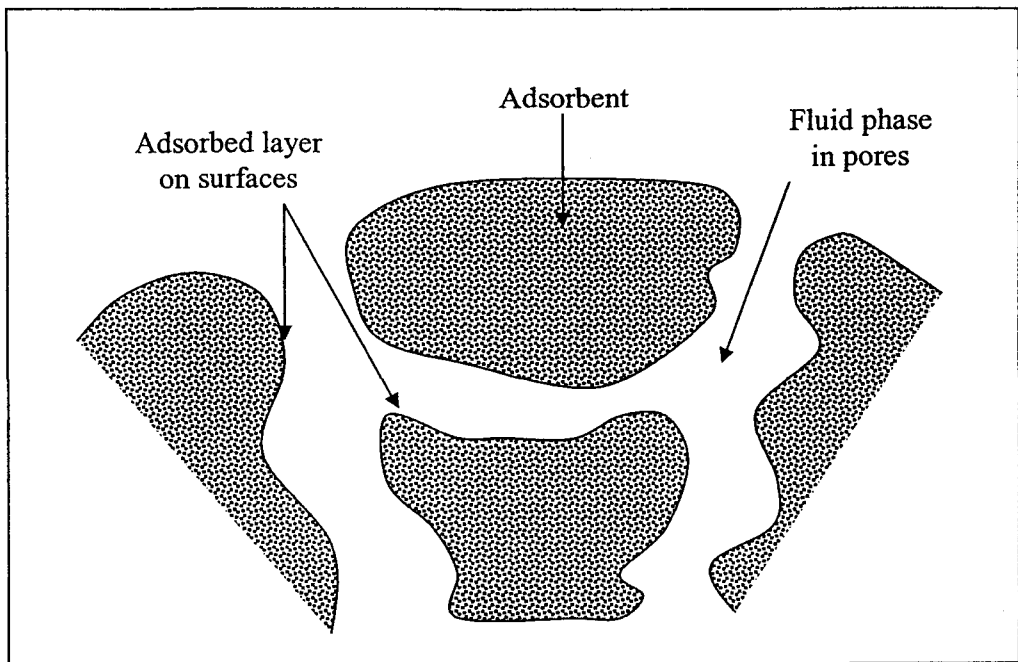


Figure 2.1 Adsorption process with solid-particle sorbent (Seader and Henley, 1998)

## 2.2 Adsorption Mechanism

Adsorption may be classified as physical adsorption or chemical adsorption depending upon the types of forces between the fluid molecules and the molecules of the solid (Seader and Henley, 1998). Physical adsorption or van der Waals adsorption, a readily reversible phenomenon, is a result of intermolecular forces of attraction between molecules of the solid and the substance adsorbed. Chemisorption, or activated adsorption, is the result of chemical interaction between

the solid and the adsorbed substance. The strength of the chemical bond may vary considerably, and identifiable chemical compounds in the usual sense may not actually form, but the adhesive force is generally much greater than that found in physical adsorption (Treyball, 1981). Under favourable conditions, both processes can occur simultaneously or alternately. Table 2.1 shows a comparison between physical adsorption and chemical adsorption (Ruthven, 1984).

Table 2.1 Comparison between physical adsorption and chemical adsorption (Ruthven, 1984)

<b>Physical Adsorption</b>	<b>Chemical Adsorption</b>
Low heat of adsorption	High heat of adsorption
Non specific	Highly specific
Monolayer or multilayer	Monolayer only
No dissociation of adsorbed species	May involve dissociation
Only significant at relatively low temperature	Possible over a wide range of temperature
Non activated, rapid and reversible	Activated, may be slow and irreversible
Non electrons transfer although polarization of sorbate may occur	Electron transfer leading to bond formation between sorbate and surface

### 2.3 Adsorbent

Solids have been known to be able to adsorb gaseous and liquids. However, only a few solids have the high adsorption capacity and sufficient selectivity to make them viable as commercial adsorbents. Of considerable importance is a large specific surface area (area per unit volume), which is achieved by adsorbent manufacturing techniques that results in solids with a microporous structure. There are many types of adsorbents available commercially such as activated carbon, activated alumina, silica gel, molecular sieve carbon, zeolite and polymeric based adsorbent (Seader and Henley, 1998).

Among these commercial adsorbents, activated carbon is the most widely used adsorbent. Over the last few decades, adsorption systems involving activated carbon have gained importance in purification and separation processes on an industrial scale. It is now considered as one of the best available technologies in removing both organic and inorganic contaminants (Girgis *et al.*, 2002).

#### **2.4 Activated Carbon**

Activated carbons are the oldest adsorbents known (Hassler, 1963). The use of activated carbon had started 3750 years before century by Egyptians and Sumerians where during that period charcoal was used for reduction of copper, zinc and tin ores for bronze manufacturing. As the time pass by, activated carbon has found new ways in various applications i.e. for medicinal purposes to adsorb odorous vapours from putrefactive wounds: decolourization agent of sugar syrup and later during World War I, activated carbon was used in the protective breathing apparatus to stop soldiers from inhaling toxic gases (Dabrowski, 2001).

Activated carbons are available in variety forms and particle sizes mainly powder, granular, pellet and bead. Powdered activated carbon is comprised of fine particles, less than about 0.2 mm in diameter, and thus presents large external surface area and small diffusion resistance. Hence the rate of adsorption is very high. Granular activated carbon on the other hand is comprised of larger carbon particles, up to about 5 mm in diameter, with smaller external surface areas compared to powdered activated carbon. Due to the fact that the granular form is more adaptable to continuous contacting, they are generally favoured for the adsorption of gaseous and vapours and for use in fixed bed filtration systems. In addition, it can be easily

regenerated, whereas this is often impossible with powdered activated carbon due to the difficulty of separating the powdered adsorbent from the fluid (Suhast *et al.*, 2007).

The market for activated carbon is indeed vast. The global consumption of activated carbons was 750,000 tonnes in year 2002. The estimated growth of worldwide demand is 4-5 % per year, with higher growth rate of 5-6 % per year projected for the United States between year 2002 and year 2005 (Zhang *et al.*, 2004). However commercially available activated carbons are very expensive, the higher the quality the greater the cost thus they may not be economical for wastewater treatment. Hence this has led to the search of new low cost adsorbent as a substitute to the existing activated carbon.

## **2.5 Activated Carbon Production Procedures**

According to Li *et al.* (2008), activated carbon can be prepared from a wide variety of raw materials which should be abundant and cheap, with high carbon content and low inorganic content. In addition raw materials should be easily activated and should have low degradation by aging (Dabrowski, 2001).

In general activated carbons are produced by carbonizing the raw materials prior to activation. The purpose of carbonization process is to enrich the carbon content and to create an initial porosity in the char. The activation process further develops the porosity and created some ordering of the structure to generate a highly porous solid as the final product (Wan Daud *et al.*, 2000).

### 2.5.1 Carbonization

Carbonization process is also known as pyrolysis. It can be defined as the chemical decomposition of a material at high temperature in an inert atmosphere. The product obtained in this process is fundamentally a solid residue with high carbon content, a combustible gas of low medium calorific value and a liquid phase composed by tars (Gañán *et al.*, 2006).

In practice, the carbonization temperature lies in the range of 500 to 900 °C. According to Rodriguez-Reinoso and Molina Sabio (1992), there are three clear stages in the carbonization process which can be determined by the temperature attained in each stage. The stages are as listed in Table 2.2 below.

Table 2.2 Stages in carbonization process (Rodriguez-Reinoso and Molina Sabio, 1992)

Stage	Temperature (K)	Process
Stage 1	300 – 470	Drying of precursors (loss of water)
Stage 2	470 – 770	Primary pyrolysis (evolution of most gases and tars and formation of the basic structure of the char)
Stage 3	770 – 1120	Consolidation of char structure with a very small weight loss

The carbonization process leaves an imprint effect on the final product. Hence to produce the essential quality of activated carbon, it is important to be careful in selecting parameters of carbonization (Wan Daud *et al.*, 2000). With reference to Mermoud *et al.*, (2006) operating conditions during pyrolysis such as heating rate, final temperature, residence time, pressure or size of the particles are known to have an influence on the morphology of the charcoal obtained as well as on

its reactivity during gasification. Therefore the process condition can be optimized to maximize the production of the pyrolytic char. Cetin *et al.* (2004) reported that the pyrolysis heating rate of the initial biomass significantly influences the reactivity of the charcoal during its gasification. Higher heating rate were found to provide more reactive charcoals during gasification by carbon dioxide.

### 2.5.2 Activation

Activation process is one of the important procedures in developing the activated carbon. Properties of the activated carbon created such as the percentage yield, surface area and porosity is highly dependent on the activation mode and the operating parameter. During the carbonization stage, the pore structure is filled with tar products, which decompose and block the pores. Throughout activation process the oxidizing gases will react with the disorganized carbon that had blocked the pore structure and as a result, the pores are opened and becomes accessible to the sorbate molecules, leading to an increase in surface area. In other word, activating the char would further create additional porosity within the solid matrix of the activated carbon.

There are two modes of activation, which are physical activation and chemical activation. However recently many researchers (Hameed *et al.*, 2009; Tan *et al.*, 2009; Mohd Din *et al.*, 2009) had made their attempt in combining both activation methods in developing a better quality of activated carbon. This method is known as physiochemical method.

### 2.5.2.1 Physical Activation

Preparation of activated carbons by a physical method normally involves two stages which are carbonization and activation. In the first stage, the carbonaceous materials are carbonized under an inert atmosphere at a moderate temperature (about 400 to 800 °C) in order to remove the volatile matters and produce chars with rudimentary pore structures. Subsequently in the second stage, the resulting chars are subjected to a partial gasification at elevated temperature (usually 800 to 1000 °C) in the presence of suitable oxidizing gases such as carbon dioxide, steam, air or their mixtures, to produce final products with well developed and accessible internal porosities (Lua *et al.*, 2006).

Figure 2.2 shows the simple thermal treatment scheme for activated carbon preparation by Guo and Lua (2002). The activated carbon was prepared from palm shell via physical activation by carbon dioxide. Carbonization was carried out for three hours under nitrogen (N<sub>2</sub>) flow at temperature of 873 K. The resulting char then was soaked with carbon dioxide (CO<sub>2</sub>) for half an hour at a temperature ranging from 773 K to 1173 K. The prepared activated carbons possessed well developed porosity, predominantly microporosity. The fairly high Brunauer-Emmet-Teller (BET) and micropore surface areas obtained render them to be suitable as effective adsorbents. The maximum BET surface area of the palm shell activated carbon was 1366 m<sup>2</sup>/g.

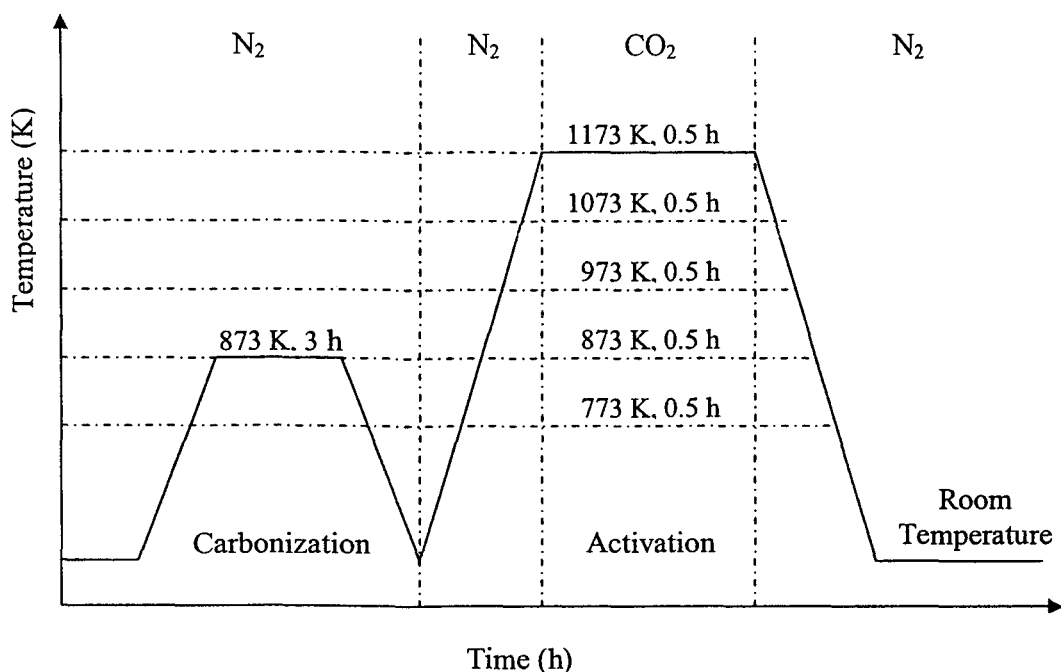


Figure 2.2 Activated carbons prepared from palm shell via physical activation scheme by  $CO_2$  (Guo and Lua, 2002)

The most common gas used for activation is carbon dioxide since it is clean, easy to handle and it facilitates control of the activation process due to the slow reaction rate at temperatures around 800 °C (Zhang *et al.*, 2004).

However, physical activation process can also be performed by one step activation method. In the one step activation process, pyrolysis and activation were carried out simultaneously in the presence of steam. The one step activation method with steam has advantages over the two step method, due to its simplicity and efficiency in the preparation of activated carbons from lignocellulosic materials. The one step method eliminates the separate carbonization step that is used in the conventional two step method and employs lower temperatures in the preparation of



the activated carbons (Şentorum-Shalaby *et al.*, 2006). Even though the single or one step pyrolysis is cheaper in cost, the two step pyrolysis is favourable because higher surface area and porous carbon can be obtained.

### 2.5.1.2 Chemical Activation

In contrast to physical activation, chemical activation is normally carried out in one step. In chemical activation the precursor is being mixed with chemical activating agents such as zinc chloride ( $\text{ZnCl}_2$ ), potassium hydroxide (KOH), phosphoric acid ( $\text{H}_3\text{PO}_4$ ) and potassium carbonate ( $\text{K}_2\text{CO}_3$ ) as dehydrating agents and oxidants. Among these dehydrating agents, zinc chloride and phosphoric acid are the most widely used chemical agents. However the use of phosphoric acid is preferred because of the environmental disadvantages associate with zinc chloride. Problem of corrosion and inefficient chemical recovery is also associates with it (Prahas *et al.*, 2008). Moreover, the carbons obtained using zinc chloride cannot be used in pharmaceutical and food industries as it may contaminate the product (Srinivasakannan *et al.*, 2004).

A number of studies have been carried out by researchers to understand the surface chemistry and reaction mechanism occurred when these chemicals are applied on certain precursors in activated carbon production. Girgis *et al.* (2002) prepared activated carbons by impregnating peanut hulls with concentrated phosphoric acid ( $\text{H}_3\text{PO}_4$ ) followed by heat treatment for three hours at 500 °C. This temperature had been found as most suitable to perform the process properly. Since heat treatment is achieved at lower temperature, a higher yield is obtained which is 36%. The chemical incorporated into the interior of the precursor particles react with

the thermal decomposition products reducing the evolution of volatiles and inhibits the shrinkage of the particles. This resulted the high conversion of precursor to carbon and once the chemical is eliminated after the heat treatment, a large internal porosity is formed.

Attia *et al.* (2008) reported that by raising the impregnation ratio or concentration of phosphoric acid it will improve the adsorption capacity due to an increase in accessible sites suitable for the accommodation of the adsorbate which is the dye molecules. Thus by raising the amounts of the impregnant incorporated inside the precursor favour the pore development with generation of relatively wide micropores. In other finding, activated carbons were developed from durian shell and used for the removal of methylene blue from aqueous solution. The activated carbon was prepared using chemical activation method with potassium hydroxide (KOH) as the activating agent. Table 2.3 shows the pore characteristics of durian shell activated carbon (DSAC) obtained in comparison with Filtrasob-400 (F-400), the commercial coal based activated carbon produced by Calgon. It was proven that the activated carbon produced via chemical activation method gives a better characteristic compared to the commercial ones (Chandra *et al.*, 2007).

Table 2.3 Pore characteristics of durian shell activated carbon (DSAC) and F-400 (Chandra *et al.*, 2007)

Pore Characteristic	Durian Shell Activated Carbon (DSAC)	Filtrasob-400 (F-400)
BET surface area (m <sup>2</sup> /g)	991.82	877.82
Micropore surface area (m <sup>2</sup> /g)	849.31	761.80
Micropore volume (cm <sup>3</sup> /g)	0.368	0.343
Total pore volume (cm <sup>3</sup> /g)	0.471	0.468

The advantage of chemical activation is low energy cost since chemical activation usually takes place at a temperature lower than that used in physical activation. Moreover, chemical activation also has better development of porous structure. The carbon yield in chemical activation is usually higher than in physical activation since the chemical agents are substances with dehydrogenation properties that inhibit the formation of tar and reduce the production of other volatile substances (Yorgun *et al.*, 2009). However the disadvantage of chemical activation is the incorporation of impurities coming from the activating agent, which may affect the chemical properties of the activated carbon (G'omez *et al.*, 2005). Some of the previous studies reported on the preparation of activated carbon via chemical activation are shown in Table 2.4.

Table 2.4 Preparation of activated carbon via chemical activation using different activating agents

Activating Agent	Precursor	Reference
Potassium Carbonate (K <sub>2</sub> CO <sub>3</sub> )	Palm shell	Adinata <i>et al.</i> , 2007
	Cork	Mestre <i>et al.</i> , 2009
Sulphuric Acid (H <sub>2</sub> SO <sub>4</sub> )	Sunflower oil cake	Karagöz <i>et al.</i> , 2008
Zinc Chloride (ZnCl <sub>2</sub> )	Coffee fruit (husk)	Oliveira <i>et al.</i> , 2008
	Rice husk	Kalderis <i>et al.</i> , 2008
	Coffee residue	Boudrahem <i>et al.</i> , 2009
Phosphoric Acid (H <sub>3</sub> PO <sub>4</sub> )	Paulownia wood	Yorgun <i>et al.</i> , 2009
	HEMP	Rosas <i>et al.</i> , 2009
	Olive-waste cakes	Baccar <i>et al.</i> , 2009
Potassium Hydroxide (KOH)	Olive Seed Waste	Skodras <i>et al.</i> , 2007
	Vetiver roots	Altenor <i>et al.</i> , 2008
	Corn Cob	Bagheri and Abedi, 2009
Sodium Hydroxide (NaOH)	Plum Kernels	Tseng, 2007

### 2.5.2.3 Physiochemical Activation

Apart from physical and chemical activation, activated carbon also can be manufacture through the combination of both activation method mentioned earlier which is known as physiochemical activation. Via physiochemical activation, the activated carbon precursor normally will be activated first with the chemical and then followed by thermal treatment.

Tan *et al.*, (2007) had prepared activated carbon using the oil palm fibre via physiochemical scheme. Potassium hydroxide (KOH) and carbon dioxide (CO<sub>2</sub>) had been chosen as the chemical and physical agents respectively. Carbonization was performed at 700 °C for two hours under nitrogen (N<sub>2</sub>) flow prior impregnation of the precursor with potassium hydroxide. Physical activation was held then under the same condition as carbonization but to a final temperature of 850 °C by carbon dioxide and activation took place for two hours. As a result of the physiochemical activation applied, a high BET surface area of prepared activated carbon was obtained which is equivalent to 1354 m<sup>2</sup>/g, with total pore volume of 0.778 cm<sup>3</sup>/g. These values were found to be much higher from the commercial activated carbon such as BDH from Merck where the BET surface area is only 1118 m<sup>2</sup>/g and total pore volume of 0.618 cm<sup>3</sup>/g. Figure 2.3, illustrates the physiochemical activation method for activated carbon preparation applied in their work.

In other study, an attempt has been made by Hu *et al.* (2001) to develop activated carbon from coconut shell by using zinc chloride in presence of carbon dioxide. Impregnation took place before carbonization. Later carbonization was performed for one hour at 800 °C while activation by carbon dioxide took several

hours at the same temperature. It was found out that, the mesopores percentage obtained was as high as 71% of total pore volume. Activating agents, zinc chloride and carbon dioxide enhance the formation of mesopores as it widened the existing pores, so that a significant amount of micropores becomes mesopores.

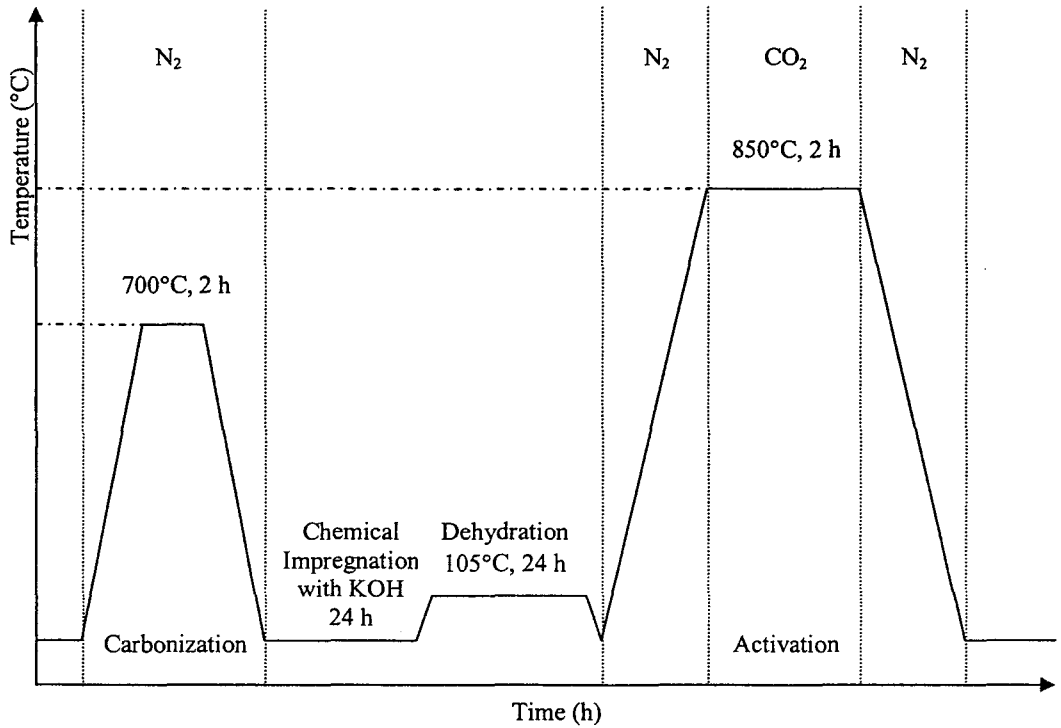


Figure 2.3 Preparation of activated carbon from oil palm fibre via physiochemical activation (Tan *et al.*, 2007)

## 2.6 Activated Carbon Precursors

Practically any carbonaceous materials, natural or synthetic, rich in carbon and low in ash are theoretically feasible for activated carbon production (Attia *et al.*, 2008). Coal, lignite and wood are examples of material which are rich in carbon. Although coal is the most commonly used precursor, agricultural waste in certain condition is a better choice (Prahas *et al.*, 2008).