Theoretical and experimental studies on activated carbons prepared from biomass for aqueous-phase adsorption

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**THEORETICAL AND EXPERIMENTAL STUDIES ON
ACTIVATED CARBONS PREPARED FROM BIOMASS
FOR AQUEOUS-PHASE ADSORPTION**

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SCHOOL OF MECHANICAL & AEROSPACE ENGINEERING

2005

**Theoretical and Experimental Studies on
Activated Carbons Prepared from Biomass for
Aqueous-phase Adsorption**

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A thesis submitted to the Nanyang Technological University
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Degree of Philosophy

2005

ABSTRACT

Preparation of activated carbons from oil-palm shells, physical activation as well as by combined steam and chemical activation was investigated in great detail to study the process parameters. In physical activation, a two-step procedure was used: pyrolysis followed by activation. Steam was used as the physical activation agent. The resulting activated carbons were studied using scanning electron microscope (SEM) for its morphology and characterized by accelerated surface area and porosimetry system to determine the pore surface areas and pore size distributions. Pyrolysis develops the rudimentary pore structure in the char. The pyrolysis parameters will influence the active surface area of the chars and therefore the reactivity of the chars. Activation, after pyrolysis, is used to increase the pore surface area and pore volume of the activated carbon.

A combined chemical and physical activation process was investigated. Potassium carbonate was used as the chemical activation agent. The results indicated that the catalytic effect of potassium and the thermal decomposition of carbonic anion in chemical activation played different roles on micropore and nonmicropore structure development. The activated carbons were used to study the adsorption of phenol aqueous solution. It was found that the adsorption capacity increased linearly with the BET surface area. This linear relationship was not applicable to activated carbons prepared under varying activation parameters. The aqueous phase adsorption capacity of the combined physically and chemically activated carbon was found not to be significantly greater than the physically activated carbons due to the blockage effect to the pore surface by the products of chemical reaction. Amongst all the activated carbons prepared, the highest BET

surface area was 1432 m²/g. For aqueous phase adsorption tests, the highest phenol adsorption capacity was 275 mg of phenol per gram of activated carbon at 30°C.

The use of the activated carbon in one component aqueous phase adsorption was studied systematically. This study included the thermodynamic, kinetic and dynamic aspects. Gas chromatography-mass spectrometry was used to analyze the chemicals in the aqueous phase. Results from the aqueous phase adsorption indicated that the equilibrium data could be correlated by the Langmuir isotherm. The correlation of the kinetic adsorption data with the Langmuir isotherm confirmed that the Langmuir equation was adequate to depict the behaviour of single component system. Batch kinetic experimental data showed a dual-rate nature of adsorption onto the activated carbon. A proposed branched pore kinetic model fitted the experimental data well and was able to predict the performance of phenol -activated carbon system. The model is called the concentration dependent branched pore kinetic model (CDBPKM).

Regression analysis to estimate the adsorption parameters was used to optimize the correlation between the experimental data and the CDBPKM model. In the CDBPKM, the concentration dependent effective diffusion coefficient was introduced into the traditional branched pore kinetic model. With this coefficient, the model can better predict the kinetic behaviour of the activated carbon in aqueous phase adsorption. CDBPKM simulated dual rates of concentration decay curves with correlation coefficients around 0.98. Theoretical study indicates that adsorption is controlled by the external mass transfer at the very early stage and then intra-particle diffusion is predominant till equilibrium is reached. Adsorption into the micropores becomes significant when the nonmicropore region is saturated. The most fundamental parameter affecting the concentration decay is the fraction of total adsorptive capacity in the

nonmicropore region. This effect indicates the importance of adsorbent surface characteristics in the adsorption process.

The potential application of activated carbon in aqueous phase adsorption was demonstrated by fixed bed adsorption study. Series of column tests were carried out for the adsorption of phenol by activated carbons. The effects of operation conditions of the fixed bed on the breakthrough curves were studied. A linear driving force model based on the solid phase concentration difference (LDFQ model) was used to simulate the fixed bed adsorption dynamics. The agreement between the model and the experimental data was good. Correlated mass transfer coefficient and fixed bed parameters provide information for fixed bed adsorption design.

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LIST OF SYMBOLS

a	Association coefficient (dimensionless)
a_m	Average area occupied by one molecule in the complete monolayer (nm^2)
A	Fixed bed cross sectional area (cm^2)
b_L	Langmuir isotherm equation constant ($\text{l} \cdot \text{mg}^{-1}$)
b_{LF}	Langmuir-Freundlich isotherm equation constant ($\text{l} \cdot \text{mg}^{-1}$)
c	Solution concentration, concentration in the aqueous phase ($\text{mg} \cdot \text{l}^{-1}$)
C	Dimensionless aqueous phase concentration ($C = \frac{c}{c_0}$)
C_s	Dimensionless aqueous phase concentration at particle surface ($C_s = \frac{c_s}{c_0}$)
c_e	Equilibrium aqueous phase concentration ($\text{mg} \cdot \text{l}^{-1}$)
c_p	Solution concentration within particle ($\text{mg} \cdot \text{l}^{-1}$)
c_s	Solution concentration at particle surface ($\text{mg} \cdot \text{l}^{-1}$)
c_0	Initial aqueous solution concentration ($\text{mg} \cdot \text{l}^{-1}$)
dH_a	Net enthalpy of adsorption, the isotheric heat of adsorption ($\text{kJ} \cdot \text{mol}^{-1}$)
d_p	Particle diameter (cm)
D_{eff}	Effective diffusion coefficient ($\text{cm}^2 \cdot \text{s}^{-1}$)
$D_{eff,0}$	Effective diffusion coefficient at zero surface coverage ($\text{cm}^2 \cdot \text{s}^{-1}$)
D_m	Molecular diffusion coefficient in dilute solution ($\text{cm}^2 \cdot \text{s}^{-1}$)
D_p	Pore diffusion coefficient ($\text{cm}^2 \cdot \text{s}^{-1}$)
D_s	Surface diffusion coefficient ($\text{cm}^2 \cdot \text{s}^{-1}$)
D_{s0}	Effective surface diffusion coefficient at zero loading ($\text{cm}^2 \cdot \text{s}^{-1}$)
E_z	Eddy diffusion coefficient or axial dispersion coefficient ($\text{cm}^2 \cdot \text{s}^{-1}$)
f	Portion of the total adsorptive capacity utilized in the nonmicropore (dimensionless)

FBiot	Modified film Biot number ($FBiot = \frac{K_f c_0 R}{\rho f D_{eff} q_0}$)
H	Column height (cm)
HJP1	Harkins and Jura parameter 1.
HJP2	Harkins and Jura parameter 2.
HJP3	Harkins and Jura parameter 3.
k	Constant, defined by quantitative measure of the binding energy and the differential heat of adsorption (dimensionless)
k_s	Particle phase mass transfer coefficient ($\text{g} \cdot \text{l}^{-1} \cdot \text{s}^{-1}$)
k_L	Langmuir isotherm equation constants ($\text{l} \cdot \text{g}^{-1}$)
k_{LA}	Langmuir isotherm equation characteristic constant ($\text{l} \cdot \text{mg}^{-1}$)
k_F	Freundlich isotherm equation characteristic constant ($\frac{\text{mg}}{\text{g}} \left(\frac{1}{\text{mg}} \right)^{n_F}$)
K	Freundlich isotherm equation constant ($\text{l} \cdot \text{g}^{-1}$)
K_b	Branched pore rate coefficient, s^{-1}
K_f	External aqueous phase mass transfer coefficient ($\text{cm} \cdot \text{s}^{-1}$)
K_F	Overall mass transfer coefficient, based on the fluid phase concentration difference (s^{-1})
K_S	Overall mass transfer coefficient, based on the particle phase concentration difference ($\text{g} \cdot \text{l}^{-1} \cdot \text{s}^{-1}$)
M	Molecule weight of solvent ($\text{g} \cdot \text{mol}^{-1}$)
m	Mass of the adsorbent (g)
m_i	Mass of raw material, i. e., oil palm shell (g)
m_t	Mass of char produced by carbonization (g)
N	Rotation speed (rpm), adsorbate uptake rate per pellet or number of adsorbate species at z ($\text{mg} \cdot \text{g}^{-1}$)
N_A	Avogadro constant ($6.02 \times 10^{23} \text{ mol}^{-1}$)
n_F	Freundlich isotherm equation constant (dimensionless)
n_{LF}	Langmuir-Freundlich isotherm equation constant (dimensionless)
N_{pt}	Number of points on a fitted experimental curve (dimensionless)
p / p_0	Relative pressure for the ith point (mmHg)

PBiot	Modified particle Biot number ($PBiot = \frac{K_b R^2}{fD_{eff0}}$)
Pe	Peclet number ($Pe = \frac{H \cdot u}{E_z}$)
q	Solid phase concentration on average ($\text{mg} \cdot \text{g}^{-1}$)
q_0	Solid phase concentration in equilibrium with c_0 ($\text{mg} \cdot \text{g}^{-1}$)
q_{av}	Amount of adsorbed on the adsorbent on volume average ($\text{mg} \cdot \text{g}^{-1}$)
q_b	Solid phase concentration in micropore region ($\text{mg} \cdot \text{g}^{-1}$)
q_e	Equilibrium solid phase concentration ($\text{mg} \cdot \text{g}^{-1}$)
q_m	Solid phase concentration in nonmicropore region ($\text{mg} \cdot \text{g}^{-1}$)
q_s	Solid phase concentration equilibrated with solution concentration on particle surface ($\text{mg} \cdot \text{g}^{-1}$)
q_{msat}	Adsorbate concentration in nonmicropore at surface saturation ($\text{mg} \cdot \text{g}^{-1}$)
Q	Dimensionless aqueous phase concentration ($Q = \frac{q}{q_0}$)
Q_{La}	Langmuir isotherm equation constant, the solid-phase concentration corresponding to a condition in which all available sites are filled, or maximum adsorption capacity, ($\text{mg} \cdot \text{g}^{-1}$)
Q_{LF}	Langmuir-Freundlich isotherm equation constant ($\text{mg} \cdot \text{g}^{-1}$)
Q_m	Dimensionless solid phase concentration in nonmicropore region ($Q_m = \frac{q_m}{q_0}$)
Q_b	Dimensionless solid phase concentration in micropore region ($Q_b = \frac{q_b}{q_0}$)
Q_s	Dimensionless solid phase concentration at particle surface ($Q_s = \frac{q_s}{q_0}$)
q^*	Equilibrium concentration defined in LDF model
r	Radial coordinate, Radial distance from center of particle (cm)
R	Particle radius (cm), Gas constant ($\text{kJ} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$), Equilibrium parameter for adsorption (dimensionless)
Re_p	Reynolds number ($Re_p = \frac{u \varepsilon_b d_p \rho}{\mu}$)
SFact	Separation factor ($SFact = \frac{mq_0}{V_f c_0}$)

S_m	Specific surface area calculated from the monolayer capacity (m^2/g)
S_s	Particle external surface area (m^2)
t	Time (s)
t_i	Thickness for i th point (nm)
t_0	Characteristic time, constant defined in equation (6.29)
T	Absolute temperature (K)
u	Interstitial velocity of the fluid in the fixed bed.
u_c	Velocity of the concentration wave front
u_s	Superficial velocity, ($u_s = Q / A_b$ where Q is the volumetric flow rate of the fluid and A_b is the cross-sectional area of the bed)
V	Molar volume of solute at normal boiling point ($\text{cm}^3 \cdot \text{mol}^{-1}$)
V_f	Solution volume, (l),
W_i	Initial mass of char before activation (g)
W_t	Mass of activated carbon at the end of activation (g)
x	Nondimensional effluent concentration $x = c / c_0$
y	Nondimensional average amount adsorbed of bed and $y = q / q_0$
z	Axial distances (cm)
ΔH^0	Standard enthalpy change of adsorption ($\text{kJ} \cdot \text{mol}^{-1}$)
ΔS^0	Standard entropy change of adsorption ($\text{kJ} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$)

Greek letters

β	Dimensionless radial variable ($\beta = \frac{r}{R}$)
$\beta_{a,h}$	Specific constant defined in Equation (5.2)
ε_b	Void fraction of the bed (ε_b is the ratio of the void volume to the total volume of the bed)
ε_p	Particle porosity
ζ	Dimensionless parameter defined in Equation (6.20) ($\zeta = \left(\frac{K_f}{k_s} \right) \left(\frac{c_0}{q_0} \right)$)
η	Transformed radial variable ($\eta = \beta^2$), Viscosity of solution (centipoise)

θ	Dimensionless time variable ($\theta = \frac{D_{eff,0}t}{R^2}$), dimensionless parameter defined in Equation (6.21) ($\theta = \frac{t - \varepsilon_b z / u}{\frac{1}{K_f} + \frac{1}{k_s(q_0 / c_0)}}$)
μ	Fluid viscosity (Pa · s)
ρ	Fluids density (kg · m ⁻³)
ρ_b	Bulk density of bed (g · cm ⁻³)
ρ_p	Adsorbent particle density, (g · cm ⁻³)
ρ_s	Adsorbent solid density, (g · cm ⁻³)
τ	Adjusted time
ψ	Proportionality factor defined in van't Hoff equation (dimensionless)

CHAPTER 1 INTRODUCTION

1.1 Background

Nowadays, the health of human beings is increasingly threatened arising from the deteriorated environment. The occurrence of various organic chemicals in the hydrosphere presents a major problem to water resources. To improve the biosphere from the catastrophic impact of a plethora of toxic chemicals, increasing effort in the use of separation and purification technologies will be necessary. Adsorption technology can provide a cheap, effective and practical solution. Comparing with other treatment methods, adsorption is amenable to a more broad range of contaminants. In particular, activated carbon adsorption has an edge over the other methods because the precursors are either waste or relatively cheap biomasses and activated carbons are very effective adsorbents for a wide range of contaminants in aqueous and gaseous media.

Activated carbons are produced from a number of biomasses. Among these are hardwoods, grain hulls, corn cobs, nut shells and others (Suarez-Garcia et al. 2002). In this research, oil-palm shell was used as the starting material for preparing the activated carbon. Figure 1-1 shows the appearance of the oil-palm fruitlet and its cross section. Oil-palm shell is one of the by-products of the palm-oil industry. The industry is important in tropical countries. For

instance, in Malaysia which is the world's largest palm-oil producing country, 9.9 million tons of solid wastes consisting of oil-palm empty bunch, fibre and fruit shell are generated every year. Conversion of these wastes into activated carbon would add value to this biomass, reduce the cost of waste disposal and in addition, the conversion can provide a potentially cheap replacement for existing commercial activated carbons.

Figure 1-1 Cross section of a oil-palm fruitlet

1.2 Significance of project

The technology options for wastewater treatment include biological, chemical and physical methods. Conventional physical and chemical methods for removal or transformation of wastes include adsorption, distillation and reverse osmosis. Selection and feasibility of a particular operation is based on the application to the solute concentration range, capacity, and cost (Buchanan and Nicell 1995; Karamanev et al. 1997). Although biological method for detoxification using different micro-organisms is feasible, it is only applicable for the low concentration range. In conventional chemical and physical methods, adsorption is the most

general operation in water treatment. For example, activated carbon is often used to pre-filter water before reverse osmosis (RO) operation. Activated carbon post-filters are also common. Comparing activated carbon adsorption with RO process, RO systems can waste a large amount of water (Dept. of the Environment 1979; Cheremisinoff 1993; Dñabrowski 1999). For distillation, energy cost can be significant (Dept. of the Environment 1979; Dabrowski 2001). Although activated carbon adsorption system must be monitored and carbon must be replaced at regular intervals, it is popular in the industry especially for high pollution concentration water source, azeotropic aqueous source, or those contaminants with a boiling point lower than water, such as some pesticides and solvents (Dñabrowski 1999). This project focused on the aqueous phase adsorption using activated carbon prepared from biomass.

1.3 Objectives of research

The objectives of this research are as follows:

- (i) To convert waste oil-palm shells to activated carbons by studying the preparation conditions so as to achieve high pore surface area and good pore structure for the activated carbons.
- (ii) To determine the effectiveness of the prepared activated carbon for aqueous phase adsorption of phenol.
- (iii) To model the adsorption kinetics using a concentration dependent multi-pore kinetic model and to validate this model using experimental data from aqueous phase adsorption studies in a batch system.

- (iv) To study the effects of different operating conditions on the fixed bed adsorption and to correlate the experimental data with a linear driving force model.

1.4 Scope of project

The scope of the project included both experimental and theoretical studies. In the experimental studies, the preparation of the activated carbons from the oil-palm shells is carried out using both physical and chemical methods. At the pyrolysis or carbonization stage, the oil-palm shell samples are subjected to different atmospheres of nitrogen atmosphere and vacuum condition. The activation is involved two-step steam activation and chemical activation with K_2CO_3 . The effects of preparation parameters on the characteristics of the activated carbons are studied and the conditions for preparing activated carbons with well-developed porosity would be determined.

The performance of the activated carbon in the liquid-solid adsorption system is investigated using batch experiments; the approach is based on the thermodynamic and kinetic aspects. The adsorption equilibrium and the adsorption mass transport of phenol onto activated carbon from aqueous solution are studied. Mass transfer governing the entire adsorption process in the batch reactor and the resulting kinetic data are analyzed in terms of the concentration decay curve. The rate of adsorption is studied for varying parameters such as initial concentrations and the weight of adsorbents. The performance of the activated carbons in a dynamic system is studied also.

The theoretical studies would include the mechanism of mass transfer during adsorption and the aqueous phase adsorption capacities. The equilibrium data would be correlated with Langmuir, Freundlich and Langmuir-Freundlich equations. A new model is presented and based on the multi-pore model. The best-fit equilibrium equation is incorporated into the concentration dependent multi-pore model to analyze the process kinetics. In the model, the intra-particle effective diffusion coefficient is based on the absolute rate theory. A concentration dependent diffusion coefficient is used to obtain a better simulation. An orthogonal collocation scheme is employed to solve the partial differential equations. Parametric sensitivity analyses are carried out to determine the effect of each operating parameter on the concentration decay curve. Finally, the theoretical study on the fixed bed adsorption system is carried out by correlating experimental data with the constant pattern linear driving force model. Through optimization, the validity of the model for describing the fixed bed adsorption system is studied.

CHAPTER 2 LITERATURE REVIEW

2.1 Activated carbon and adsorption process

Historically, adsorption had been widely used in many instances as a separation process. Using charcoal to remove odour and taste from water was recorded in Sanskrit manuscripts 2 millennia ago. The Swedish scientist Carl Wilhelm Scheele made the first scientific study and discovered the adsorptive capacity of certain types of charcoal in 1773. Charcoal was found to decolourize tartaric acid in 1785. In 1794, charcoal was first applied to the refinement of sugar (Jankowska et al. 1991). By 1901, scientists had developed ways to synthesize activated carbon from coal that had adsorptive and decolourizing capacity (Smisek and Cerny 1970). The need for developing efficient adsorbents against toxic agents during the First World War led to the successful production of activated carbon in granular form. Later on, adsorption was found to be useful in industry for separation and purification.

The term “adsorption” is believed to have been first introduced by Kayser in 1881 to describe his observations of the condensation of gases on free surfaces, a phenomenon discovered independently by both Scheele and Fontana some years earlier (Tien 1994). One may view the adsorption phenomenon as follows. Consider a heterogeneous system composed of a fluid

phase (liquid or gaseous) and a solid surface. It is assumed that the fluid phase is a solution consisting of several different chemical species and that the fluid and solid phase are in thermodynamic equilibrium. A species present in the fluid phases is said to be adsorbed on the solid surface if the concentration of the species in the fluid-solid boundary region is higher than that in the bulk of the fluid. It is obvious that adsorption is a surface phenomenon and that its definition rests upon concentration measurements and carries no implications of mechanisms. Adsorption takes place because of the interaction between the species present in the fluid phase and the solid surface.

Adsorption at the liquid-solid interface is of great importance in industry and daily life like water treatment. Although the liquid phase adsorption was first discovered, the gas phase adsorption was studied most extensively including works of Irving Langmuir (1932). Liquid-phase adsorption, in general, is a more complex phenomenon than gas-phase adsorption, although most of the isotherm expressions discussed for gas phase adsorption can be readily extended to liquid phase. For example, one may envision monolayer coverage in liquid adsorption, but the adsorbed molecules are not necessarily tightly packed with identical orientation. Other complications include the presence of solvent molecules and the formation of micelles from adsorbed molecules. Furthermore, the liquid phase adsorption is characterized by the exchange between the adsorbates (Tien 1994).

2.2 Fundamentals of adsorption at liquid-solid phase

The material in the adsorbed state is called the adsorbate. When adsorption occurs at the interface between a fluid phase and a solid, the solid is usually called the adsorbent. Certain

adsorption phenomena can be related to the expulsion of solute from one phase and its indifferent accumulation at the interface of that phase (Weber and DiGiano 1996). There are two types of adsorption which are referred to as solvent-motivated (entropy-driven) and sorbent-motivated adsorptions. Adsorbent motivated adsorption occurs strictly as the result of the specific attraction of a surface or interaction for a chemical species, such as the adsorption of phenol from water by activated carbon.

Since adsorption occurs on surfaces, thus adsorbents are characterized first by surface properties such as surface area (Suzuki 1990). A large specific surface area is preferable for providing large adsorption capacity, but the creation of a large internal surface area in a limited volume inevitably gives rise to large numbers of small sized pores between adsorption surfaces. On the other hand, the porosity development should be taken into account for application. Two physical properties of the adsorbent, namely, the surface area and the distribution of different sized pores, should be considered in order to optimize the adsorption process. The results of the study by Hsieh and Teng (2000) demonstrated the importance of mesopores in enhancing the adsorption capacity of microporous carbons in aqueous solutions, especially for the adsorption of large molecule adsorbates. The size of pore structure determines the accessibility of adsorbate molecules to the adsorption surface; so the pore size distribution is another important property for characterizing adsorption capacity of adsorbents. The capacities of carbon for contaminant compounds are significantly affected by the pore structures of activated carbon as well as the size of the adsorbate. Therefore, a suitable carbon adsorber to remove specified compounds is an important issue for the treatment process (Hsieh and Teng 2000). To obtain suitable carbon adsorber, it depends on the precursors for the activated carbons and the activated carbon preparation process.

2.3 Activated carbon preparation

Activated carbon can be prepared from a large number of sources by a variety of methods. The Merck Index divides these into four basic forms: (1) animal charcoal, obtained by charring bones, meat, blood, etc.; (2) gas black, furnace black, or channel black, obtained by the incomplete combustion of natural gas; (3) lamp black, obtained by burning various fats, oils, resins, etc.; and (4) activated charcoal, prepared from biomass (Budavari 1996)

2.3.1 Biomass

Biomass can generally be defined as any hydrocarbon material which mainly consists of carbon, hydrogen, oxygen and nitrogen. The major organic components of biomass can be classified as cellulose, hemi-cellulose and lignin. Biomass resources include various natural and derived materials, such as woody and herbaceous species, wood wastes, bagasse, agricultural and industrial residues, waste paper, municipal solid waste, sawdust, bio-solids, grass, waste from food processing, animal wastes, aquatic plants and algae, etc. Table 2-1 shows a list of activated carbons prepared from biomass.

The method most frequently used for preparing active carbons involves pyrolysis of the precursor in an inert atmosphere followed by activation. Another method for activated carbon preparation, namely, chemical activation, also plays an important role. Both methods can be utilized purposely to tune the surface characterization of activated carbon products for their specified applications. The surface characteristics of the activated carbon can be generalized

into the BET surface area. Although activated carbon from biomass for adsorption has been existing for centuries and voluminous researches have focused on this field, the pursuing of new adsorbents and the development of adsorbent surface characteristics have never ceased.

Table 2-1 Activated carbons prepared from biomass in the literature

Material	BET surface area (m ² /g)	Pore volume (cm ³ /g)		Reference
		Total	Micropore	
Apricot stones	1190	0.83	0.50	(Savova et al. 2001)
Cherry stones	875	0.66	0.28	(Savova et al. 2001)
Grape seeds	497	0.58	0.12	(Savova et al. 2001)
Almond shells	998	0.82	0.40	(Savova et al. 2001)
Nut shells	743	0.67	0.21	(Savova et al. 2001)
pistachio-nut shells	778	0.466	0.22	(Lua et al. 2004)
Oil palm stones	1366	N.A.	N.A.	(Lua and Guo 2001)
Eucalyptus globulus	1193	0.56	0.40	(Arriagada et al. 1994)
Coconut shell	2390	1.665	0.868	(Hu et al. 2003)
Palm stones	1291	0.785	0.463	(Hu et al. 2003)

Although the physical, chemical, surface and adsorptive properties of activated carbons have been investigated significantly, there appears to be little information on such characterization of steam-activated carbons from oil-palm shells. Therefore, information on the surface characteristics of steam-activated carbons from oil-palm shell is not available. Further, the performance of these activated carbons to adsorb contaminants in water has not been reported.

2.3.2 Pyrolysis or carbonization process

The preparation of activated carbons involves two stages, i.e., pyrolysis or carbonization, followed by activation. Each stage has its effects on the characteristics of the final activated

carbon products. Activated carbons prepared under different processes characterized different pore structures and therefore different applications in adsorption. For example, activated carbons produced by CO₂ activation consist predominantly of micropores which are suitable for gas-phase adsorption such as adsorption of SO₂, H₂S or NO_x. On the other hand, activated carbons produced by steam activation will tend to have more mesopores which are suitable for aqueous-phase adsorption such as phenol, benzene, or dye adsorption. Conventional pyrolysis or carbonization consists of the slow, irreversible, thermal decomposition of the organic components in biomass in the absence of oxygen. Pyrolysis or carbonization leads to an array of solid, liquid and gas products. The method has been used for commercial production of a wide range of fuels, solvents, chemicals and other products from biomass feed stocks. Pyrolysis or carbonization has traditionally been used for the production of charcoal. The char obtained has a porous structure and a surface area that is appropriate to use in activation (Yaman 2004).

The pyrolysis parameters have influence on activation and the final product (Bansal et al. 1988). As for the packed bed reactor, the effects of the operation conditions are fundamental. These relevant parameters include: pyrolysis atmosphere, the final temperature selected, the process holding time, the rate of temperature increase, the carrier gas flow rate and the material particle size.

2.3.2.1 Effect of environment

Cao *et al.* (2002) studied activated carbon preparation from bark residuals under atmospheric and vacuum pyrolysis. Two vacuum levels were used in the study. The Pyrocycling™ process,

a semi-continuous process, was performed at a temperature of 450°C and a total pressure of 20 kPa. In their study, the pressure of batch process was as low as 1.3 kPa. They found that under the same activation conditions, vacuum pyrolytic charcoal yields more activated carbon with a higher specific surface area compared to charcoal from atmospheric pyrolysis. These findings suggested that the vacuum pyrolysis could be an attractive method for the production of activated carbon.

Lua and Yang (2005) studied the effects of pyrolysis atmosphere on the chemical activation of pistachio-nut shells. It was observed that after pyrolysis under vacuum conditions, the chars yielded activated carbons in which the characteristics were better than those pyrolysed in nitrogen atmosphere. The BET surface areas of the carbons activated under nitrogen atmosphere and vacuum conditions were 1635.37 and 1647.16 m² / g, respectively.

2.3.2.2 Effect of temperature

Pyrolysis temperature is an important parameter. It determines the amount of energy supplied for thermal degradation and migration of the volatile molecules out of the raw material. Generally, during pyrolysis, the basic microstructure is formed at 500°C, however, some of these pores are blocked by the products and could be available only when high-temperature treatment is given (Bansal et al. 1988).

According to the work of Cagnon *et al.* (2003), in the case of coconut shells subjected to high IHTT (intermediate heat treatment temperature, i.e. the temperature of pyrolysis), the two-step procedure leads to activated carbons with a well developed microporosity even at low

burn-off. Results suggested that activated carbons obtained from coconut shells could be optimized by carbonizing above 700°C and then cooling down to room temperature, before proceeding with the activation. It was observed that chars obtained by carbonizing coconut shells at low IHTTs presented underdeveloped porosity, with tars deposited at the entrance of the initial micropore network structure. Changes in surface characteristics of Brazil nut shells (*Bertholletia excelsa*) due to pyrolysis at different temperatures were examined (Bonelli et al. 2001). Surface characteristics obtained with nitrogen adsorption indicated that the surface area reached a maximum value at 600°C and slightly decreased at the highest temperature of 850°C.

Guo and Lua (2000) studied the effect of pyrolysis temperature on the BET and micropore surface areas of the chars prepared from oil-palm shells. Results showed that the reaction commenced at 400°C. As the temperature increased from 500 to 800°C, increasingly greater volatile matters were released progressively during pyrolysis thereby resulting in the development of some new pores, and hence the BET surface area of the char increased progressively. With further increase of temperature to 900°C, the BET surface area decreased due to some of the pores being sealed off as a result of the sintering effect at high temperature. In summary, a high temperature is needed to remove volatile matters and enhance porosity before detrimental effects set in at a threshold temperature.

2.3.2.3 Effect of hold time

Lua *et al.* (2004) studied the feasibility of preparing effective adsorbents from pistachio-nut shell. In their investigation, the effect of holding time during pyrolysis on the surface area and

pore volume was analyzed. It was observed that the surface area, the pore volume and the solid density showed similar trends with increasing holding time. Increasing the hold time during pyrolysis from 1 to 2 hours increased the properties values progressively, but thereafter these values decreased when the hold time was further increased for up to 3 hours. The results indicated that as the hold time during pyrolysis increased, the rudimentary pore structure within the char varied due to the trade off between increasing release of the volatile matter and sealing-off of pores with an intermediate melt.

2.3.2.4 Effect of heating rate

Low heating rate during pyrolysis results in lower volatilization and higher char yield because of better stabilization of the polymeric components. Carbonization of a typical coking coal from the Pittsburgh seam, Edenborn mine was studied (Warren 1935) based on the effects of heating rate during carbonization. Given data showed that tar yield increased, coke yield decreased, and gas yield decreased in proportion to the logarithm of the heating rate. A mechanism of coking was formulated. It suggested that the coal existed in an unstable molecular configuration and experienced molecular rearrangement during the increase of temperature. These rearrangements resulted in more stable forms and required a substantial period of time to reach their completion. Hence, if the samples were heated rapidly to the temperature required for the actual decomposition, there would be less opportunity for the completion of the rearrangements. The molecules would break down in greater parts to form liquids while slow heating up would allow time for the rearrangement to be completed and the molecules decomposed subsequently would be in a more stable form to start with and yield lower liquid and higher solids.

2.3.2.5 Effect of nitrogen flow rate

Nitrogen gas is usually used to provide an inert atmosphere for pyrolysis and to assist in removing the volatile matter released from the samples. The nitrogen flow affects the residence time of the vapour phase produced by pyrolysis. Rapid flow removes the products quickly from the reaction zone and hence minimizes secondary reactions such as cracking and char formation.

There were some studies on the effect of carrier gas flow rate like pyrolysis of cardunculus L. studied by Encinar *et al.* (2000). In the study, the kinetics of pyrolysis were determined for the temperature range of 300–800°C, the particle size of about 0.63–1 mm, the nitrogen flow rate of about 200 cm³/min, and the initial sample mass of about 5 g. For these conditions, mass-transfer limitations were found to be insignificant. This was confirmed by the fact that the pyrolysis behaviour was not affected by changing the gas flow rate or particle size. A conclusion was drawn that yields of three phases (solid, liquid and gaseous) were strongly dependent on temperature but practically independent of particle size and nitrogen flow rate under the conditions of the study.

2.3.2.6 Effect of particle size

It is of practical interest to examine the effect of changing particle size on pyrolysis products since pretreatment of feedstock by size classification is relatively inexpensive. It was generally assumed (Beaumont and Schwob 1984; Chan *et al.* 1988), that an increase in particle size caused greater temperature gradients inside the particle, so that at a given time,

the core temperature was lower than that of the surface and that possibly gave rise to an increase in solid yields with a concomitant decrease in liquids and gases.

The effects of different initial material sizes on the properties of chars produced were studied (Lua and Guo 1998). In this study, extracted oil palm fibres with a larger particle size (1.0–2.0 mm) had the smallest BET and micropore surface areas. The extracted oil palm fibres with the particle size range of 0.5–1.0 mm had the highest BET and micropore surface areas. It was concluded that particle size would have a major influence on the process rate and particle size of starting material played an important role in the development of pore structures.

2.3.3 Activation process

The product of pyrolysis has a weakly developed porous structure; activation is generally applied to improve it in practice. The objective of the activation process is to enhance the volume and to enlarge the diameters of the pores that were created during the pyrolysis process and to create some new pores (Jankowska et al. 1991).

2.3.3.1 Effect of activation agents

There are two different methods for activation, namely, physical and chemical. The physical activation process comprises treatment of the solid residue obtained in the pyrolysis with oxidizing gas, generally steam or carbon dioxide, at high temperature. Chemical treatment is

also common in which chemicals are mixed with the source material in order to cauterise the fine pores. The chemicals that are mostly used include zinc chloride, potassium hydroxide and so on.

The gases used in the physical activation step are mainly CO₂ and steam (Sanchez et al. 2001; Lua et al. 2004; Mui et al. 2004). In activation, the gas acts as an oxidizing agent and produces a porous structure in the char as it reacts with the carbon to form gaseous reaction products. The pores thus produced in the char give the active carbon its surface area and adsorptive properties.

Alcaniz-Monge *et al.* (1994) prepared petroleum pitch-based activated carbon fibres in either 0.1 MPa CO₂ or 0.05 MPa H₂O at 1160 K. They observed that activation rate in H₂O (up to 50% carbon burn-off) was about two times faster than that in CO₂. Activated carbons prepared by CO₂ activation exhibited a larger micropore volume and a narrower micropore size distribution than those prepared from H₂O activation. Similar experimental results were found in another study (Molina-Sabio et al. 1996) for the development of microporosity in activated carbons prepared from olive stones. Walker (1996) reviewed the works of the Spanish University at Alicante by comparing the virtues of carbon dioxide and steam as activating agents and made a comparative study from the viewpoint of the activation mechanism. He attributed differences in activation results for CO₂ and H₂O to two reasons. One of them is that activation in CO₂ proceeds at a less rapid rate than that in H₂O. The second reason is the diffusion coefficients of carbon dioxide and water molecules. Walker referred to the works of Koresh and Soffer (1980), from their studies on diffusion in molecular sieve carbons and concluded that H₂O has a smaller critical molecular dimension

than CO₂. Thus, the diffusion of H₂O in the process would be larger than that for CO₂. As activation proceeds, resulting in pore enlargement, and diffusion changes to Knudsen diffusion, H₂O is still expected to exhibit a higher diffusion coefficient because of its lower molecular mass as compared to that of CO₂. They presented the C-H₂O reactions in detail as follows:

where C_f is a carbon-free active site, C(O) is oxygen surface complex, and C(H) is chemisorbed hydrogen.

Rodriguez-Reinoso *et al.* (1995) used a two-stage carbonization and activation process to compare the roles of steam and CO₂ as activation agents. Activated carbon was prepared from carbonized olive stones. They found that microporosity widening occurred from the early stages of the activation process when steam was used as an activating agent at either 750 or 800°C. In contrast, microporosity widening occurred later with CO₂ as an activating agent. Steam was found to produce a wider range of pore size distribution than CO₂, with a large development of mesoporosity and macroporosity, both of which are useful for adsorbing larger molecules and providing transport routes to the micropores. This similar conclusion was reported from a study of granular activated carbons prepared from rockrose (Pastor-Villegas and Duran-Valle 2002). For nonmicropore development and low activation temperature, steam is preferred over carbon dioxide. Using immersion microcalorimetry of liquids with different molecular sizes, Molina-Sabio *et al.* (1996) presented different effects of steam and carbon dioxide activation on the development of microporosity and micropore size distribution for activated carbons prepared from oil stones. The experimental results

showed that carbon dioxide activation mainly caused the creation of microporosity and exhibited a larger micropore volume and narrow pore size distribution than those prepared with steam. Steam activation widens the microporosity from the early stages of the activation process; the resulting activated carbons exhibit a lower micropore volume.

In terms of their physical, chemical and adsorptive properties, steam-activated almond shell granular activated carbons were given the edge over carbon dioxide-activated granular activated carbons. Under identical pyrolysis and activation temperature, hold time, the average BET surface area of steam activated almond shell granular activated carbons is 20 % plus larger than those of carbon dioxide activated granular activated carbons. The estimated costs of production indicate that steam-activated, unoxidized and oxidized carbons appear to be the most economical granular activated carbons to manufacture and also the most economical for removal of organic compounds (Toles et al. 2000). Taking into account of the advantages of steam activation and the applications of activated carbons, steam will be utilized in the physical activation studies.

2.3.3.2 Effect of activation temperature

The influence of temperature, in the range of 500-900°C, on the pore structure of granular activated carbons prepared from oil palm stones in carbon dioxide was investigated by Lua and Guo (2001). The effects of activation temperature and hold time on the BET surface area of the activated carbons were studied. For a hold time of 15–45 min, the BET surface area increased progressively with increasing activation temperature. For the case of a hold time of 60 min, it showed a decrease in the surface area at higher activation temperatures.

Yang and Lua (2003) investigated the characteristics of activated carbons prepared from pistachio-nut shells in CO₂. The studies showed that increasing the activation temperature enhanced the existing pores and formed new pores in the samples by continual devolatilization of the chars and carbon burn-off due to the carbon–CO₂ reaction, resulting in increasing BET surface area, micropore volume, and nonmicropore volume of the activated carbons. At 775°C, the formation of micropores had reached the maximum. Beyond that, the micropore volume commenced to decline due to increased widening of micropores to mesopores or even macropores, resulting in steep declines at 825°C. On the other hand, the nonmicropore volume continued to increase with increasing temperature, even up to 825°C, due to the pore widening effect.

Pastor-Villegas and Duran-Valle (2002) studied the influence of the activation temperature on the pore structure of granular activated carbons prepared from rockrose (*Cistus ladaniferus* L.) by physical activation. The textural structure development was compared among the different activation reagents. In general terms, the volume of narrow micropores was higher for the activated carbons in carbon dioxide than for those activated in steam. This pore volume first increased up to 850°C and then decreased to 950°C in the series of activated carbons prepared by steam activation. In contrast, the variation was of little significance in the series of activated carbons prepared by carbon dioxide activation. The temperature also showed little influence on the volume of wide micropores, which was similar in both series of activated carbons.

2.3.3.3 Effect of hold time in activation

The significant influences of hold time on the surface area and pore size distribution of the activated carbons were investigated. Lua and Guo (2001) studied the preparation and characterization of the activated carbons from oil-palm stones by carbon dioxide activation. At a fixed temperature of 900°C, increasing the hold time from 15 to 30 min increased the BET surface area and micropore surface area. When the hold time was increased to 60 min at 900°C activation temperature, the BET and micropore surface areas and the pore volume decreased. In another case, dwell time affected the characteristics of the activated carbons obtained from pistachio-nut shells (Yang and Lua 2003). Initially, with increasing dwell time, the BET surface area and micropore volume of the activated carbons increased. The micropore volume and BET surface area reached the maximum at a dwell time of 1.5 and 2 hours respectively and then with elongation of dwell times both the BET surface area and micropore volume decreased. Development of mesopores has also been observed with increasing activation times in the case of CO₂ activation of coconut shells (Yoshizawa et al. 2000). The porous properties of the activated carbons produced from waste tyres in steam activation after carbonization was studied (Ariyadejwanich et al. 2003). The properties showed that varying the activation time from 1 to 4 hours, the burn-off in activation, BET surface area and mesopore volume increased with increasing holding time.

Activated carbon prepared from corn cob was studied by Chang *et al.* (2000). The experimental results showed that the levels of development and widening of microporosity were dependent on the activation time. In the case of steam activation at 900°C, the surface area and the total pore volume at 60 min of soaking time are smaller than those at 50 min.

This might be attributed to the fact that, for the burn-off time of 60 min, destruction of high porosity by external ablation of carbon particles was more pronounced than development and widening of microporosity. As a result, the BET surface area and total pore volume are reduced.

2.3.3.4 Chemical activation

In chemical activation, the starting material is impregnated with the activating agent in the form of concentrated solution by mixing or kneading. The chemical-impregnated material is then heated at a temperature around 400°C to 800°C. The most popular chemicals used in the chemical activation include alkali hydroxide (Yang and Lua 2003), alkali salts (Hayashi et al. 2000; Hayashi et al. 2002) or transition metal salts (Hu et al. 2001).

The characteristics of activated carbons with chemical activation can be affected by two parameters: one is the mass ratio of chemical to raw material, and the other is the temperature of the process. Conceptually, the chemical activation refers to the thermal treatment of impregnated materials in a nitrogen atmosphere. Recently, the combination between the chemical impregnation and physical activation was investigated. The results indicated that with the combined activation, a developed nonmicropore would prevail in the porous structure of the carbons (Hu and Srinivasan 2001). Guo and Lua (Guo 1999; Guo and Lua 1999) investigated the effects of activation temperature on the BET surface area of activated carbons with combined chemical and CO₂ activation. It was observed that increasing the activation temperature from 500°C up to 800°C increased the BET surface area, beyond which the surface area decreased. The tendency of the change in the specific surface area with

activation temperature resembled among the researchers. The specific surface areas of the prepared activated carbons from all the nutshells increased with an increase in carbonization temperature between 773 and 1073 K and decreased at the temperature of 1173 K (Hayashi et al. 2002).

The effect of temperature in the combined activation on the mesoporosity was investigated (Hu and Srinivasan 2001). Coconut shells and palm seeds were used as raw materials to obtain activated carbons with high surface area by simultaneous treatment with zinc chloride and carbon dioxide as the chemical and physical agents, respectively. It was concluded that an increase in temperature resulted in increased mesoporosity, higher pore volumes and surface areas and larger pore diameters.

2.4 Characterization of activated carbon

Activated carbons have variable surface characteristics like BET surface area and pore size distributions; providing sources of heterogeneity. The structural characteristic of activated carbon plays an important role in adsorption processes, and numerous methods have consequently been developed and applied for the characterization of this property. These methods include mercury porosimetry, scanning electron microscopy and gas as well as liquid phase adsorption. Among these various methods, gas adsorption is most often used for characterizing the structural heterogeneity of activated carbons (Ismadji and Bhatia 2001).

2.4.1 Gas phase adsorption

Gas adsorption on solid surfaces and in pore spaces is a complex phenomenon. The adsorption involves mass and energy interaction like phase changes. Many theories have been put forth in description. The theories can be used to treat data from adsorption measurements and provide parameters characterizing the process and the samples. Therefore, the basic ideas and background of theories are applied in characteristic studies for the activated carbon samples (Webb and Orr 1997).

A large proportion of the atoms of a particle are in or near the surface. This causes particles to exhibit distinctively different properties from the same material in bulk form. The difference depends on the magnitude of particle surface areas and the nature of their porosity (Webb and Orr 1997). The adsorbent properties of activated carbons are essentially attributed to their large surface area, a well-developed porous structure and a favourable pore size distribution. These surface characteristics make the internal surface accessible and enhance the adsorption rate (Legrouri et al. 2005). For example, the pore size limits the size of the molecules that can be adsorbed whilst the surface area limits the amount of material which can be adsorbed. The above characteristics will be used as criteria for preparation process optimization.

The surface area of activated carbon is generally evaluated by the BET theory (Brunauer et al. 1938; Toles et al. 1997). The surface area of nonmicropore can be determined by the t-plot method (Lippens and de Boer 1965; Satterfield 1993). The t-plot is an empirical method used to determine the surface area of the mesopores by analyzing the gas phase adsorption isotherm. So, porosity is generally characterized by analyzing the gas phase adsorption

isotherms using the BET and t-plot methods to determine the BET surface area, the nonmicropore surface area and the micropore surface area. This technology is adopted by most of the researchers (Merchant and Petrich 1993; Tseng and Tseng 2006; Qian et al. 2007). The results can be compared easily. Besides these traditional kinetic or the phenomenological approach, a molecular based statistical thermodynamic theory, the density functional theory, can be used to relate the adsorption isotherms to the microscopic properties of the sample like the pore size and so on.

1) BET surface area

The characteristics of porous materials are characterized in terms of their specific surface areas. The precise measurement of the specific surface area of solids is by means of gas adsorption. The specific surface area can be quantified in terms of the BET surface area. The BET (named after Brunauer, Emmett and Teller in (Brunauer et al. 1938)) surface area is described in the standard DIN 66131 and in the IUPAC Recommendations of 1984. This specific surface area is related to the volumetric static measurement of the adsorption isotherm. The BET isotherm can be expressed as follows:

$$\frac{q}{q_s} = \frac{C(p/p_s)}{(1-p/p_s)(1-p/p_s + Cp/p_s)} \quad (2.1)$$

where q is the sorbate concentration, q_s is the saturation limit for monolayer coverage of sorbate, p is the sorbate pressure, C is a constant related to the heat of adsorption of different layers and p_s is the saturation pressure of the gas. The BET isotherm has been found to provide a good representation of the experimental physical adsorption isotherm. The BET

isotherm can be rewritten into a linear form as $\frac{p}{(p_s - p)q} = \frac{1}{q_s C} + \frac{C-1}{q_s C} \frac{p}{p_s}$. Then, a plot of $\frac{p}{(p_s - p)q}$ versus p/p_s should yield a straight line with intercept $\frac{1}{q_s C}$ and slope $\frac{C-1}{q_s C}$. The value of C and q_s can then be obtained from a plot of a straight line, or regressive line, through the points within the relative pressure range from 0.05 to 0.3. From these values, the monolayer capacity (in mol/g) can be calculated according to $n_m = 1/(\frac{1}{q_s C} + \frac{C-1}{q_s C})$. The specific surface area S_m is calculated from the monolayer capacity by assessing a value a_m for the average area occupied by each molecule in the complete monolayer. Micromeritics uses 0.162 nm^2 for the area occupied by a nitrogen molecule and 0.21 nm^2 for krypton at liquid nitrogen temperature (77K), 0.142 nm^2 for argon at liquid argon temperature, and 0.17 nm^2 for carbon dioxide at ice water temperature. Then through the formula, $S_m = n_m \cdot a_m \cdot N_A$. Where N_A is the Avogadro constant, the BET surface area can be obtained.

2) t-plot

Experimental isotherms can be analyzed by the t-plot method to get information for the micropore volume and external surface area of the activated carbon samples (Lippens and de Boer 1965; Satterfield 1993). The t-plot is an empirical method that allows a semi-quantitative analysis of the nonmicropore surface area and so on. It is a method provided to correlate the isotherms to the average thickness of the adsorbed layer. The basic principle of the t-plot is to compare the adsorption isotherm under test to a standard isotherm corresponding to a nonporous reference solid in a reduced form.

The critical part of the t-plot is how to obtain standard isotherms for nonporous particles and then set up a precise analysis. The applicable and most frequently employed of the thickness equations for the i th point is from Harkins and Jura (1944) which is in the form of

$$t_i = \left[\frac{HJP1}{HJP2 - \log_{10} \left(\frac{p}{p_0} \right)} \right]^{HJP3} \quad (2.2)$$

where t_i is the thickness for the i th point, $HJP1$, $HJP2$ and $HJP3$ are the parameters defined in Harkins and Jura equation, and p/p_0 is the relative pressure for the i th point.

The t-plot method plots quantity adsorbed (V_a) against thickness (t) derived from the thickness equation. A least square analysis fit is performed on the thickness and volume adsorbed. The values of external surface area and micropore volume can be calculated from the slope and intercept of the correlation between volume adsorbed and thickness of adsorbed layer. The y-intercept obtained by extrapolating the linear portion of the t-plot yields the micropore volume (volume in pores of diameter less than 2 nm). The slope of the linear region provides the surface area represented by nonmicropores (diameter greater than 2 nm).

3) DFT method

One way of determining the distribution of pores is offered by Density Functional Theory (DFT). A significant feature is that the density functional theory method applies over the complete range of the isotherm and is not restricted to a confined range of relative pressures or pore size. Density functional theory offers a practical alternative to molecular dynamic and

Monte Carlo simulations. As all these methods, DFT method is based on the fundamental thermodynamic law that such a system will adopt a configuration of minimum free energy at equilibrium. Background on the application of density functional theory to the adsorption process is described by Tarazona (1985).

Density functional theory describes the thermodynamic grand potential as a functional of the single particle density distribution. Therefore, by definition, calculating the density profile that minimizes the grand potential energy yields the equilibrium density profile. The solution of equation yields the equilibrium density profile. The quantity adsorbed per unit area of surface is obtained by integrating the equilibrium density profile over the spatial coordinate r (that is, from the wall outward) and subtracting the quantity of adsorptive that would be present in the absence of wall forces (that is, the contribution of the bulk gas). In this way, solution of the equation of state leads to a method of characterization.

2.4.2 Aqueous phase adsorption

Activated carbons have chemical structure as well as physical structure. The activated carbons adsorption capacity is determined by porous structure and chemical structure of their surface. There are methods to study the adsorbent surface chemistry. These methods include physical, chemical and physicochemical techniques like Boehm titration, potentiometric titration, temperature-programmed desorption (TPD), thermodesorption, X-Ray Photoelectron Spectroscopy (XPS) and Fourier Transform Infrared Spectroscopy (FTIR). Unfortunately, none of the methods is able to provide completely reliable information. Boehm titration is considered to be a good method for evaluating surface acidity. It is simple, fast and usually

gives reasonable reproducibility. Its major deficiency is that all groups with a pK_a in the range of the oxygen-containing species are classified as oxygen-containing acids. Therefore, the presence of other surface groups (for example nitrogen, phosphorus, or sulfur) will overestimate oxygenated surface groups number. Another method measuring acid–base interactions is potentiometric titration (Contescu et al. 1997). Unlike the Boehm method, potentiometric titration allows the specific pK_a of various groups to be obtained. As many different heteroatom configurations can result in a similar pK_a (which also depends on the unknown activity of the solution), the exact classification of species is impossible. This uncertainty can be examined with comparing results obtained from TPD. TPD or thermodesorption has been developed to evaluate the active surface area (ASA) of carbons (Laine et al. 1963). TPD data can confirm the results of titrations qualitatively. However, the number of detected groups is found to be larger by a factor of 2. The measurement is higher because titration methods are able to detect acids and bases having a certain pK_a value only, whereas during thermal desorption, all surface groups, regardless of their chemical nature, should decompose. The TPD method has a shortcoming. It can only be used to evaluate the surface chemistry of carbons obtained by carbonization at high temperature. The weakness of XPS method is the difficulty in identifying the type and distribution of functional groups unambiguously. In the case of other spectrum techniques like FTIR and X-ray diffraction, activated carbons generated at lower temperatures can be measured only. For other samples, quantitative evaluation of the surface chemistry using FTIR or XRD is an extremely difficult task due to continued background absorption.

CHAPTER 3 INSTRUMENTATION AND EXPERIMENTAL SET-UP

3.1 Instrumentation

3.1.1 Thermal analysis

A thermogravimetric analyzer (TA-50, Shimadzu) was used to determine the proximate analysis and the pyrolysis kinetics of the oil palm shell. The proximate analysis provides information on the composition of moisture, volatile matter, fixed carbon and ash within the shell. The volume flow rate of the carrier gas was 30 ml/min. The samples were heated in a nitrogen stream in the temperature range from ambient to 900°C with a heating rate of 10°C/min. A plot of residual mass versus temperature was obtained. From these data, such as the derivative thermogravimetric (DTG) data and the characteristic temperatures, that is, the temperature of maximum mass loss rate, the initial decomposition temperature and the final decomposition temperature can be determined.

3.1.2 Fine particle analysis - characterization of surface area and pore structure

The accelerated surface area and porosimetry (ASAP2010, Micromeritics) was used to provide surface area and porosimetry information of the carbon samples. The principle of physical adsorption is used in the system. Based on the adsorption isotherms, the material characteristics, such as BET surface area, the micropore surface area, the micropore volume, the total pore volume, and the pore size distribution can be determined. During the analysis, a sample is placed in the evacuated space. The sample is kept at a fixed temperature as a dose of pure nitrogen gas is admitted into the space surrounding the sample. The pressure within the space is recorded over time. The pressure will fall rapidly from its initial value and gradually approach a steady reading called the equilibrium pressure. Consequently, the amount of gas adsorbed is related to the quantity of gas removed from the bulk gas phase by the solid surface. These raw adsorption data can then be processed to yield surface characteristics based on adsorption theory and methods.

3.1.3 Scanning Electron Microscopy

Scanning electron microscopy (SEM) was used to provide a direct image of the topographical nature of the surface. SEM provides surface information from all the emitted secondary electrons. It allows one to visualize objects on the order of nanometers. SEM makes use of a beam of electrons carefully focused by electromagnetic lenses. A detector is used to resolve back-scattered (reflected) electrons, secondary (given-off) electrons, and Auger electrons to create an image. The secondary electron yield is confined near the beam impact area, which permits images to be obtained at relatively high resolution.

3.1.4 Gas Chromatography/Mass Spectrometer

Gas chromatography (GC) with mass spectrum detector is used to determine organic concentrations. Chromatography encompasses a series of techniques. The techniques separate components of a mixture by a series of equilibrium operations. The separation of the entities is a result of their partitioning (differential sorption) between two different phases, one stationary with selectivity and the other a moving phase in contact with the first. Gas chromatography is used widely in the analytical and preparation separations. In this study, a gas chromatography cum mass spectrometry system (6890 GC/5970N MSD, Agilent) was used to determine the adsorbate concentration in the aqueous phase. This technique was based on EPA method 8720. EPA method 8720 is a standard. It is used to determine the concentration of semi-volatile organic compounds in water samples by gas chromatography/mass spectrum.

3.2 Experimental setup

3.2.1 Activated carbon preparation

3.2.1.1 Pyrolysis system

Pyrolysis of the raw oil-palm shell was conducted in a vertical stainless-steel reactor (dimensions are 38 mm o.d., 32 mm i.d. and 190 mm long). The reactor was placed in an electrical furnace. A continuous nitrogen flow provided an inert reaction environment. For the

case of pyrolysis under vacuum, the vacuum prevented any extra-particle secondary reactions of the primary volatile products. Figure 3-1 shows the set-up of the pyrolysis system for char preparation.

Figure 3-1 Pyrolysis system for char preparation

1. Gas cylinder, 2. Gas volume flow meter, 3. Metal mesh, 4. Sample, 5. Furnace, 6. Reactor, 7. Exhaust line

3.2.1.2 Activation system

Steam was used as the activation reagent in the study. The activation system was similar to that of pyrolysis except for a different reactor and an additional steam pipeline. The dimensions of the reactor are 25.5 mm o.d., 18 mm i.d., and length of 330 mm for activation. Figure 3-2 shows the set-up of the activation system for activated carbon preparation.

Extensive studies have been carried out to investigate the effects of various experimental conditions on the characterization of active carbon. Based on the BET surface area and pore volume values of final AC, effects of each condition were investigated by the local optimization.

Figure 3-2 Activation system for activated carbon preparation

1. Steam generator, 2. Mass flow meter for steam, 3. Furnace, 4. Reactor, 5. Metal mesh, 6. Sample, 7. Gas volume flow meter, 8. Gas cylinder

3.3 Design of experiment – activated carbon preparation

3.3.1 Effects of pyrolysis conditions

3.3.1.1 Pyrolysis procedure

The raw oil-palm shells were crushed and sieved to a size range of 2-2.8 mm. The shells were ready to be used after drying at 383K in an electrical oven for 24 hours. About 20 g of raw materials were placed on a 120 μm metal mesh, which was located at the centre of the reactor. Nitrogen gas of 99.9995% purity at a pre-selected flow rate ($150\text{cm}^3/\text{min}$) was used as the inert gas flushing through the reactor right from the beginning of the pyrolysis process. The furnace temperature was increased at a certain heating rate ($5^\circ\text{C}/\text{min}$ to $40^\circ\text{C}/\text{min}$) from room temperature to a selected temperature (400°C to 900°C) and held at this temperature for a period of time (0.5 to 2.5 hours). After pyrolysis, the furnace was cooled to room temperature

with N₂ flushing through the sample. The resulting char was collected for subsequent activation.

About 2 g of char were used in the steam activation. The activation was conducted at an activation temperature of 900°C and a hold time of 60 minutes with a heating rate of 10°C·min⁻¹ and a steam flow rate of 1.4 kg/hour at 2.1x10⁵ N/m². The effects of pyrolysis parameters on the characteristics of the final activated carbon were studied for these fixed activation conditions. The experimental parameters for the pyrolysis process are given in Table 3-1.

For pyrolysis under vacuum conditions, the shells were placed in another vertical stainless steel reactor (dimensions are 64 mm o.d., 57 mm i.d. and 400 mm long), which was connected to a mechanical vacuum pump. This reactor was placed into an electrical furnace (Model 2416, Carbolite). The pyrolysis conditions were similar to those for pyrolysis under N₂ except that the whole process, including heating up and cooling down periods, was under vacuum. The experimental parameters are shown in Table 3-2.

The surface characteristics of the activated carbons were determined using an accelerated surface area and porosimetry system (ASAP 2010, Micromeritics) based on N₂ adsorption at 77K. Using the Brunauer-Emmett-Teller (BET) equation, data from the isotherms were used to determine the surface area (Gregg and Sing 1982). The t-plot method was used to calculate the micropore volume and the nonmicropore surface area. The total pore volume was estimated to be the liquid volume of adsorbate (N₂) at a relative pressure of 0.985. The difference between the total pore volume and the micropore volume is the non-micropore volume.

3.3.1.2 Experimental parameters for pyrolysis

A local maximum value refers to a point in the experimental space being studied, within the constraints of the matrix experiment, where the response to a given parameter is at a maximum value. The methodology to obtain the local optimum pyrolysis conditions for activation is illustrated in Table 3-1 below. One pyrolysis parameter was varied at a time while the rest of the parameters remained constant.

Table 3-1 Experimental parameters for pyrolysis

A) Effect of Temperature

Sample No.	Temperature, °C	Holding Time, hrs	Heating Rate, °C/min	N2 flow rate, cm ³ /min	Particle size, mm
1	400	2	10	150	2.0-2.8
2	500	2	10	150	2.0-2.8
3	600	2	10	150	2.0-2.8
4	650	2	10	150	2.0-2.8
5	700	2	10	150	2.0-2.8
6	750	2	10	150	2.0-2.8
7	800	2	10	150	2.0-2.8
8	850	2	10	150	2.0-2.8
9	900	2	10	150	2.0-2.8

B) Effect of Holding Time

Sample No.	Temperature, °C	Holding Time, hrs	Heating Rate, °C/min	N2 flow rate, cm ³ /min	Particle size, mm
10	Optimum pyrolysis temperature from Part A	0.5	10	150	2.0-2.8
11		1	10	150	2.0-2.8
12		1.5	10	150	2.0-2.8
13		2	10	150	2.0-2.8
14		2.5	10	150	2.0-2.8
15		3.0	10	150	2.0-2.8

C) Effect of Heating Rate

Sample No.	Temperature, °C	Holding Time, hrs	Heating Rate, °C/min	N2 flow rate, cm ³ /min	Particle size, mm
16	Optimum pyrolysis temperature from Part A	Optimum holding time from Part B	5	150	2.0-2.8
17			10	150	2.0-2.8
18			20	150	2.0-2.8
19			30	150	2.0-2.8
20			40	150	2.0-2.8

D) Effect of Nitrogen Flow Rate

Sample No.	Temperature, °C	Holding Time, hrs	Heating Rate, °C/min	N2 flow rate, cm ³ /min	Particle size, mm
21	Optimum pyrolysis temperature from Part A	Optimum holding time from Part B	Optimum heating rate from Part C	50	2.0-2.8
22				100	2.0-2.8
23				150	2.0-2.8
24				200	2.0-2.8
25				250	2.0-2.8

E) Effect of Particle Size

Sample No.	Temperature, °C	Holding Time, hrs	Heating Rate, °C/min	N2 flow rate, cm ³ /min	Particle size, mm
26	Optimum pyrolysis temperature from Part A	Optimum holding time from Part B	Optimum heating rate from Part C	Optimum N ₂ flow rate from Part D	1.0-2.0
27					2.0-2.8
28					2.8-4.0
29					4.0-4.75
30					4.75-6.3

A similar methodology was used to obtain the optimum conditions for pyrolysis under vacuum.

3.3.2 Effect of activation conditions

3.3.2.1 Physical activation process

The optimum pyrolysis conditions determined in section 3.3.1.2 were used to obtain the chars which were subsequently subjected to a physical activation process. The parameters for the physical activation were optimized by varying one parameter at a time while the remaining parameters remaining fixed; similar to the methodology used for the pyrolysis parameters. Table 3-2 lists the procedure to study the effects of activation parameters.

Table 3-2 Experimental parameters for activation process**A) Effect of steam flow rate**

Sample No.	Steam flow rate, kg/h	Holding Time, hrs	Temperature, °C
A1	0.68	1	900
A2	1.13	1	900
A3	1.36	1	900
A4	1.81	1	900

B) Effect of hold time

Sample No.	Steam flow rate, kg/h	Holding Time, hrs	Temperature, °C
A5	Optimum steam flow rate from A	0.5	900
A6		1	900
A7		1.5	900
A8		2	900
A9		2.5	900
A10		3	900

C) Effect of temperature

Sample No.	Steam flow rate, kg/h	Holding Time, hrs	Temperature, °C
A7	Optimum steam flow rate from A	Optimum hold time from B	750
A8			800
A9			850
A10			900
A11			950
A12			970
A13			1000

3.3.2.2 Chemical activation process

For chemical activation, the oil-palm shell was impregnated with the chemical reagent (potassium carbonate) for a certain weight ratio of the chemical to the oil-palm shell. 50 ml of DI water was added to 20 g of the mixture. The mixture solution was shaking in a water bath at 80°C overnight. The slurry was removed from the bottle for oven drying at 110°C for 24 hours. The impregnated oil-palm shell slurry were placed in the reactor and heated in a nitrogen stream up to the pre-set final temperature for activation. Steam was then introduced into the reactor at this final temperature for activation. The activated carbon products were washed with 0.1 M HCl and then DI water till the pH value was 6-7. The objective of the

experiment is to maximize surface characteristics of the activated carbons. The parameters studied for the chemical activation process were the weight ratio of chemical to oil-palm shell, the activation temperature, and the hold time to determine the local optimized values. Table 3-3 lists the values of the parameters used in the chemical activation process.

Table 3-3 Experimental values of the parameters for chemical activation processes

Chemical activation (Heating rate: 10°C/min)	
Ratio of chemicals to oil palm shell	0, 0.125, 0.25, 0.5, and 1
Activation temperature	650, 700, and 750°C
Hold time	0.5, 1.0, 1.5, 2.0, and 2.5 hours

Potassium chloride and sodium carbonate were also used as chemical reagents for activation and a comparison between the three reagents was conducted.

3.3.3 Aqueous phase adsorption tests

Aqueous phase adsorption tests were carried out for phenol solution with a concentration of approximately 200 mg/l. phenol, as the detective system, is used because it is a typically small molecular contaminant. Another reason for using phenol is that phenol derivatives are the predominant liquid products from oil palm shell pyrolysis. To develop preparation process to be an environmentally friendly one, phenol aqueous phase adsorption was investigated and the solution was taken as the detective system.

Initially, 50 ml of prepared phenol solution was transferred to a 100 ml conical flask. The flask was placed in a water bath maintained at $30 \pm 0.5^\circ\text{C}$. When the temperature of the

adsorbate solution had stabilized at a pre-set value, a known weight of adsorbent was added into the flask and agitation at a speed of 150 rpm. When equilibrium had reached, 1 ml of the supernatant was removed from the flask with a pipette for analysis. The phenol concentration was determined by a gas chromatograph-mass spectrometer (6890N GC-5973MSD system, Agilent).

3.4 Material and chemical

The chemicals, potassium carbonate, potassium chloride, sodium carbonate and phenol used in this study, was supplied by Merck & Co., Inc., Germany. De-ionized water was generated from Milli-Q® gradient Systems (Millipore Co.).

CHAPTER 4 EXPERIMENTAL RESULTS AND DISCUSSION

4.1 Pyrolysis kinetic study

Oil-palm shells were used as the raw materials for preparing activated carbons. The ultimate and proximate analyses of the raw oil-palm shell are given in Tables 4-1 and 4-2, respectively.

Table 4-1 Ultimate analyses of oil-palm shell

C (wt, %)	H (wt, %)	N (wt, %)	O (wt, %)
53.7	5.6	0.2	40.5

Table 4-2 Proximate analyses of oil-palm shell

Moisture (wt, %)	Volatile content (wt, %)	Fixed carbon (wt, %)	Ash (wt, %)
4.82	65.85	28.36	0.97

From the above analyses, the oil-palm shell appeared to be a suitable precursor for preparing high-quality activated carbons due to its high carbon contents but low ash contents.

Kinetic analysis of heterogeneous decomposition of oil-palm shell in nitrogen was studied. Thermogravimetric curves and differential thermogravimetric analysis (DTG) curves derived

from TG curves were used to evaluate pyrolysis kinetics (Yaman 2004). The TG and the DTG curves under nitrogen environment are shown in Figure 4-1.

Figure 4-1 Thermogravimetric analyses on oil-palm shell

The DTG curve exhibits four peaks. The small peak at the temperature range of 290-450K shows the evaporation of the sorbed water. Table 4.1 shows that the moisture content in the oil-palm shell to be about 5%. Following the evaporation of water, the first significant mass loss due to decomposition commenced slowly and accelerated rapidly in the temperature range of 470-491K. A second significant mass loss, for the temperature range of 503-658K, followed the first one and reached an overall mass loss of more than 70%. From the DTG curve, it could be observed that at least two different processes occurred when the raw shell decomposed. They have been determined to be ascribed to the pyrolysis of hemicellulose and cellulose, accompanied by lignin pyrolysis, which generally occurs slowly over a very broad range of temperatures (Antal and Varhegyi 1995). However, a small peak occurred at 1100K which indicated a slightly increased rate of decomposition of the lignin.

4.2 Pyrolysis

4.2.1 Pyrolysis under nitrogen atmosphere

4.2.1.1 Reaction rate in pyrolysis

The reaction rate in pyrolysis can be expressed in terms of conversion from the raw oil-palm shell to char. The conversion ratio (CR) of pyrolysis is defined as the ratio of weight loss to the initial raw material weight, viz., $CR = \frac{m_i - m_t}{m_i}$ where m_i is the weight of the initial raw material, (oil-palm shell) and m_t is the weight of char after pyrolysis. In pyrolysis kinetic study using thermogravimetric analysis, the weight loss of the sample or the conversion ratio of process is an indication of the thermal degradation occurring during the process. Figures 4-2 to 4-6 show the conversion rate under different conditions. In this study, the operating parameters are varied one at a time while the rate of the parameters remaining fixed.

Figure 4-2 shows that the conversion ratio during pyrolysis increases progressively with increasing temperature from 400°C to 650°C. It is to be expected because a higher temperature increase the amount of volatiles being released from the carbon structures, hence the conversion ratio increases. For pyrolysis temperatures above 650°C, there are no further releases of volatiles because the thermal decompositions of cellulose and hemicellulose have been completed. Hence the conversion ratio remains relatively flat.

Figure 4-2 Conversion ratio during pyrolysis versus temperature

Figure 4-3 Conversion ratio during pyrolysis versus hold time

Figure 4-4 Conversion ratio during pyrolysis versus heating rate

Figure 4-5 Conversion ratio during pyrolysis versus nitrogen flow rate

Figure 4-6 Conversion ratio during pyrolysis versus size particle

(Particle size series. 1: 1-2mm, 2: 2-2.8mm, 3: 2.8-4mm, 4: 4-4.75mm, 5: 4.75-6.3mm)

Figure 4-3 shows that increasing the hold time from 0.5 to 3 hr has relatively negligible effect on the conversion ratio during pyrolysis. This implied that most of the volatiles were evolved within the first half an hour of pyrolysis. The effect of heating rate on the conversion ratio during pyrolysis is shown in Figure 4-4. The conversion ratio increases slightly with increasing heating rate. A higher heating rate during pyrolysis brings about a higher reaction rate and results in more volatile matters being released during pyrolysis; hence a higher conversion ratio is obtained. These results agreed with the conclusions of other researchers although the variances of heating rate value were not as significant as the heating rate in a flash pyrolysis (Bansal et al. 1988; Encinar et al. 2000). The “flash pyrolysis” refers to a very rapid pyrolysis in which the biomass is subjected to the pyrolysis temperature quite instantaneously. Figure 4-5 shows that increasing nitrogen flow rate has no effect on the conversion ratio during pyrolysis. It was surmised that a flow rate of 50 cm³/min of nitrogen was sufficient to carry all volatiles away from the sample; above which there is no significant change. Increasing the particle size of the raw material has no effect on the conversion ratio

for the 1 to 6.3 mm particle sizes studied as shown in Figure 4-6. For this narrow size range, the paths through which these volatiles were released might not differ significantly.

4.2.1.2 Reaction rate in activation

The reaction rate in activation can be expressed in terms of the burn-off of the char. This burn-off of char provides an evaluation of its reactivity during activation. The burn-off (θ) measures the loss in weight of the char during activation and is defined as $\theta = \frac{W_i - W_t}{W_i}$ where W_i is the initial mass of char and W_t is the mass of activated carbon at the end of activation. For identical activation conditions, the burn-off of char was studied for varying pyrolysis parameters; one parameter was varied at a time while the rest of the parameters remained the same.

Figure 4-7 shows the burn-off of char prepared at different pyrolysis temperatures. At the pyrolysis temperature of 400°C, a substantial amount of volatiles in the char was not released during pyrolysis because of its low temperature. Hence, a substantial amount of volatiles were released during activation that resulted in a high burn-off of about 50%. Increasing the pyrolysis temperature to 500°C increased the amount of volatiles released during pyrolysis and hence this improved the rudimentary pore development in the char. Therefore, the burn-off decreased because less volatile were released during activation. Further increase in the pyrolysis temperature to 650°C decreases the burn-off. Again, the decrease in burn-off with increasing pyrolysis temperature was due to the reduced release of volatiles during activation. The results concurred with other studies such as those of Bansal *et al.* (1988). Bansal *et al.* reported that the burn-off of char prepared at different temperatures and concluded that when

the chars were prepared at temperatures lower than the activation temperature, they underwent further pyrolytic decomposition during activation, resulting in weight loss independent of the activating gas. Thus, the low-temperature chars gasify at a much faster rate in the initial stages of the activation process.

Figure 4-7 Burn-off of char for varying pyrolysis temperature

Figure 4-8 Burn-off of char for varying pyrolysis hold time

Figure 4-9 Burn-off of char for varying pyrolysis heating rate

Figure 4-10 Burn-off of char for varying nitrogen flow rate during pyrolysis

Figure 4-11 Burn-off of char for varying particle size

(Particle size series. 1: 1-2mm, 2: 2-2.8mm, 3: 2.8-4mm, 4: 4-4.75mm, 5: 4.75-6.3mm)

When the pyrolysis temperature is above 650°C, increasing pyrolysis temperature results in further variations in burn-off. Over 650°C, the volatile release during pyrolysis was nearly completed. Hence, the increase in the burn-off from 650 to 750°C was mainly due to the carbon loss or combustion during the activation process. For pyrolysis temperatures greater than 750°C, shrinkage of the pores reduced pore passages restricted the diffusion of the steam within the char structure, resulting in smaller amounts of carbon combusted. Therefore, the burn-off in Figure 4-7 decreases with increasing pyrolysis temperature from 750 to 900°C.

The effects of pyrolysis hold time, heating rate and nitrogen flow rate on the burn-off of char during activation for the particle size range 2-2.8 mm are shown in Figures 4-8, 4-9 and 4-10 respectively. The relatively flat curves implied that varying values of these parameters had no effect on the burn-off of char during activation. This was to be expected as the amounts of volatiles present in the chars for each pyrolysis parameter (ref. Figures 4-3, 4-4 and 4-5) were roughly the same and therefore the same amounts of volatiles were released during activation

for the same activation conditions. Additionally, the amount of carbon combusted during activation is same for the constant activation conditions used in these tests. Figure 4-11 shows the effect of particle size on the burn-off of char. Particle size 2-2.8 mm yield the highest burn-off because of the greater accessibility of steam into the internal pores of the char for a smaller size. However, for the raw shell particle sizes 1-2 mm, the burn-off is lower than that of 2-2.8 mm for the following reason. For the 1-2 mm particle size, the chars were powdery and hence during activation, the steam could not easily penetrate into the interior of this powdery lump, resulting in reduced burn-off than expected.

4.2.1.3 Adsorption analyses

Figure 4-12 shows a typical nitrogen adsorption isotherm at 77K for the steam activated carbon prepared from oil-palm shell. The 2-2.8 mm particle size shell was pyrolyzed in nitrogen atmosphere at 750°C temperature, 2 hours hold time, 10°C/min heating rate and 150 cm³/min nitrogen volume flow rate. The char was activated at 900°C temperature, 1 hour hold time, 10°C/min heating rate and 1.36 kg/h of steam flow rate.

The isotherm is characterized by a hysteresis loop. The hysteresis loop is a characteristic of the non-microporous structure of porous materials and is caused by the condensation of nitrogen molecules in the pores (Webb and Orr 1997). The characteristics of the porous structure can be deduced from the adsorption isotherm. Fig. 4-12 indicates that there is a widening of the porosity by an increase in the mesoporosity, as inferred from the opening of the knee of the isotherm and the higher slope of the plateau. The effects of pyrolysis parameters on the pore structures of the activated carbons were studied.

Figure 4-12 Adsorption and desorption isotherms of the activated carbon prepared from oil-palm shell

Table 4-3 shows the pore characteristics of the activated carbons pyrolyzed in nitrogen atmosphere for different pyrolysis temperatures.

Table 4-3 Effect of pyrolysis temperature on the pore characteristics of the activated carbons pyrolysed in nitrogen atmosphere

Preparation conditions *	BET surface area (m ² /g)	Micropore surface area (m ² /g)	Nonmicropore surface area (m ² /g)	Total pore volume (cm ³ /g)	Percentage of nonmicropore surface area (%)
N400-2-10-150-2~2.8-900-1	716.49	590.09	126.40	0.37	18
N500-2-10-150-2~2.8-900-1	789.80	624.13	165.67	0.41	21
N600-2-10-150-2~2.8-900-1	700.93	566.70	134.23	0.36	19
N650-2-10-150-2~2.8-900-1	660.29	545.10	115.19	0.33	17
N700-2-10-150-2~2.8-900-1	700.51	568.32	132.19	0.35	19
N750-2-10-150-2~2.8-900-1	793.64	637.03	156.61	0.41	20
N800-2-10-150-2~2.8-900-1	743.45	611.36	132.09	0.37	18
N850-2-10-150-2~2.8-900-1	639.22	534.32	104.90	0.32	16
N900-2-10-150-2~2.8-900-1	543.26	451.17	92.09	0.27	17

* The preparation conditions are denoted as follows: pyrolysis temperature (°C)-pyrolysis hold time (hours)-pyrolysis heating rate (°C/min)-nitrogen flow rate during pyrolysis (cm³/min)-particle size of oil-palm shell (mm)-activation temperature (°C)-activation hold time (hours). N refers to the pyrolysis atmosphere in nitrogen.

The development of porosity in the oil-palm-shell activated carbon was strongly dependent on the temperature at which the char was prepared. Increasing the pyrolysis temperature from 400 to 500°C increases the amount of volatiles released during pyrolysis and improves the rudimentary pore development, and therefore the BET and the nonmicropore surface areas increase. A further increase in temperature to 650°C shows an unexpected decrease in the BET and nonmicropore surface areas. This was due to the formation of an intermediate melt in the char which blocked the pores and hindered carbon burn-off during activation, thereby resulting in decreased pore development. Barton *et al.* (1999) found this intermediate melt being a liquid crystalline material and named it as the carbonaceous mesophase. They studied the liquid phase formed during the carbonization of the graphitizing precursors and concluded that the polynuclear aromatic hydrocarbons are stacked into parallel arrays. However, increasing the pyrolysis temperature from 650°C to 750°C increases the BET and nonmicropore surface areas. It was due to, at these higher pyrolysis temperatures, the intermediate melt vaporized from the pore structure and thereby cleared the blocked pores. This phase was the results of the release of volatiles with a higher molecular mass than those released at 400-500°C. Further increases in the carbonization temperature up to 900°C result in decreasing BET surface area and nonmicropore surface area. These arose from the shrinkage in the pore structure at these extreme high carbonization temperatures and restricted the diffusion of water molecules for the steam-carbon reaction, resulting in reduced pore development. The results coincided with other studies of activated carbon preparation from biomasses (Daud et al. 2000; Bonelli et al. 2001; Lua et al. 2004).

Table 4-3 shows that there are two peaks, at 500°C and 750°C, which yield comparable surface characteristics. The two peaks for the surface characteristics of the activated carbons under two different pyrolysis temperatures verified that the releases of lignin and cellulose

were not simultaneous but consecutively. The pyrolysis temperature of 750°C was selected for subsequent tests as most of the volatiles would have been released.

Table 4-4 shows the effect of hold time on the pore characteristics of the activated carbons pyrolyzed in nitrogen atmosphere. The maximum BET and nonmicropore surface areas were obtained at a pyrolysis hold time of 2 hours. Increasing the hold time from 0.5 to 2 hours increases the BET and nonmicropore surface areas. This was a result of increasing rudimentary pore development in the char with pyrolysis hold time, which allowed a better diffusion of steam molecules through the pores for the steam-carbon reaction. However, increasing pyrolysis hold time from 2 to 3 hours decreases the BET and micropore surface areas. This might again be due to the shrinkage in the pore structure of the char with prolonged pyrolysis hold time and restricted the diffusion of the water molecules for the steam-carbon reaction, thereby reducing pore development in the activated carbon. The optimum hold time of 2 hours for pyrolysis was used for subsequent tests.

Table 4-4 Effect of hold time on the pore characteristics of the activated carbon pyrolysed in nitrogen atmosphere

Preparation conditions *	BET surface area (m ² /g)	Micropore surface area (m ² /g)	Nonmicropore surface area (m ² /g)	Total pore volume (cm ³ /g)	Percentage of nonmicropore surface area (%)
N750-0.5-10-150-2~2.8-900-1	676.12	562.80	113.32	0.34	17
N750-1.0-10-150-2~2.8-900-1	741.60	600.37	141.23	0.38	19
N750-1.5-10-150-2~2.8-900-1	761.21	618.93	142.28	0.39	19
N750-2.0-10-150-2~2.8-900-1	793.64	637.03	156.61	0.41	20
N750-2.5-10-150-2~2.8-900-1	772.84	613.02	159.82	0.40	21
N750-3.0-10-150-2~2.8-900-1	688.43	559.09	129.34	0.35	19

* Please refer footnote in Table 4-3.

The effects of heating rate and nitrogen flow rate during pyrolysis and the particle size on the pore characteristics of the activated carbons are given in Tables 4-5 to 4-7. Varying one parameter at a time while the other parameters remained constant during pyrolysis, these

parameters were similarly optimized as previously carried out for the temperature and hold time during pyrolysis.

Table 4-5 Effect of heating rate on the pore characteristics of the activated carbon pyrolysed in nitrogen atmosphere

Preparation conditions *	BET surface area (m ² /g)	Micropore surface area (m ² /g)	Nonmicropore surface area (m ² /g)	Total pore volume (cm ³ /g)	Percentage of nonmicropore surface area (%)
N750-2-5-150-2~2.8-900-1	668.28	544.06	124.22	0.34	19
N750-2-10-150-2~2.8-900-1	793.64	637.03	156.61	0.41	20
N750-2-20-150-2~2.8-900-1	781.04	644.21	136.83	0.39	18
N750-2-30-150-2~2.8-900-1	751.32	591.99	159.33	0.39	20
N750-2-40-150-2~2.8-900-1	730.60	591.98	138.62	0.37	19

* Please refer footnote in Table 4-3.

Table 4-5 shows that a heating rate of 10°C/min yields the maximum BET and non-micropore surface areas.

Table 4-6 Effect of nitrogen flow rate on the pore characteristics of the activated carbon pyrolysed in nitrogen atmosphere

Preparation conditions *	BET surface area (m ² /g)	Micropore surface area (m ² /g)	Nonmicropore surface area (m ² /g)	Total pore volume (cm ³ /g)	Percentage of nonmicropore surface area (%)
N750-2-10-50-2~2.8-900-1	767.74	620.87	146.87	0.39	19
N750-2-10-100-2~2.8-900-1	733.11	599.71	133.40	0.37	18
N750-2-20-150-2~2.8-900-1	771.14	616.44	154.70	0.39	20
N750-2-30-200-2~2.8-900-1	729.42	606.52	122.90	0.36	17
N750-2-40-250-2~2.8-900-1	762.93	616.21	146.72	0.39	19

* Please refer footnote in Table 4-3.

Table 4-6 shows the effect of nitrogen flow rate during pyrolysis on the pore characteristics of the activated carbons. Varying flow rates do not have any significant effect on the BET and micropore surface areas. However, a flow rate of 150 cm³/min yields the largest BET surface area and this flow rate was used in the subsequent tests.

Table 4-7 Effect of particle size on the pore characteristics of the activated carbon pyrolysed in nitrogen atmosphere

Preparation conditions*	BET surface area (m ² /g)	Micropore surface area (m ² /g)	Nonmicropore surface area (m ² /g)	Total pore volume (cm ³ /g)	Percentage of nonmicropore surface area (%)
N750-2-10-50-1~2-900-1	569.49	485.44	84.05	0.276	15
N750-2-10-100-2~2.8-900-1	771.14	616.44	154.70	0.394	20
N750-2-20-150-2.8~4-900-1	626.76	519.62	107.14	0.313	17
N750-2-30-200-4~4.75-900-1	531.51	453.65	77.86	0.258	15
N750-2-40-250-4.75~6.3-900-1	530.00	450.00	80.00	0.252	15

* Please refer footnote in Table 4-3.

The effect of particle size on the pore characteristics of the activated carbons pyrolysed in nitrogen atmosphere is shown in Table 4-7. The five particle size ranges under study were 1-2 mm, 2-2.8 mm, 2.8-4 mm, 4-4.75 mm and 4.75-6.3 mm. Decreasing particle size increases the BET and the non-micropore surface areas because of the greater accessibility of steam into the internal pores of the char for a smaller size. However, the particle range of 1-2 mm shows a smaller BET or non-micropore surface area than that of the 2-2.8 mm size. This was due to the powdery chars which restricted the diffusion of the steam during activation as explained earlier for the burn-off phenomenon for this size range in section 4.2.1.2. The particle size range of 2-2.8 mm yields the largest BET and non-micropore surface areas and this size range was used for subsequent tests.

4.2.1.4 Surface morphology

Figures 4-13 to 4-15 show the scanning electron micrographs of the surfaces of the raw oil-palm shell, char and activated carbon respectively. These micrographs show the pore structures, from the elementary porous structure of the shell, to the rudimentary pore structure of the char and then finally into the developed porous structure of the activated carbon. Figure

4-13 shows the botanical pores on the surface of the shell that provide the sites for the macropore development of the char in Figure 4-14. In Figure 4-14, a fraction of voids is completely open while the others are in an intermediate phase, accumulated with tar-like deposits. These deposits are the products of thermal decomposition and transferred from the internal structure. After activation, Figure 4-15 shows the regular pores on the surface of the activated carbon. These micrographs show that the intrinsic ostioles in the biomass make it possible to develop the porous structure of the activated carbon. Figure 4-16 shows another view of the surface morphology of the activated carbon.

Figure 4-13 Surface morphological structure of oil-palm shell (x1100)

Figure 4-14 Surface morphological structure of char pyrolysed in nitrogen (x2400)

Figure 4-15 Surface morphological structure of activated carbon pyrolysed in nitrogen (x14000)

Figure 4-16 Surface morphology of the activated carbon (x14000)

4.2.1.5 Aqueous phase adsorption

In section 4.2.1.3, the effect of the pyrolysis parameters on the activated carbons were evaluated on the basis of their pore characteristics. Another criterion used was on the basis of the adsorption capacity of the activated carbon. These activated carbons, prepared as per those described in section 4.2.1.3, were subjected to adsorption tests using aqueous phenol solutions. The adsorption capacity of the activated carbons to 200 mg/dm³ of initial phenol concentration at 30°C was determined. Figure 4-17 to 4-21 show the effects of the different pyrolysis parameters on the phenol adsorption capacity. The BET surface area was also plotted in these figures for comparison purposes.

The effect of i) pyrolysis temperature, ii) pyrolysis hold time, iii) pyrolysis heating rate, iv) nitrogen flow rate during pyrolysis, and v) initial particle size on the phenol adsorption capacity and the BET surface area of activated carbons pyrolyzed in nitrogen are shown in Figures 4-17,4-18,4-19,4-20 and 4-21, respectively. The trends of the adsorption capacity follow closely to those BET surface area for each of the pyrolysis parameters under study. This is to be expected because the adsorption capacity depends directly on the pore surface area of the adsorbent (Suzuki 1990). The discussion on the variations of the BET surface area with the pyrolysis parameters has been presented in section 4.2.1.3.

Figure 4-17 Effect of pyrolysis temperature on the adsorption capacity and the BET surface area of activated carbons pyrolysed in nitrogen atmosphere

Figure 4-18 Effect of pyrolysis hold time on the adsorption capacity and the BET surface area of activated carbons pyrolysed in nitrogen atmosphere

Figure 4-19 Effect of pyrolysis heating rate on the adsorption capacity and the BET surface area of activated carbons pyrolysed in nitrogen atmosphere

Figure 4-20 Effect of nitrogen flow rate during pyrolysis on the adsorption capacity and the BET surface area of activated carbons pyrolysed in nitrogen atmosphere

Figure 4-21 Effect of initial particle size on the adsorption capacity and the BET surface area of activated carbons pyrolysed in nitrogen atmosphere (particle size series. 1: 1-2mm, 2: 2-2.8mm, 3: 2.8-4mm, 4: 4-4.75mm, 5: 4.75-6.3mm)

To correlate the adsorption capacity and the pore characteristics, a plot of the phenol adsorption capacity versus the BET surface area is shown in Figure 4-22 for all the activated carbons with different pyrolysis conditions. Generally, the adsorption capacity of phenol increases linearly with the BET surface area of the activated carbons. In the figure, a regression line is drawn through the experimental data points and its correlation coefficient is 0.93. The dashed lines shown indicate 95% confidence limits.

Figure 4-22 Correlation between adsorption capacity and BET surface area for activated carbons pyrolysed in nitrogen atmosphere

The pore size distributions of the activated carbons for two varying pyrolysis parameters are shown in Figures 4-23 and 4-24. Figure 4-23 shows the effect of pyrolysis temperature while Figure 4-24 shows the effect of initial particle size. For Figure 4-23, a pyrolysis temperature of 750°C should yield the largest BET surface area (ref. Table 4-3). For all the pyrolysis temperatures shown in Fig 4-23, the pores in the activated carbons range from 2 to 11 nm. Pyrolysis temperatures of 500 and 750°C generally yield the most pores for the whole size range while the pyrolysis temperature of 900°C generally yields the least number of pores. For Figure 4-24, an initial particle size range of 2-2.8 mm yields the largest BET surface area

(ref. Table 4-7). For the different initial shell sizes, the particle size range of 2-2.8 mm produces the most pores in the whole size range of 2 to 11 nm. For the rest of the pyrolysis parameters, the pore size distributions are quite similar and therefore they are not shown here.

Figure 4-23 Effect of temperature on pore size distribution of AC pyrolysed in nitrogen

Figure 4-24 Effect of particle size on pore size distribution of AC pyrolysed in nitrogen

4.2.2 Pyrolysis under vacuum

4.2.2.1 Reaction rate in pyrolysis

Pyrolysis under vacuum consists of the thermal decomposition of the precursor under reduced pressure. The complex organic molecules in the raw material decompose into primary fragments during pyrolysis. These fragments, consisting of hydrocarbon volatiles of hemicellulose, cellulose and lignin, are removed from the reactor by a vacuum pump. In this way, secondary degradation reactions are minimized. First of all, the conversion ratio during the pyrolysis under vacuum was determined and then compared to that for pyrolysis under nitrogen atmosphere for each pyrolysis parameter.

(a)

(b)

Figure 4-25 Comparison of conversion rate in pyrolysis in different atmosphere

Figure 4-25 (a) shows the effect of the pyrolysis temperature on the conversion ratio of the oil-palm shell to char for pyrolysis under nitrogen and vacuum conditions. For the nitrogen atmosphere, the release of the volatiles from the carbon structure of the shell is dependent on the prevailing pyrolysis temperature. At about 400-500°C, volatiles of hemicelluloses and cellulose are released, thereby contributing to the increasing conversion ratio with increasing temperature. Further increases in pyrolysis temperature from 500 to 650°C, volatiles of lignin are released and therefore the conversion ratio increases further. At about 700°C, the release of volatiles is nearly completely and hence the conversion ratio remains nearly constant for increasing pyrolysis temperature from 700 to 900°C. However, for the vacuum pyrolysis conditions, the boiling points of the volatiles are lower due to a reduced pressure in the reactor. Most of the volatiles are released for a pyrolysis temperature of about 400°C and hence the conversion ratio is higher than that for the nitrogen atmosphere case. This difference is present up to about 700°C when the release of volatiles for the nitrogen

atmosphere case is nearly complete. Thereafter, the conversion ratio curves for both cases become almost identical for pyrolysis temperatures from 700-900°C. The effect of pyrolysis hold time, pyrolysis heating rate and initial particle size on the conversion ratio are shown in Figures 4-25 (b), (c) and (d) respectively. Since the pyrolysis temperature was 750°C, most of the volatiles had been released and therefore the conversion ratio remained constant for increasing values of these pyrolysis parameters for both nitrogen and vacuum conditions.

4.2.2.2 Reaction rate in activation

Similar to the burn-off of chars for pyrolysis under nitrogen atmosphere in section 4.2.1.2, the effects of the pyrolysis conditions on the burn-off of chars pyrolysed in vacuum were studied. For these tests, the activation conditions were fixed as follows: 1.36 kg/h steam flow rate, 900°C activation temperature and 1 hour hold time. The pyrolysis parameters were varied one at a time while the rest of the parameters remained the same for each parameter studied.

Figure 4-26 shows the burn-offs of chars which were subjected to vacuum pyrolysis. In addition, the burn-off of chars subjected to nitrogen pyrolysis are also shown so that a comparison between the burn-offs of these two types of chars can be studied and analyzed. Figure 4-26(a) shows the burn-off of chars versus the pyrolysis temperature for the two pyrolysis atmospheres. For the vacuum pyrolysis case, the burn-off for the pyrolysis temperatures from 400 to 675°C remains rather high. The burn-off during this activation process is mainly due to the steam-carbon reaction and the continual release of residual volatiles still remaining in the chars. However, for pyrolysis temperatures greater than 675°C, the burn-off decreases continuously until a pyrolysis temperature of 900°C. This decreasing trend is probably due to the increasing shrinkage of pore within the carbon structure for

increasing pyrolysis temperature such that the steam-carbon reaction progressively decreases. At a pyrolysis temperature of 900°C, the burn-offs for both vacuum and nitrogen atmospheres have converged to a common point. The burn-off must be due to the steam-carbon reaction as all the volatiles must have been released at this pyrolysis temperature. This low burn-off would be attributed to the severe shrinkage of pores within the carbon structure, inhibiting the carbon-steam reaction, the higher burn-off for the nitrogen atmosphere than the vacuum case at 400°C pyrolysis temperature would be the higher continual devolatilization during activation for the former case which has more volatiles left in the char (ref. Figure 4-25(a)).

Figure 4-26 Comparison of burn-off of chars for two different atmospheres

The effects of pyrolysis hold time, pyrolysis heating rate and initial particle size on the burn-off of chars are shown in Figure 4-26 (b), (c) and (d) respectively. For these pyrolysis parameters, the burn-off of chars for the nitrogen atmosphere is always smaller than that for the vacuum condition. The pyrolysis temperature for the nitrogen case was 750°C. At this temperature under normal atmospheric pressure, sintering of the volatiles occurs, followed by polymerization and finally condensation. These reactions result in carbonaceous deposits on the surface and inside the char particles, and thereby clogging up the rudimentary pores within the carbon structure. Hence, during activation, the blocked pores restrict the diffusion of the steam molecules for the carbon-steam reaction and therefore reducing the carbon burn-off. On the other hand, for the vacuum pyrolysis condition, the pyrolysis temperature was 675°C. Due to a reduced pressure, the boiling points of these hydrocarbon volatiles are lowered and at 675°C, the detrimental effects of carbonaceous deposits were minimized. The problem of blocked pore was small and the carbon-steam reaction was more effective and hence a higher carbon burn-off. For the effect of particle size in Figure 4-26 (d), it is also observed that the 1-2 mm particle size range yields a lower burn-off than that of the 2-2.8 mm particle size for the vacuum pyrolysis case. The reason is similar to that given in section 4.2.1.2, i.e., the powdery chars that hinder the diffusion of steam molecules for the steam-carbon reaction. The variations of the burn-off with increasing hold time, pyrolysis heating rate and particle size for the vacuum condition are similar to those of the nitrogen atmosphere, which had been discussed in section 4.2.1.2. Another interesting point to note is the difference in the burn-off between the vacuum condition and the nitrogen atmosphere; this difference decreases with increasing pyrolysis temperature greater than 750°C. The release of volatiles in the nitrogen conditions is more spontaneous and the associated problems of sintering, polymerization and condensation are avoided, facilitating the carbon-steam reaction in these chars for the nitrogen pyrolysis case.

4.2.2.3 Adsorption analyses

The effects of pyrolysis parameters on the pore characteristics of activated carbons pyrolysed under vacuum condition were studied. Using a local optimization scheme in which one particular pyrolysis parameter was varied while the other pyrolysis parameters remained constant; the effects of varying values of this particular parameter on the pore surface area of the activated carbons were analyzed. The value of this particular parameter that yielded the highest surface area would be chosen. This optimizing process would then be applied to choose the values of the remaining parameters. The activation conditions for the chars were fixed for this optimization process.

Table 4-8 shows the effect of pyrolysis temperature on the pore characteristics of the activated carbons pyrolysed under vacuum condition. The range of pyrolysis temperatures used was 400 to 900°C. For the pyrolysis temperature of 400°C, the BET and the non-micropore surface areas were found to be amongst the lowest for the pyrolysis temperatures studied. This could be attributed to the fact that the release of volatiles was not complete and thereby inhibited the steam-carbon reaction during the activation process. At a high pyrolysis temperature of 900°C, it yielded the lowest BET and non-micropore surface areas. The shrinkage of pores restricted the diffusion of the steam molecules into the pores of the chars and therefore reduced the steam-carbon reaction. A pyrolysis temperature of 675°C produced the highest BET and non-micropore surface areas and this pyrolysis temperature was used for subsequent tests.

Table 4-8 Effect of pyrolysis temperature on the pore characteristics of the activated carbons pyrolysed under vacuum condition

Preparation conditions *	BET surface area (m ² /g)	Micropore surface area (m ² /g)	Nonmicropore surface area (m ² /g)	Total pore volume (cm ³ /g)	Percentage of nonmicropore surface area (%)
V400-2-10-2~2.8-900-1	797.97	618.21	179.76	0.42	23
V500-2-10-2~2.8-900-1	929.43	683.39	246.04	0.51	26
V525-2-10-2~2.8-900-1	980.66	724.72	255.94	0.55	26
V550-2-10-2~2.8-900-1	939.55	689.90	249.65	0.51	27
V600-2-10-2~2.8-900-1	857.31	645.84	211.47	0.46	25
V650-2-10-2~2.8-900-1	946.77	694.97	251.80	0.52	27
V675-2-10-2~2.8-900-1	988.35	715.63	272.72	0.55	28
V700-2-10-2~2.8-900-1	953.73	692.88	260.85	0.53	27
V750-2-10-2~2.8-900-1	873.84	656.05	217.79	0.47	25
V800-2-10-2~2.8-900-1	892.57	675.14	217.43	0.48	24
V850-2-10-2~2.8-900-1	839.55	659.50	180.05	0.44	21
V900-2-10-2~2.8-900-1	692.74	575.79	116.95	0.35	17

* The preparation conditions are denoted as follows: pyrolysis temperature (°C)-pyrolysis hold time (hour)-pyrolysis heating rate (°C/min)-particle size of oil-palm shell (mm)-activation temperature (°C)-activation hold time (hour). V refers to the pyrolysis under vacuum.

Table 4-9 shows the effect of hold time on the pore characteristics of the activated carbons pyrolysed under vacuum condition. Tests were carried out for hold time of 0.5, 1.0, 1.5, 2.0, 2.5 and 3 hours. Variations in the BET and non-micropore surface areas for these hold times were not greatly significant. However, a hold time of 2 hours yielded the highest surface areas and therefore this hold time was used for subsequent tests.

Table 4-9 Effect of hold time on the pore characteristics of the activated carbons pyrolysed under vacuum condition

Preparation conditions *	BET surface area (m ² /g)	Micropore surface area (m ² /g)	Nonmicropore surface area (m ² /g)	Total pore volume (cm ³ /g)	Percentage of nonmicropore surface area (%)
V675-0.5-10-2~2.8-900-1	939.72	688.39	251.33	0.53	27
V675-1.0-10-2~2.8-900-1	946.53	693.73	252.80	0.54	27
V675-1.5-10-2~2.8-900-1	937.11	693.98	243.13	0.52	26
V675-2.0-10-2~2.8-900-1	988.13	715.65	272.48	0.57	28
V675-2.5-10-2~2.8-900-1	948.95	681.69	267.26	0.53	28
V675-3.0-10-2~2.8-900-1	925.59	690.02	235.57	0.52	25

* Please refer footnote in Table 4-8

Table 4-10 shows the effect of pyrolysis heating rate on the pore characteristics of the activated carbons pyrolysed under vacuum condition. The heating rates used were 5,10,20,30 and 40°C/min. Varying heating rate had very little effect on the BET and non-micropore surface areas. A heating rate of 10°C/min had a slight edge over the rest of the heating rates and it was used for subsequent tests.

Table 4-10 Effect of pyrolysis heating rate on the pore characteristics of the activated carbons pyrolysed under vacuum condition

Preparation conditions*	BET surface area (m ² /g)	Micropore surface area (m ² /g)	Nonmicropore surface area (m ² /g)	Total pore volume (cm ³ /g)	Percentage of nonmicropore surface area (%)
V675-2.0-5-2~2.8-900-1	980.37	737.98	242.39	0.54	25
V675-2.0-10-2~2.8-900-1	1031.79	753.77	278.02	0.59	27
V675-2.0-20-2~2.8-900-1	1012.45	737.88	274.57	0.58	27
V675-2.0-30-2~2.8-900-1	1019.48	737.09	282.39	0.57	28
V675-2.0-40-2~2.8-900-1	1010.40	734.80	275.60	0.57	27

* Please refer footnote in Table 4-8

Table 4-11 shows the effect of particle size on the pore characteristics of the activated carbons pyrolysed under vacuum condition. Decreasing particle size increased the BET and non-micropore surface areas of the activated carbons except for the smallest size range of 1-2 mm. A smaller particle enhanced the diffusion of the steam molecules into the pores in the interior carbon structure for the steam-carbon reaction to take place.

Table 4-11 Effect of particle size on the pore characteristics of the activated carbons pyrolysed under vacuum condition

Preparation conditions*	BET surface area (m ² /g)	Micropore surface area (m ² /g)	Nonmicropore surface area (m ² /g)	Total pore volume (cm ³ /g)	Percentage of nonmicropore surface area (%)
V675-2-10-1~2-900-1	843.68	574.98	268.70	0.50	32
V675-2-10-2~2.8-900-1	989.59	631.85	357.74	0.62	36
V675-2-10-2.8~4-900-1	854.76	616.20	238.56	0.49	28
V675-2-10-4~4.75-900-1	829.14	589.67	239.47	0.48	29
V675-2-10-4.75~6.3-900-1	690.79	486.10	204.69	0.39	30

* Please refer footnote in Table 4-8

The particle size of 2-2.8 mm produced the highest BET and non-micropore surface areas once again; the smallest particle of 1-2 mm should yield better results than powdery state of the chars which partly obstructed the access of steam for the steam-carbon reaction during activation.

For each varying pyrolysis parameters, the activated carbons produced by nitrogen atmosphere and vacuum condition were analyzed. Comparing the data for pyrolysis temperature (Tables 4-3 and 4-8), pyrolysis hold time (Tables 4-4 and 4-9), heating rate during pyrolysis (Tables 4-5 and 4-10) and initial particle size (Tables 4-7 and 4-11), the vacuum pyrolysis condition produced higher quality activated carbons in term of BET and non-micropore surface areas than the nitrogen pyrolysis atmosphere.

Table 4-12 Reproducibility tests for experiment V675-2-10-2~2.8-900-1

	Experimental Run 1	Experimental Run 2	Experimental Run 3	Experimental Run 4	Standard deviation
BET surface area (m ² /g)	988	988	1032	990	22

4.2.2.4 Surface morphology

Scanning electron micrographs on the surface of a char and an activated carbon pyrolysed in vacuum are shown in Figures 4-27 and 4-28 respectively. The char was prepared under vacuum at a pyrolysis temperature of 675°C, a hold time of 2 hours and a heating rate of 10°C/min. the activated carbon was obtained by subjecting this type of char to steam activation at 900°C and 1 hour hold time. Deposits on the char surface could be seen but none was observed on the surface of the activated carbon.

Figure 4-27 Surface morphological structure of char pyrolysed under vacuum (x1800)

Figure 4-28 Surface morphological structure of activated carbon pyrolysed under vacuum (x5120)

4.2.2.5 Aqueous phase adsorption

The activated carbons prepared under vacuum pyrolysis condition were subjected to aqueous phenol adsorption to determine the adsorption capacities of activated carbons prepared under i) varying pyrolysis temperature, ii) varying pyrolysis hold time, iii) varying pyrolysis heating rate, and iv) varying initial particle size. The initial phenol solution concentration was 200 mg/dm³. The flask containing the activated carbon and the phenol solution was placed in an orbital shaker with a shaking speed of 150 rpm. The initial phenol temperature was 30°C. the effects of pyrolysis temperature, pyrolysis hold time, pyrolysis heating rate and particle size on the phenol adsorption capacity of the activated carbons are shown in Figures 4-29,4-30,4-31 and 4-32 respectively.

In these figures, the BET surface area data were also plotted. This would enable the variations in the phenol adsorption capacity and the BET surface area with the pyrolysis parameters to be examined simultaneously. Generally, the trends of these two properties are similar as shown in Figures 4-29 to 4-32. Similar to Figures 4-17, 4-18, 4-19 and 4-21. This is to be expected because the adsorption capacity of the activated carbon is directly proportional to the pore surface area, i.e. the BET surface area especially for aqueous phase adsorption. Comparing the adsorption capacities of activated carbons pyrolysed in nitrogen atmosphere (Figure 4-17, 4-18, 4-19 and 4-21), the activated carbons pyrolysed under vacuum showed higher adsorption capacities for the corresponding pyrolysis parameter.

The effects of temperature, hold time and particle size on BET surface area and aqueous phase adsorption capacity are similar. Comparing with other effects, the difference between effects of heating rate on BET surface area and that on aqueous phase adsorption is

fundamental. Generally, heating rate changed the process of dehydration and the stabilization of the polymeric components during pyrolysis or carbonization (Bansal et al. 1988). Different heating rate changed the molecule arrangement on chars' surface. Under vacuum, the effect of heating rate on molecule arrangement is accentuated. This can be explained through the controlling step in the ramp period. In the nitrogen, the porosity development by volatile release is the controlling step. So the difference between effects of heating rate on BET surface area and that on aqueous phase adsorption is slight in the nitrogen atmosphere. While under vacuum, the structure rearrangement is predominant because of the minimization of volatile release effect under pressure gradient provided by vacuum. The experimental results of heating rate effect indicated both porosity development and molecule rearrangement happened in pyrolysis affected active surface of chars.

Figure 4-29 Effect of pyrolysis temperature on the adsorption capacity and the BET surface area of activated carbons pyrolysed under vacuum

Figure 4-30 Effect of pyrolysis hold time on the adsorption capacity and the BET surface area of activated carbons pyrolysed under vacuum

Figure 4-31 Effect of pyrolysis heating rate on the adsorption capacity and the BET surface area of activated carbons pyrolysed under vacuum

Figure 4-32 Effect of initial particle size on the adsorption capacity and the BET surface area of activated carbons pyrolysed under vacuum (particle size series. 1: 1-2mm, 2: 2-2.8mm, 3: 2.8-4mm, 4: 4-4.75mm, 5: 4.75-6.3mm)

Pyrolysis parameters affect aqueous phase adsorption capacity and BET surface area of activated carbon both. As Figure 4-29, 4-30 and 4-32 indicated, the trends of those effects are similar. A correlation between aqueous phase adsorption capacity and BET surface area was investigated. As shown in Figure 4-33(a), as for the activated carbons prepared in this section, the BET surface area and aqueous phase adsorption capacity can be correlated with a linear regression in which R equal to 0.94 and the dashed lines refer to the 95% confidential regions for prediction. So BET surface area can be a criterion to evaluate the effects of those parameters except for effects of heating rate.

The data from Figures 4-22 and 4-33(a) were combined together and shown in Figure 4-33(b). The activated carbons pyrolysed under vacuum conditions have higher BET surface areas than those pyrolysed under nitrogen. The regressed data for both the vacuum and nitrogen

pyrolysis conditions show good agreement and linearity trend. Hence, the aqueous phase phenol adsorption capacity is generally directly proportional to the BET surface area.

(a)

(b)

Figure 4-33 Correlation between adsorption capacity and BET surface area for activated carbons pyrolysed under (a) vacuum, and (b) nitrogen and vacuum.

The effects of pyrolysis temperature and initial particle size on the pore size distributions of the activated carbons pyrolysed under vacuum and shown in Figures 4-34 and 4-35

respectively. The pore sizes are mainly in the mesopore regions which are suitable for aqueous phase adsorption.

Figure 4-34 Effect of pyrolysis temperature on the pore size distribution of activated carbons pyrolysed under vacuum

Figure 4-35 Effect of initial particle size on the pore size distribution of activated carbon pyrolysed under vacuum

4.3 Summary of pyrolysis conditions

A systematic series of tests were carried to determine the optimum pyrolysis conditions in order to maximize the pore surface areas of the activated carbons. Two different pyrolysis environments were studied; vacuum pyrolysis and pyrolysis in nitrogen atmosphere. The pyrolysis parameters studied were i) temperature, ii) hold time, iii) heating rate, iv) nitrogen flow rate (for nitrogen pyrolysis only), and v) initial particle size of the oil-palm shell. The activation conditions for the chars were fixed for these tests, i.e., i) temperature of 900°C, ii) hold time of 1 hour, iii) heating rate of 10°C/min, iv) steam flow rate of 22.68 g/min. varying one pyrolysis parameter at a time whilst the rest of the pyrolysis parameters remained fixed, the local optimum values of the pyrolysis parameters could be obtained based on the highest pore surface area of the activated carbon.

For pyrolysis in nitrogen atmosphere, the optimum pyrolysis conditions are i) temperature of 750°C, ii) hold time of 2 hours, iii) heating rate of 10°C/min, iv) nitrogen flow rate of 150 ml/min, and v) initial particle size of 2-2.8 mm. for pyrolysis under vacuum conditions, the optimum pyrolysis conditions are i) temperature of 675°C, ii) hold time of 2 hours, iii) heating rate of 10°C/min, and iv) initial particle size of 2-2.8 mm.

4.4 Activation process

4.4.1 Physical activation

In the physical activation process, the chars were subjected to steam as the activation agent. The chars were prepared by pyrolysis in nitrogen atmosphere or vacuum condition. The optimum pyrolysis conditions are given in the preceding section 4.3. The activation parameters studied were the steam flow rate, hold time and activation temperature. To optimize the activation process to produce activated carbons of high pore surface areas, the activation parameters were varied one at a time whilst the remaining parameters were fixed. After optimizing one parameter, this optimum value would be used when optimizing the next parameter. This process would be repeated until all the parameters were optimized. The criterion for selecting the optimum value of each parameter was based on the BET surface area.

4.4.1.1 Adsorption analyses

The first activation studied was the steam flow rate. Table 4-13 shows the effect of steam flow rate during activation on the pore surface characteristics of the activated carbons. The mass flow rate of steam into the activation reactor was varied from 0.68 to 1.81 kg/h (or 1.5 to 4.0 lb/hr) while the rest of the parameters remained constant.

Table 4-13 Effect of steam flow rate during activation on the pore surface characteristics of the activated carbons

Preparation condition *	BET surface area (m ² /g)	Micropore surface area (m ² /g)	Nonmicropore surface area (m ² /g)	Total pore volume (cm ³ /g)	Percentage of nonmicropore surface area (%)
Pyrolysis in nitrogen atmosphere					
N750-2-10-150-2~2.8-0.68-900-1	NA	NA	NA	NA	NA
N750-2-10-150-2~2.8-1.13-900-1	976.68	734.47	242.21	0.52	25
N750-2-10-150-2~2.8-1.36-900-1	771.14	616.44	154.70	0.39	20
N750-2-10-150-2~2.8-1.81-900-1	443.53	369.82	73.71	0.26	16
Pyrolysis under vacuum					
V675-2-10-2~2.8-0.68-900-1	NA	NA	NA	NA	NA
V675-2-10-2~2.8-1.13-900-1	1059.63	702.04	357.58	0.62	34
V675-2-10-2~2.8-1.36-900-1	989.59	631.85	357.74	0.62	36
V675-2-10-2~2.8-1.81-900-1	484.56	386.13	98.43	0.22	20

* The preparation conditions are denoted as follows: pyrolysis temperature (°C)-pyrolysis hold time (hour)-pyrolysis heating rate (°C/min)-nitrogen flow rate during pyrolysis (cm³/min)-particle size of oil-palm shell (mm)-activation temperature (°C)-activation hold time (hour). N refers to the pyrolysis atmosphere in nitrogen while V refers to the pyrolysis under vacuum.

For both types of chars, a steam flow rate of 1.13 kg/h produced activated carbons with the highest BET and non-micropore surface areas. When the steam flow rate was 0.68 kg/h, the reaction was severe or drastic such that there was excessive carbon burn-off, leaving very little residue for any analyses to be conducted. The reason might be that the low steam flow rate was not sufficient to flush the air in the reactor and the pipeline and hence resulted possibly in the combustion of char with air. Increasing the steam flow rate from 1.13 to 1.81 kg/h generally decreased the BET and non-micropore surface areas of the activated carbons. An excessive high steam flow rate reduced the reaction temperature of the char and hence resulted in low steam-carbon reaction and underdeveloped pore structures. This observation is also supported by Lv. *et. al.* (2004). In summary, a steam flow rate of 1.13 kg/h was used for subsequent tests.

The effects of hold time and temperature during activation on the pore surface characteristics of the activated carbons are shown in Table 4-14. Chars pyrolysed in nitrogen atmosphere and under vacuum condition were used.

Table 4-14 Effect of hold time and temperature during activation on the pore surface characteristics of the activated carbons

Preparation condition	BET surface area (m ² /g)	Micropore surface area (m ² /g)	Nonmicropore surface area (m ² /g)	Total pore volume (cm ³ /g)	Percentage of nonmicropore surface area
Effect of hold time: pyrolysis in nitrogen atmosphere					
N750-2-10-150-2~2.8-1.13-900-0.5	635.31	518.95	116.36	0.32	18
N750-2-10-150-2~2.8-1.13-900-1.0	932.59	661.21	271.38	0.51	29
N750-2-10-150-2~2.8-1.13-900-1.5	1308.79	852.6	456.19	0.79	35
N750-2-10-150-2~2.8-1.13-900-2.0	1209.83	797.80	412.03	0.68	34
N750-2-10-150-2~2.8-1.13-900-2.5	1135.12	793.28	341.85	0.62	30
Effect of hold time: pyrolysis under vacuum condition					
V675-2-10-150-2~2.8-1.13-900-0.5	979.67	695.16	284.51	0.55	29
V675-2-10-150-2~2.8-1.13-900-1.0	1059.63	702.04	357.58	0.62	34
V675-2-10-150-2~2.8-1.13-900-1.5	1075.99	711.28	364.71	0.63	34
V675-2-10-150-2~2.8-1.13-900-2.0	1048.48	710.89	335.58	0.60	32
V675-2-10-150-2~2.8-1.13-900-2.5	994.49	706.47	288.03	0.58	29
Effect of temperature: pyrolysis in nitrogen					
N750-2-10-150-2~2.8-1.13-750-1.5	421.73	358.78	62.94	0.20	15
N750-2-10-150-2~2.8-1.13-800-1.5	739.21	621.96	117.25	0.36	16
N750-2-20-150-2~2.8-1.13-850-1.5	938.7	791.87	146.83	0.46	16
N750-2-30-150-2~2.8-1.13-900-1.5	1308.79	852.6	456.19	0.79	35
N750-2-20-150-2~2.8-1.13-950-1.5	1432.94	605.45	827.5	0.95	58
N750-2-30-150-2~2.8-1.13-970-1.5	1316.92	490.4	826.52	0.94	63
Effect of temperature: pyrolysis under vacuum					
V675-2-10-150-2~2.8-1.13-750-1.5	443.33	370.12	73.22	0.22	17
V675-2-10-150-2~2.8-1.13-800-1.5	490.77	401.86	88.91	0.25	18
V675-2-10-150-2~2.8-1.13-850-1.5	657.91	518.87	139.04	0.34	21
V675-2-10-150-2~2.8-1.13-900-1.5	1192.29	777.99	414.3	0.72	35
V675-2-20-150-2~2.8-1.13-950-1.5	1382.95	573.27	809.68	0.99	59
V675-2-30-150-2~2.8-1.13-970-1.5	1256.71	499.66	757.05	0.93	60

Increasing hold time during activation generally increases the pore surface area and pore volume of the activated carbons as shown in Table 4-14. A longer hold time enhances the pore development due to the steam-carbon reaction. A hold time of 1.5 hours yields the highest BET and nonmicropore surface areas. However, for hold times greater than 1.5 hours, the pore surface area and pore volume decrease with increasing hold time because of pore

widening and thinning of pore walls, mainly converting mesopores to macropores. For excessive long hold times, the pore walls would collapse and two or more pores would combine and form into one large pore, thereby decreasing the pore surface area. For the same hold time of 1.5 hour, the chars pyrolysed in nitrogen atmosphere yield activated carbons with higher BET and non-micropore surface areas than those chars pyrolysed under vacuum condition. A hold time of 1.5 hour was used for subsequent tests to determine the optimum activation temperature.

The effect of activation temperature on the pore characteristics of the activated carbons is shown in Table 4-14. The range of activation temperatures used was 750 to 970°C. Increasing the temperature from 750 to 950°C increases all pore surface areas and pore volume of the activated carbons except for the micropore surface area which peaks at 900°C. Increasing temperature creates new pores and enhances pore development through the steam-carbon reaction. However, excessive pore widening and pore wall thinning effects set in at a temperature of 970°C, resulting in a decrease in the BET and pore surface areas and pore volume.

As a consequence of pore widening at high activation temperatures, the activation temperature had a significant influence on the microporosity of the activated carbons. Table 4-14 shows that for activation temperatures of 900°C and less, the activated carbons had predominantly microporous structures but for temperatures greater 900°C, the activated carbons had changed to predominantly non-microporous in nature. Therefore, the pore structure development in activated carbons can be tailored by controlling the degree of activation through varying the activation temperatures. Similar results had been reported by other studies (Kovacik et al. 1995; Teng et al. 1996).

For the two pyrolysis conditions, an activation temperature of 950°C produced the highest BET and non-micropore surface areas. In the case of pyrolysis in nitrogen atmosphere, the highest BET surface area was 1432.95 m²/g; while in the case of pyrolysis under vacuum condition, the highest BET surface area was 1382.95 m²/g. Hence, the optimum activation conditions were a steam flow rate of 1.13 kg/h, a hold time of 1.5 hour hold time and an activation temperature of 950°C.

4.4.1.2 Aqueous phase adsorption

The activated carbons prepared were subjected to phenol adsorption tests to determine their adsorptive capacities. Figure 4-36 and 4-37 show the effects of hold time on the phenol adsorption capacity and the BET surface area of activated carbons pyrolysed in nitrogen atmosphere and under vacuum condition respectively. In Figure 4-36, the BET surface area peaks at an activation hold time of 1.5 hour whereas the adsorption capacity peaks from 1 to 2 hours of activation hold time. In Figure 4-37, both the BET surface area and the adsorption capacity peak at an activation hold time of 1.5 hour. The activation capacity remains at its peak for the next half hour increase in hold time but the BET surface area decreases. These minor differences between the BET surface area and the adsorption capacity further indicate that the active sites for aqueous phase adsorption are not equivalent to those functioning in measuring the BET surface area with gas phase adsorption.

Figure 4-38 and 4-39 show the effects of activation temperature on the phenol adsorption capacity and the BET surface area of activated carbons pyrolysed in nitrogen atmosphere and under vacuum condition respectively.

Figure 4-36 Effect of hold time on the adsorption capacity and the BET surface area of activated carbons pyrolysed in nitrogen atmosphere

Figure 4-37 Effect of hold time on the adsorption capacity and the BET surface area of activated carbons pyrolysed under vacuum condition

Figure 4-38 Effect of activation temperature on the adsorption capacity and the BET surface area of activated carbons pyrolysed in nitrogen atmosphere

Figure 4-39 Effect of activation temperature on the adsorption capacity and the BET surface area of activated carbons pyrolysed under vacuum condition

In figure 4-38, both the adsorption capacity and the BET surface area peak at an activation temperature of 950°C. With a small increase in the activation temperature to 970°C, a slight drop in the BET surface area is seen but the adsorption capacity remains constant. In Figure 4-39, the BET surface area peaks at an activation temperature of 950°C whereas the maximum phenol adsorption capacity is at an activation temperature of 900°C. Although, the general trend is that the adsorption capacity increases with increasing BET surface area, the aforementioned deviations between the adsorption capacity and the BET surface area indicate that the active sites for the processes for measuring these two properties are different.

Comparing Figure 4-36 with Figure 4-37, and Figure 4-38 with Figure 4-39, the activated carbons pyrolysed under vacuum condition generally result in higher phenol adsorption capacity than those pyrolysed in nitrogen atmosphere for the same activation temperature or activation hold time. It may be surmised that the pores of the char pyrolysed in nitrogen atmosphere may be blocked even after activation.

4.4.1.3 Pore size distributions

The pore size distributions of the chars and activated carbons were obtained from nitrogen adsorption isotherms using density functional theory. Figure 4-40 shows typical pore size distributions of char and activated carbon. In fact, this char was pyrolysed in a nitrogen stream at 750°C for a hold time of 2 hours, a heating rate of 10°C/min and a nitrogen flow rate of 150 cm³/min. The initial particle size range of the oil-palm shells is 2-2.8 mm.

Figure 4-40 Typical pore size distributions of char and activated carbon

The char was subsequently activated by steam at 950°C and a hold time of 1.5 hour. The pore size distribution of the char (in dot line) shows that the peak size is about 1 nm. After activation, the pore size distribution of the activated carbon shows a broader spectrum of sizes: sizes which are larger as well as smaller than those of the char. This verifies that during activation, new porosities are developed and existing pores are enhanced into larger pores. Therefore, the char provides the rudimentary pore structure, which is then further developed during activation.

Figures 4-41 and 4-42 show the pore size distributions of the activated carbons pyrolysed in nitrogen atmosphere and under vacuum condition respectively. The pore width is plotted as a function of the activation temperature and the incremental surface area. The peaks shown indicate the dominant pore size for each curve. Generally, increasing the activation temperature from 750 to 850°C increases the peaks of these curves, verifying the development of new pores due to the steam-carbon reaction.

Figure 4-41 Pore size distribution of activated carbon pyrolysed in nitrogen Atmosphere

Figure 4-42 Pore size distribution of activated carbon pyrolysed under vacuum condition

For activation temperatures of 850°C and higher, less peaks emerge in the larger pore sizes. This development may be attributed to the severe steam-carbon reaction which sets in at high temperatures and causes widening of existing pores.

4.4.2 Chemical activation

In the chemical activation process, potassium carbonate was mixed with the oil-palm shell in different mass ratios. The mixture was then subjected to steam in the reactor. Hence, the shells were subjected to both physical and chemical activation.

4.4.2.1 Adsorption analyses

The effects of the ratio of potassium carbonate to the oil-palm shell masses on the surface characteristics of the activated carbons were studied for three activation temperatures of 650, 700 and 750°C as shown in Figures 4-43, 4-44 and 4-45 respectively. Generally, chemical activation with potassium carbonate increases and enhances pore development; the BET and the micropore surface areas of the chemically activated carbons are always higher than those which are only physically activated, i.e., no potassium carbonate added. For mass ratios less than 0.25, increasing mass ratio increases the BET and the micropore surface areas due to the combined effects of physical and chemical activation. The rudimentary pores in the char are further developed and new pores are generated.

Figure 4-43 Effect of ratio of potassium carbonate to oil-palm shell masses on the surface characteristics of activated carbon at 650°C

Figure 4-44 Effect of ratio of potassium carbonate to oil-palm shell masses on the surface characteristics of activated carbon at 700°C

Figure 4-45 Effect of ratio of potassium carbonate to oil-palm shell masses on the surface characteristics of activated carbon at 750°C

For mass ratio greater 0.25 in Figures 4-43 to 4-45, increasing mass ratio decreases the BET and the micropore surface areas; at the same the average pore size appears to increase marginally. This may indicate pore widening with increasing mass ratio greater than 0.25 and the subsequent merging of pores that will reduce the BET and micropore surface areas. Another possible reason is that at these relative high mass ratios, the potassium carbonate chemicals obstruct the passages of the external surface area to the diffusion of water molecules of steam and thereby reduce the steam-carbon reaction. It then depends on the potassium carbonate (K_2CO_3) – carbon reaction to enhance pore development and produce new pores. Another significant result shown in Figure 4-43 to 4-45 is the increase in the BET surface area with increasing activation temperature from 650°C to 750°C. This phenomenon is the result of increased reaction rate with increasing activation temperature, which will be discussed next.

The effect of activation temperature on the physical and chemical activation of the oil-palm shell will be studied in detail. Figure 4-46 shows the effect of activation temperature on the BET surface area for varying ratio of potassium carbonate to oil-palm shell masses. Increasing activation temperature definitely increases the BET surface area of the activated carbons for all mass ratios greater than zero. A higher activation temperature increases the reaction rate of the combined steam-carbon and K_2CO_3 - carbon reactions, giving rise to more pores. Besides the BET surface area, increasing activation temperature also increases the micropore surface area, except for mass ratio of 0.25 (Figure 4-47), and it also increases the non-micropore surface area (Figure 4-48). An interesting observation was made in that at an activation of 750°C , the activated carbons were transformed into powders due to the extreme high reactions. This would be due to excessive carbon burn-off which led to the collapse of the carbon structure.

Figure 4-46 Effect of activation temperature on the BET surface area of activated carbon for varying ratio of potassium carbonate to oil-palm shell masses

Figure 4-47 Effect of activation temperature on the micropore surface area of activated carbon for varying ratio of potassium carbonate to oil-palm shell masses

Figure 4-48 Effect of activation temperature on the nonmicropore surface area of activated carbon for varying ratio of potassium carbonate to oil-palm shell masses

4.4.2.2 Aqueous phase adsorption

Potassium carbonate activated carbons from oil-palm shells were activated at 700°C for various mass ratios. The effect of the mass ratio on the BET surface area of the activated carbon had been discussed in section 4.4.2.1 with reference to Figure 4-44. The activated carbons were then used to determine their performance on the adsorption of phenol. Figure 4-49 shows the effect of the ratio of potassium carbonate to the oil-palm shell masses on the BET surface area and the phenol adsorption capacity. The trend of the adsorption capacity is similar to that of the BET surface area. It is to be expected as the adsorption capacity is proportional to the pore surface area for physical adsorption.

Figure 4-49 Effect of ratio of potassium carbonate to oil-palm shell masses on the BET surface area and the aqueous phase phenol adsorption capacity

4.4.2.3 Chemical activation - a comparative study of some chemicals

A comparative study was carried out to determine the effects of some chemicals on the pore surface characteristics of the oil-palm-shell activated carbons subjected to chemical activation. The chemicals investigated were potassium chloride, potassium carbonate and sodium carbonate. The individual chemical was mixed with the oil-palm shell in a mass ratio of 0.25:1. The mixture was activated in the presence of steam at a temperature of 700°C for 1 hour hold time. Table 4-15 shows the pore surface area characteristics of activated carbons subjected to various chemicals during activation.

Table 4-15 Pore surface area characteristics of activated carbons subjected to various chemicals during activation

Preparation conditions *	BET surface area (m ² /g)	Micropore surface area (m ² /g)	Nonmicropore surface area (m ² /g)	Total pore volume (cm ³ /g)	Percentage of nonmicropore surface area (%)
AKCl-0.25-2~2.8-700-1	498.55	429.44	69.10	0.248	14
APC-0.25-2~2.8-700-1	710.56	515.06	195.50	0.339	28
ASC-0.25-2~2.8-700-1	326.62	178.43	148.19	0.174	45

* KCl refers to potassium chloride, PC refers to potassium carbonate, SC refers to sodium carbonate.

The combined steam and chemical activation using potassium carbonate yields the highest BET surface area whilst that using sodium carbonate yields the lowest BET surface area but the largest amount of non-micropores. The presence of the carbonate anion gives rise to the release of CO₂ from thermal decomposition which results in the CO₂ - carbon reaction. This additional activation, besides the steam activation, will tend to widen the pores and contribute to the increase in the non-micropores. Hence, both the potassium carbonate and sodium carbonate in Table 4-15 yield higher proportion of non-micropores than potassium

chloride. However, comparing between potassium carbonate and sodium carbonate, the potassium cation seems to contribute to the development of micropores. It is further deduced from the potassium chloride test that it produces the most micropores amongst the three tests. Incidentally, potassium chloride was chosen as one of the chemicals to determine whether it would give the same effect as zinc chloride which is shown to retard tar formation and contribute to pore development.

4.5 Summary of activation conditions

Using an experimental optimization procedure, the local optimum conditions for producing oil-palm-shell activated carbons with the largest BET surface area and pyrolysed in nitrogen stream were as follows: raw oil-palm shell size range of 2-2.8 mm; pyrolysis conditions-temperature of 750°C, 2 hour hold time, 10°C/min heating rate, nitrogen flow rate of 150 cm³/min; and activation conditions – temperature of 950°C, 1.5 hours hold time, steam flow rate of 1.13 kg/h. This activated carbon had a BET surface area of 1432 m²/g and an adsorption capacity of 150mg of phenol per gram of activated carbon.

The local optimum conditions for pyrolysis under vacuum condition were as follows: raw oil-palm shell size of 2-2.8 mm; pyrolysis conditions-temperature of 675°C, 2 hour hold time, 10°C/min heating rate; and activation conditions – temperature of 950°C, 1.5 hours hold time, steam flow rate of 1.13 kg/h. The resulting activated carbon had a BET surface area of 1383 m²/g and an adsorption capacity of 200 mg of phenol per gram of activated carbon.

Although the activated carbon pyrolysed in nitrogen stream yielded a maximum BET surface area of 1432 m²/g, the one pyrolysed in vacuum condition produced the larger phenol

adsorption capacity of 275 mg phenol per gram of activated carbon with a lesser BET surface area of 1309 m²/g.

CHAPTER 5 KINETIC MODELLING AND BATCH STUDIES IN AQUEOUS PHASE ADSORPTION

5.1 Introduction

The occurrence of various organic chemicals in hydrosphere presents a major problem in the usage of water resources. Hydroxybenzene or phenol and its analogous, recognized as priority pollutants, enter the environment through numerous chemical industries, viz., coal conversion, petroleum refining, textile, pharmaceutical, timber, mining, paper and pulp, as well as large-scale use of herbicides, insecticides and pesticides in agriculture (US report 1998). Phenols are also released as intermediate products during microbial degradation of pesticides or some other xenobiotics (Hottenstein et al. 1995). Complete removal of these carcinogenic compounds or in some cases reduction of the load of such solutes to an acceptable concentration has become a major challenge to preserve the quality of aquatic life. The promising options for the treatment of phenolic wastes are through biological, chemical and physical methods. Although biological method for detoxification using different microorganisms is feasible, it is only applicable for the low concentration range. Conventional physical and chemical methods for removal or transformation of phenolic wastes include adsorption, ion exchange and membrane processes. Selection and feasibility of a particular operation are based on its application to the solute concentration range, capacity, cost, reusability and reproducibility (Buchanan and Nicell 1995; Karamanev et al. 1997).

Adsorption process has been employed extensively in large scale for chemical and environmental separation engineering. Adsorption of proteins on solid surfaces and their interaction are major concerns in a number of fields such as biology, medicine, biotechnology and food processing, and play an important role from various points of view (Nakanishi et al. 2001; Chen et al. 2003). For its large specific surface area, activated carbon is a general adsorbent for the removal of many toxic compounds in environmental (Tancredi et al. 2004; Dabrowski et al. 2005) and pharmaceutical applications (Kamp et al. 2005). Besides conducting adsorption tests to determine the effectiveness of any adsorbents, kinetic modelling is also needed to understand the physics of the adsorption process.

It is desirable to optimize the performance of the activated carbon, to elucidate the mechanisms of adsorption and to develop branched pore kinetic model (BPKM). The concentration dependent model is based on the present knowledge of the internal structure of the activated carbon. It is expected to give an accurate description of the adsorption process from initial contact through to equilibrium. The activated carbon prepared from the oil-palm shell is used in water treatment. As stated in Chapter 4 for steam activation, the activated carbon has an advantage of having a well-developed nonmicropore structure. This advantage is expected to be used in the treatment of wastewater containing semi-volatile organic compounds like phenol. In this chapter, besides the experimental studies on the adsorption of phenol from water, modelling of adsorption kinetics of phenol on heterogeneous porous adsorbents will be described.

5.2 Literature Review on adsorption modeling

Adsorption at solution-carbon interface is already widely used on a large scale for water treatment (McCafferty et al. 2000). Experimental studies on the adsorption of the phenol aqueous solution and activated carbon system including a large number of equilibrium studies have been carried out. (Tancredi et al. 2004; Dabrowski et al. 2005).

5.2.1 Adsorption equilibrium

Adsorption isotherms are important to relate the mechanics in which the adsorbates will interact with the adsorbents. The Langmuir equation, the empirical Freundlich equation and the three parameter Langmuir-Freundlich equations are used to characterize the adsorption isotherms of activated carbons.

5.2.1.1 Langmuir Model

For solid-liquid systems, Langmuir equation is usually written as

$$q_e = \frac{Q_{La} b_L c_e}{1 + b_L c_e} \quad (5.1)$$

where q_e is the amount of solute adsorbed per unit weight of adsorbent at equilibrium, Q_{La} is the solid-phase concentration corresponding to a condition in which all available sites are filled, or monolayer saturation adsorption capacity, and c_e is the liquid-phase equilibrium concentration. Generally, the objective of applying model fitting is to determine b_L and Q_{La} . A nonlinear regression technique may be preferred using equation (5.1).

5.2.1.2 Freundlich model

Despite the sound theoretical basis of the Langmuir model, the isotherm often fails to describe experimental solution sorption data adequately. At approximately the same time as Langmuir was developing the monolayer model for adsorption from gas phase, Heinrich Freundlich and other investigators suggested that data for sorption from solution were best described by a general exponential concentration-dependent relationship. The Freundlich isotherm equation is

$$q_e = k_F c_e^{n_F} \quad (5.2)$$

where k_F and n_F are characteristic constants. The parameter k_F can be taken as an indicator of sorption capacity at a specific solution-phase concentration, that is, a specific capacity. The exponent n_F can be shown to be a joint measure of the cumulative magnitude and diversity of energies associated with a particular adsorption reaction.

The treatment and analysis of equilibrium sorption data generally need to select an appropriate isotherm model and an evaluation of the constants for that model. The first step is often influenced by the intended use of the data and model parameters. The choice of a model based in part upon the usefulness of model parameters. For example, the Freundlich k_F term has been used widely to quantify extent of sorption and provides an easy way to compare different adsorbents or conditions for a particular system. Similarly, if an indication of ultimate adsorption capacity is desired, the monolayer saturation term, Q_{La} , may be of interest.

5.2.1.3 Langmuir-Freundlich model

The Langmuir-Freundlich model is characterized by the symmetrical shape of its site energy distribution allowing straightforward illustration of the effects of parameter variations.

$$q_e = \frac{Q_{LF} (b_{LF} c_e)^{1/n_{LF}}}{1 + (b_{LF} c_e)^{1/n_{LF}}} \quad (5.3)$$

This model is also a popular one for describing the adsorption. The Langmuir-Freundlich model was analyzed by Sips (1948) who found that the energy distribution function corresponds to a symmetrical quasi-Gaussian function. At low concentrations, the model reduces to Freundlich model and in the case of a homogeneous surface, it reduces to the Langmuir model (Quinones and Guiochon 1998). Since the Langmuir-Freundlich model has more than two adjustable parameters, it is not easily fitted to the experimental data by linear regression or graphical means. In this case, it is necessary to apply nonlinear least-squares analysis.

5.2.2 Adsorption kinetics - existing activated carbon adsorption models

The mechanisms of solute adsorption onto various adsorbents can be subdivided into reaction-based systems and diffusion based systems. In the adsorption of phenol, which has large molecules and a long contact time to equilibrium, the adsorption mechanism is likely to be diffusion control. Noll *et al.* (1992) summarized in a literature that the adsorption on a solid takes place in three stages. These are external diffusion, actual adsorption process and internal diffusion. External diffusion refers to the mass transfer by diffusion of adsorbate molecules from the bulk fluid phase through a stagnant boundary layer surrounding each adsorbent particle to the external surface of the solid. The actual adsorption process refers to

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the process whereby the molecules in the pores are adsorbed onto the solid phase. This stage is relatively fast. The internal diffusion refers to the transfer of adsorbate to the interior of the particle by the migration of the adsorbate molecules from the relative small external surface of the adsorbent to the surface of pores within each particle and/or by the diffusion of the adsorbate molecules through the pores of particles. Suzuki (1990) pointed out, depending on the structure of adsorbent, several different types of diffusion mechanisms become dominant and sometimes two or three of them compete or cooperate. In addition, the dominant mechanism depends on a combination of adsorbate and adsorbent and adsorption conditions such as temperature and concentration range.

In adsorbent particles with bi-dispersed pore structures, such as activated carbon, nonmicropores act as paths for adsorbate molecules to reach the interior of particle. In this case, molecular diffusion taking place in the nonmicropore is called pore diffusion. On the internal pore surface, an adsorbed molecule may hop along the surface when it attains sufficient activation energy and when an adjacent adsorption site is available. Although the mobility of adsorbed phase will generally be smaller than that in solution, the concentration is very much higher; so a significant contribution to the flux is possible. When adsorbed molecules are mobile on the surface of the adsorbent, e.g., volatile hydrocarbon on activated carbon, diffusion due to migration of the adsorbed molecules may contribute more than pore diffusion to intra-particle diffusion. This type of diffusion is referred to as surface diffusion. In another case, when the size of an adsorbate molecule is closed to the size of the micropore, diffusion of the molecule becomes restricted and the rate of transport in the micropore may have a significant effect on the overall adsorption rate. This type of diffusion in the micropore can be taken as an activated process that depends heavily on adsorbate properties.

Kinetics of the process describes the rate at which molecules are transferred from the solution to the pores of the carbon particle. Therefore, mechanisms of adsorption kinetics include film diffusion, pore diffusion, and surface diffusion. Kinetic models account for external (film transfer) and internal (pore or surface diffusion) effects (Noll et al. 1992). Based on the particular adsorption system, different types of diffusion mechanisms become dominant and sometimes two or three of them compete or cooperate. Different models were proposed for different adsorption systems in literature including surface diffusion model, pore diffusion model, and combined diffusion model.

5.2.2.1 Surface diffusion model

This model (Chang et al. 2004; Lee and McKay 2004) depicts the diffusion of an adsorbate through an external film to the outer surface of a particle; at this surface, adsorption occurs instantaneously and equilibrium is assumed to establish between adsorbed in the fluid and that on the surface. The adsorbed material then diffuses into the pores in the adsorbed state. A mass balance for a spherical particle results in the following mass transfer equations:

$$\frac{\partial q}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} (r^2 D_s \frac{\partial q}{\partial r}) \quad (5.4)$$

$$K_f (c - c_s) = D_s \rho_s \frac{\partial q}{\partial r} \quad \text{at } r = R \quad (5.5)$$

$$\frac{\partial q}{\partial r} = 0 \quad \text{at } r = 0 \quad (5.6)$$

where D_s is the surface diffusion coefficient, r is the radial coordinate, t is the time, and ρ_s is the particle solid density, q is the average solid phase concentration, K_f is the external

aqueous phase mass transfer coefficient, c is the solution concentration in the aqueous phase, c_s is the solution concentration at particle surface, R is the particle radius.

5.2.2.2 Pore diffusion model

In the pore diffusion model (Arslanoglu and Arslan 2005; Jayne et al. 2005), it is assumed that the adsorbate diffuses into the pores in the fluid phase and is taken up by adsorption on the walls of the pores. It assumes that there are uniformly distributed sinks for adsorption within the pores. The molecule cannot diffuse along the walls of the pores in the adsorbed state. If one assumes particle is in spherical shape, the solution is dilute, and local equilibrium is achieved, then the equations describing the adsorbate mass transfer are as follows:

$$\varepsilon_p \frac{\partial c_p}{\partial t} + \rho_p \frac{\partial q}{\partial t} = \frac{\varepsilon_p}{r^2} \frac{\partial}{\partial r} (r^2 D_p \frac{\partial c_p}{\partial r}) \quad (5.7)$$

$$K_f (c - c_s) = \varepsilon_p D_p \frac{\partial c_p}{\partial r} \quad \text{at } r = R \quad (5.8)$$

$$\frac{\partial c_p}{\partial r} = 0 \quad \text{at } r = 0 \quad (5.9)$$

$$c_p = c_{p0} \quad \text{when } t = 0 \quad (5.10)$$

where D_p is the pore diffusion coefficient, c_p is the solution concentration within particle, ε_p is the particle porosity and c_{p0} is the initial solution concentration within particle, ρ_p is the adsorbent particle density.

5.2.2.3 Combined diffusion model

In this model (Cheung et al. 2001), the heterogeneous systems consisting of the adsorbent particles, are formed by a porous solid phase and a fluid phase filling the void fraction of the adsorbent. The internal diffusion can be expressed by two simultaneous diffusion mechanisms.

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Mass balance for the spherical particle which includes pore diffusion and surface diffusion, results in the following partial differential equations:

$$\varepsilon_p \frac{\partial c_p}{\partial t} + \rho_p \frac{\partial q}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left[r^2 \left(\varepsilon_p D_p \frac{\partial c_p}{\partial r} + D_s \rho_p \frac{\partial q}{\partial r} \right) \right] \quad (5.11)$$

$$K_f (c - c_s) = D_s \rho_p \frac{\partial q}{\partial r} + \varepsilon_p D_p \frac{\partial c_p}{\partial r} \quad \text{at } r = R \quad (5.12)$$

$$\frac{\partial c_p}{\partial r} = 0 \quad \frac{\partial q}{\partial r} = 0 \quad \text{at } r = 0 \quad (5.13)$$

$$c_p = c_{p0} \quad \text{when } t = 0 \quad (5.14)$$

In the dilute solution range of an adsorption system having a favourable isotherm, Equation (5.11) can be reduced to:

$$\frac{\partial q}{\partial t} = \frac{D_s}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial q}{\partial t} \right) + \frac{\varepsilon_p}{\rho_p} \frac{D_p}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial c_p}{\partial r} \right) \quad (5.15)$$

In the preceding models, the system description depends on whether it is a single or double mass transfer resistance. The use of a single effective diffusion parameter has been reported to result in a systematic lack of fit in the batch kinetic analyses. When a double intra-particle parameter surface diffusion model was fitted to data from a batch kinetic experiment using a nonlinear least squares fitting, the model was able to describe only the data for the early stage and the fitted coefficient was a function of the time. The observed poor fitting can be explained because the models are constrained to approach the equilibrium. However, the experimental data show a rapid initial uptake but level off after this period to a slower rate. The data indicated that another internal mass transfer resistance or a variable internal diffusion coefficient become rate controlling factor at long time periods. In correlation to experimental results, to match the rapid initial rate, a large diffusion coefficient was required and consequently the models predicted a rapid approach to equilibrium. The simplest way to account for this non-uniformity effect is to consider a particle to be composed of two regions:

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a nonmicropore and a micropore region, each of which is characterized by its diffusion coefficient.

For the above mentioned models, the authors ignored the complexity of internal pore structure. They assumed that a single or double effective diffusion parameters act throughout the adsorption period and that all adsorption sites within the carbon particle are identical except for the radial direction. Although these are features of homogeneous adsorbents, these models were used for activated carbon adsorption simulations even though it is accepted that activated carbons have heterogeneous surface properties and a wide range of pore size distribution (Choy et al. 2004). In general, activated carbon has pores with different sizes. The pores are polydispersed and arranged randomly. In certain cases, the difference in pore size may be significant, resulting in a different intra-particle mass-transfer mechanism (Tien 1994). Several authors including Beck and Schultz (1970) have demonstrated that the effective diffusion parameter in small pores is a strong function of the pore diameter to the solute diameter ratio, and that diffusion rates decrease with decreasing pore size. Since activated carbons have a wide range of pore sizes, a corresponding range of diffusion rates would be expected. Rapid saturation of the fast diffusing pores would result in a net decrease in effective diffusion rate as adsorption proceeds. Consequently, a large diffusion parameter results in rapid attainment of equilibrium and a small coefficient in slow attainment.

In phenol adsorption studies, a rapid initial uptake phase followed by a slow approach to equilibrium is required. To correlate with experimental data, an aqueous phase activated carbon adsorption can be described by a branched pore kinetic model (BPKM) or multi-pore model. The branched pore kinetic model (BPKM) for aqueous phase activated carbon adsorption was proposed by Peel *et al.* (1981). The model depicted activated carbon adsorption as a dual mechanism rather than as a single mechanism process. In order to

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simulate the polydispersed or continuous pore size distributions of the activated carbon, the branched pore kinetic model divides the carbon pellets into rapidly and slowly diffusing regions. This division can also be reflected by the very different rates of diffusion in the two regions. It is difficult to deduce either the dimensions or relative proportions of the non-micropore and micropore regions. The regions are loosely termed as non-micropore and micropore regions. The fraction, f , is the amount of adsorption in the non-micropore region as compared to the total adsorptive capacity in the whole region. The initial rapid adsorptive uptake takes place in the non-micropore region. The remaining fraction, $1-f$, constitutes the adsorption in the micropore region. The model assumes that the distribution of both regions is radially and the diffusion between these two regions is expressed with a linear driving force between the local non-micropore and micropore concentrations. The assumption of the adsorption model for such a particle consists of three resistances in series: (1) diffusion of solute from solution, across the external liquid boundary layer onto the adsorbent surfaces, then (2) diffusion into and adsorbing in the non-micropore region and (3) diffusion into and adsorbing in the micropore region. Ko *et al.* (2002; 2003) and Yang and Al-Duri (2001) studied the branched pore diffusion model (BPDM) and applied it to the single component adsorption of dye onto activated carbon in batch stirred vessels.

In the applications of the BPKM (Peel *et al.* 1981; Yang and Al-Duri 2001; Ko *et al.* 2003) simulations, the effective intra-particle diffusion coefficient or surface diffusion coefficient was assumed to be a constant and the values of the diffusion coefficients were determined by fitting the model to the experimental concentration decay curve. It was noticed that although the simulation could cover a wide range of system conditions, the correlated diffusion coefficient in the non-micropore region increased with the initial aqueous solution concentration. Furthermore, the diffusion coefficient can be mathematically related to the

amount of surface loading. In this project, an improvement is implemented to obtain more accurate simulations for the adsorption system using a group of experimental data.

5.3 Model description

A model is proposed to combine the branched pore kinetic model and the concentration dependent intra-particle effective diffusion coefficient. In the existing model, the concentration dependent surface diffusion coefficient is assumed as a constant. In the proposed model, an effective intra-particle diffusion mechanism is used to describe the intra-particle diffusion in the non-micropore area. The effective diffusion coefficient is given by an exponential expression which correlates the concentration dependence of effective diffusion coefficient to the surface coverage of adsorbate molecules. The model is an approximation to the microscopic description of the diffusion process. It has been developed in this work virtually dividing the carbon particle into two regions of different diffusion rates. The regions are termed as nonmicropore region and micropore region. It should be noticed that these terms should not be confused with their conventional usage to define certain pore size ranges. Relatively rapid diffusion and adsorption occur in the nonmicropores, and the remaining slow approach to equilibrium occurs in the micropores.

In the CDBPKM, the adsorption mechanism is taken to be diffusion control. The control processes include external diffusion, adsorption process and internal diffusion. The bulk concentration is considered to be homogeneous under well stirred condition. External diffusion occurs in the stagnant film layer around the adsorbent particle. The particle of activated carbon is considered as spherical and the pore structure of the adsorbent particles is assumed to be bi-dispersed, consisting of nonmicropore and micropore regions. The

micropores are assumed to be homogeneously distributed throughout the particle and to branch off from the larger nonmicropore network which is responsible for radial transport. A schematic diagram of the model for mass transfer in one particle is shown in Figure 5-1. However, it is not possible to define the dimensions of the nonmicroporous sub-units when dealing with activated carbons. Thus, a lumped parameter approach is used to describe diffusion in the nonmicropores. An effective diffusion mechanism is assumed to be responsible for transport in the non-micropores. The effective diffusion is composed of pore diffusion and surface diffusion.

Figure 5-1 Mass transfer schematic for one particle in activated carbon aqueous phase adsorption system

In the current proposed model, an effective intra-particle diffusion mechanism is assumed to describe the intra-particle diffusion in the non-micropore region. In terms of an activation process, the effective diffusion coefficient of the intra-particle diffusion depends on the

energy barrier for the diffusion of the adsorbate in the particle. In describing the relationship between effective diffusion coefficient and solid phase concentration, different modelling approaches are available. For the purpose of selecting suitable concentration dependent effective diffusion coefficient model, Yang *et al.* (2003) reviewed the most commonly used modelling methods. The exponential expression was adopted. The expression correlated the concentration dependence of effective diffusion coefficient to the surface coverage of adsorbate molecules through the heat of the adsorption process (Gilliland et al. 1974; Sudo et al. 1978). The effective diffusion coefficient is expressed as

$$D_{eff} = D_{eff0} \exp\{k(q / q_{sat})\} \quad (5.16)$$

where D_{eff} is the effective diffusion coefficient, D_{eff0} is the effective diffusion coefficient at zero surface coverage, k is a constant defined by the quantitative measure of the binding energy and the differential heat of adsorption, q is the solid phase concentration, and q_{sat} is the solid phase concentration at surface saturation. In the model, the diffusion between micropore and nonmicropore region is expressed with a linear driving force between the local nonmicropore and micropore concentrations.

5.3.1 Mathematical Development

Incorporating the aforementioned mechanisms and assumptions into the mass balances on the bulk and adsorbent phases, a system of differential algebraic equations for the adsorbate, i.e., the governing equations of the concentration dependent branched pore kinetic model (CDBPKM), are established.

The macroscopic mass conservation equation of the adsorbate in the aqueous phase is

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$$V_f \frac{dc}{dt} = -m \frac{dq_{av}}{dt} \quad (5.17)$$

where m is the mass of the adsorbent, V_f is the solution volume and c is the aqueous phase concentration at time t . The amount adsorbed in the solid phase, q_{av} , is given by:

$$q_{av} = \frac{3}{R^3} \int_0^R [fq_m + (1-f)q_b] r^2 dr \quad (5.18)$$

where f is the part of the total adsorptive capacity utilized in the nonmicropore, q_m and q_b are the solid phase concentrations in the non-micropore and micropore regions respectively, R is the adsorbent particle radius, and r is the radial distance from the centre of the adsorbent particle. The non-micropore mass balance equation is

$$f \frac{\partial q_m}{\partial t} + (1-f) \frac{\partial q_b}{\partial t} = \frac{fD_{eff,0}}{r^2} \frac{\partial}{\partial r} (r^2 \exp\{k(q_m / q_{msat})\} \frac{\partial q_m}{\partial r}) \quad (5.19)$$

where $D_{eff,0}$ is the effective surface diffusion coefficient at zero loading, q_{msat} is the adsorbate concentration in the non-micropore region at surface saturation, and k is a constant. The micropore mass balance equation is

$$(1-f) \frac{\partial q_b}{\partial t} = K_b (q_m - q_b) \quad (5.20)$$

where K_b is the branched pore rate coefficient.

The coupling between the aqueous and solid phases, achieved by equating the fluxes at the solid-aqueous interface, is

$$K_f (c - c_s) = fD_{eff,0} \exp\{k(q_m / q_{msat})\} \rho_s \left(\frac{\partial q_m}{\partial r} \right)_{r=R} \quad (5.21)$$

where K_f is the external aqueous phase mass transfer coefficient, c_s is the aqueous phase concentration at the particle surface at time, t , and ρ_s is the solid density of the adsorbent.

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The Langmuir isotherm is used for the local equilibrium at the interface between the aqueous and the adsorbent solid phases.

$$q_e = \frac{k_{LA}c_e}{1 + b_Lc_e} \quad (5.22)$$

In addition, the following initial and boundary conditions apply:

$$\begin{aligned} q_m(r, 0) &= 0 \\ q_b(r, 0) &= 0 \\ c(t = 0) &= c_0 \\ q_m(R, t) &= q_s(t) \\ \frac{\partial q_m}{\partial r}(0, t) &= 0 \end{aligned} \quad (5.23)$$

The governing equations are first rendered dimensionless by the following dimensionless parameters:

$$\begin{aligned} C &= \frac{c}{c_0} \\ C_s &= \frac{c_s}{c_0} \\ Q &= \frac{q}{q_0} \\ \beta &= \frac{r}{R} \\ \theta &= \frac{D_{eff,0}t}{R^2} \end{aligned} \quad (5.24)$$

where c_0 is initial aqueous solution concentration, q_0 is solid phase concentration in equilibrium with c_0 , C is dimensionless aqueous phase concentration, Q is dimensionless aqueous phase concentration, β is transformed radial variable and θ is dimensionless time variable.

In dimensionless form, the derivative items can be expressed as:

$$\frac{\partial q_m}{\partial t} = \frac{D_{eff,0}q_0}{R^2} \frac{\partial Q_m}{\partial \theta} \quad (5.25)$$

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$$\frac{\partial q_b}{\partial t} = \frac{D_{eff,0} q_0}{R^2} \frac{\partial Q_b}{\partial \theta} \quad (5.26)$$

To fine-tune the grids near particle surface, the independent variable can be transformed

$$\eta = \beta^2 \quad (5.27)$$

Introducing the derivative items, equation (5.19) becomes

$$\frac{\partial Q_m}{\partial \theta} + \frac{(1-f)}{f} \frac{\partial Q_b}{\partial \theta} = \frac{1}{\eta^2} \frac{\partial}{\partial \eta} [\eta^2 \exp\{k(Q_m / Q_{msat})\} \cdot \frac{\partial Q_m}{\partial \eta}] \quad (5.28)$$

The RHS of (5.28) expands to

$$\frac{\partial Q_m}{\partial \theta} + \frac{(1-f)}{f} \frac{\partial Q_b}{\partial \theta} = \frac{\partial}{\partial \eta} [\exp\{k(Q_m / Q_{msat})\}] \cdot \frac{\partial Q_m}{\partial \eta} + \exp\{k(Q_m / Q_{msat})\} \cdot \left[\frac{1}{\eta^2} \frac{\partial}{\partial \eta} \left(\eta^2 \frac{\partial Q_m}{\partial \eta} \right) \right] \quad (5.29)$$

Equation (5.29) becomes

$$\frac{\partial Q_m}{\partial \theta} + \frac{(1-f)}{f} \frac{\partial Q_b}{\partial \theta} = 2\eta \cdot \frac{\partial}{\partial u} [\exp\{k(Q_m / Q_{msat})\}] \cdot 2\eta \cdot \frac{\partial Q_m}{\partial u} + \exp\{k(Q_m / Q_{msat})\} \cdot \left[2\eta \cdot \frac{1}{u} \frac{\partial}{\partial u} \left(2\eta \cdot u \frac{\partial Q_m}{\partial u} \right) \right] \quad (5.30)$$

Finally

$$\frac{\partial Q_m}{\partial \theta} + \frac{(1-f)}{f} \frac{\partial Q_b}{\partial \theta} = 4u \frac{\partial}{\partial u} [\exp\{k(Q_m / Q_{msat})\}] \cdot \frac{\partial Q_m}{\partial u} + \exp\{k(Q_m / Q_{msat})\} \cdot \left[4u \frac{\partial^2 Q_m}{\partial u^2} + 6 \frac{\partial Q_m}{\partial u} \right] \quad (5.31)$$

Similarly, introducing the dimensionless parameters in equation (5.24) into the partial differential equation (PDE) systems, equations (5.17), and (5.19) to (5.21) are transformed into dimensionless form

$$\frac{\partial Q_m}{\partial \theta} + \frac{(1-f)}{f} \frac{\partial Q_b}{\partial \theta} = 4\eta \frac{\partial}{\partial \eta} [\exp\{k(Q_m / Q_{msat})\}] \cdot \frac{\partial Q_m}{\partial \eta} + \exp\{k(Q_m / Q_{msat})\} \cdot \left[4\eta \frac{\partial^2 Q_m}{\partial \eta^2} + 6 \frac{\partial Q_m}{\partial \eta} \right] \quad (5.32)$$

$$\frac{\partial C}{\partial \theta} = -SFact(f \int_V \frac{\partial Q_m}{\partial \theta} dV + (1-f) \int_V \frac{\partial Q_b}{\partial \theta} dV) \quad (5.33)$$

$$\frac{\partial Q_b}{\partial \theta} = PBiot \frac{f}{1-f} (Q_m - Q_b) \quad (5.34)$$

$$\left(\frac{\partial Q_m}{\partial \eta} \right)_{u=1} = \left(\frac{FBiot}{2} \right) \exp\{-k(Q_m / Q_{msat})\} (C - C_s) \quad (5.35)$$

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where

$$FBiot = \frac{K_f c_0 R}{\rho f D_{eff,0} q_0} \quad (5.36)$$

$$PBiot = \frac{K_b R^2}{f D_{eff,0}} \quad (5.37)$$

$$SFact = \frac{m q_0}{V_f c_0} \quad (5.38)$$

The Langmuir equation can be written as:

$$Q_m \Big|_{u=1} = \frac{c_s k_{LA} c_0}{q_0 + c_0 q_0 b_{LA} c_s} \quad (5.39)$$

The initial and boundary conditions become

$$\begin{aligned} Q_m(\eta, 0) &= 0 \\ Q_b(\eta, 0) &= 0 \\ C(0) &= 1 \\ Q_m(1, t) &= Q_s(t) \end{aligned} \quad (5.40)$$

where Q_m is dimensionless solid phase concentration in nonmicropore region, Q_b is dimensionless solid phase concentration in micropore region. Q_s is dimensionless solid phase concentration at particle surface. $PBiot$ is the modified particle Biot number, $FBiot$ is the modified film Biot number, and $SFact$ is the separation factor.

The orthogonal collocation method (OCM) was then employed to solve the differential algebraic equations in the concentration dependent branched pore kinetic model (CDBPKM). The method of orthogonal collocations on fixed elements was first introduced by Villadsen and Michelsen (1978) and then applied to adsorption processes in various instances (Lee et al. 1999; McKay 2001; Arora et al. 2005). This scheme requires that the normalized space coordinate r in the interval $[0,1]$ is divided into N spatial domains with N interior collocation points plus the point at the boundary. After the discretization of the coordinates in the N spatial domains, the approximation of the unknowns can be expressed by the polynomial functions. Substituting the discretized items into the equations, these are calculated by

integrating the following system of ODEs and algebraic equations. In the CDBPKM, there are four major parameters, namely, the external mass transfer coefficient, K_f , the effective diffusion coefficient at zero surfaces loading, $D_{eff,0}$, the parameter k , the micropore rate coefficient K_b , and the fraction of total adsorptive capacity in nonmicropore region f . The shape of the theoretical concentration decay curves will result from the non-linear combination of these parameters. An optimizing subroutine based on the Levenberg-Marquardt nonlinear regression was employed to search for the best combination of those parameters.

5.4 Experimental study

Adsorption is a complicated surface phenomenon, which has not been adequately understood. Therefore, extensive experimental investigations are essential for a successful application of this process.

5.4.1 Equilibrium experiments

The equilibrium adsorption capacities of the activated carbons for phenol at various initial adsorbate concentrations were measured to determine the adsorption isotherms for phenol. The aqueous phase adsorption studies were carried at five different temperatures of 298K, 303K, 313K, 318K and 323K. For each temperature, five different phenol concentrations were studied. 50 ml of each solution was poured into a 125ml conical flask. An accurately weighed amount of activated carbon was added into each flask. The activated carbons were washed with boiling deionized water and subsequently dried at 110°C for 24 hours before use. An additional flask with a known phenol solution, but without any activated carbon, was used

as the control experiment. By verifying that the initial and final concentrations of this control flask remaining the same, it is confirmed that phenol loss through volatilization and adsorption onto the walls of the flask was negligible. All the six flasks were placed in a shaker bath (DK-SB020, Daiki) operating at 900 degrees per second for 168 hours. By determining the phenol solution concentration before and after the adsorption test, the amount of phenol adsorbed by the activated carbons could be found. The phenol concentration was determined by a gas chromatograph-mass spectrometer (6890N GC-5973MSD system, Agilent).

5.4.2 Kinetic experiments

To study the adsorption kinetics with time, the adsorption of phenol by the oil-palm-shell activated carbons was carried out in a batch process. In particular, the effect of the initial solution concentration on the rate of phenol adsorption was investigated. An accurate weighed amount of activated carbon was added to 50 cm³ of phenol solution in a 100 cm³ conical flask. The flask was then agitated in a thermostatic orbital shaker at a temperature and a rotational speed of 900 degrees per second over a period of 6 days. The phenol concentration was determined by the same gas chromatograph-mass spectrometer mentioned earlier. The technique used was based on the EPA method 8720. The amount of phenol adsorbed was determined by the mass balance procedure.

5.5 Results Discussion

5.5.1 Adsorption study

5.5.1.1 Equilibrium isotherms

The adsorption isotherms of phenol onto the oil-palm-shell activated carbons at various solution temperatures are shown in Fig 5-2. The adsorption curves fitted from the Langmuir, the Freundlich and the Langmuir-Freundlich equations are also shown in the figure. Generally, increasing solution temperature decreases the adsorption capacity of the adsorbent and hence the equilibrium solid phase concentration decreases. This is to be expected due to the exothermic effect of adsorption; the molecular motions of the adsorbate molecules increase with temperature and thereby reduce the sorption of these molecules onto the pore surfaces. The Langmuir and the Langmuir-Freundlich curves provide good agreement with the experimental adsorption data for the whole range of solution concentrations while the Freundlich curve shows less agreement with the experimental data.

Figure 5-2 Aqueous phase phenol adsorption isotherms at different temperatures and their correlations to the various isotherm equations

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In order to compare the validity of the three isotherm equations quantitatively, the normalized and non-normalized RMS (root mean square) residuals were computed and were used as criteria for determining the effectiveness of a particular model to fit the adsorption isotherm data. The usage of these two criteria is based on the calculation of errors. For nonnormalized RMS residual, it is more sensitive to errors at high equilibrium solution concentrations as it weighs the actual error at all points. However, the normalized RMS residual is based on the relative error and therefore it weighs all points equally. The formulae of the normalized RMS and the nonnormalized RMS residuals are

$$\text{Normalized RMS residual} = 100 \times \sqrt{\frac{1}{N_{pt}} \cdot \sum_{i=1}^{N_{pt}} \left(\frac{q_{ei,exp} - q_{ei,calc}}{q_{ei,exp}} \right)^2} \quad (5.41)$$

$$\text{Nonnormalized RMS residual} = \sqrt{\frac{1}{N_{pt}} \cdot \sum_{i=1}^{N_{pt}} (q_{ei,exp} - q_{ei,calc})^2} \quad (5.42)$$

Table 5-1 shows the adsorption parameters as obtained from the three isotherm equations for the oil-palm-shell activated carbons using various adsorption temperatures. As the adsorption capacity decreases with increasing solution temperature, the constants k_L , K_F and Q_{LF} in the Langmuir, Freundlich and Langmuir-Freundlich equations respectively, also generally decrease with increasing temperature. The data for the error residuals also confirm the Langmuir and the Langmuir-Freundlich equations provide better agreement for the experimental data points than the Freundlich equation.

Table 5-1 Adsorption parameters derived from Langmuir, Freundlich and Langmuir-Freundlich equations for various adsorption temperatures

Temperature (K)	Langmuir				Freundlich				Langmuir-Freundlich				
	k_{LA} (l.g ⁻¹)	b_L (l.mg ⁻¹)	NRMS (%)	NNRMS	k_F ($\frac{\text{mg}}{\text{g}} (\frac{\text{l}}{\text{mg}})^{1/n_F}$)	1/n _F	NRMS (%)	NNRMS	Q_{LF} (mg/g)	b_{LF} (l/mg)	1/n _{LF}	NRMS (%)	NNRMS
298.15	5.90	0.015	4.77	6.73	36.88	0.39	15.74	20.33	336.01	0.021	1.41	3.13	7.23
303.15	5.22	0.014	9.10	10.08	31.41	0.41	16.36	18.44	315.15	0.020	1.43	6.18	10.23
313.15	2.75	0.009	5.95	6.33	16.90	0.46	7.79	10.52	335.54	0.008	0.96	5.60	6.29
318.15	3.46	0.014	5.64	6.12	26.42	0.35	14.31	13.96	294.43	0.009	0.79	7.71	8.83
323.15	3.17	0.017	5.28	6.17	26.63	0.26	12.67	12.46	295.00	0.005	0.59	9.08	10.00

5.5.1.2 Evaluation of adsorption enthalpy

The adsorption enthalpy can be obtained from the van't Hoff equation which is

$$\ln(q_e / c_e) = -\frac{\Delta H^0}{RT} + \left(\frac{\Delta S^0}{R} - \ln \psi \right) \quad (5.43)$$

where R is the universal gas constant, T is the temperature of the adsorption system, ΔH^0 and ΔS^0 are the enthalpy change and entropy change during adsorption, respectively, and ψ is the proportionality factor. If ΔH^0 , ΔS^0 and ψ are constant, a plot of $\ln\left(\frac{q_{eq}}{c_{eq}}\right)$ versus $\frac{1}{T}$

will yield a straight line with a slope of $-\Delta H^0 / R$ and hence ΔH^0 can be calculated. Figure

5-3 shows the plot of $\ln\left(\frac{q_{eq}}{c_{eq}}\right)$ versus $\frac{1000}{T}$ for five different solution temperatures. The data

are extracted from the five phenol adsorption isotherms given in Fig.5-2. A linear relationship

is obtained, in which the slope is $-\frac{\Delta H^0}{R}$. Hence, an average enthalpy change of -26.93 kJ/mol

was obtained for all the adsorption tests presented in Fig.5-2. The negative value for ΔH^0 indicates that the phenol adsorption is an exothermic process.

Figure 5-3 Plot of $\ln\left(\frac{q_e}{c_e}\right)$ versus $\frac{1000}{T}$

This value of enthalpy change is in good agreement with the absolute value of 25 kJ/mol obtained by Salvador and Merchan (1996) for the adsorption of phenol from an aqueous solution by a typical activated carbon. Moreover, this value also agrees with results of other studies. Fritz Stoeckli *et. al.* (2001) examined the enthalpies of immersion of some typical and well-characterized activated carbons into the aqueous solutions of phenol with a calorimeter. The absolute values ranged from 19.1 kJ/mol to 30.5 kJ/mol.

5.5.2 Application of the CDBPKM

The experimental data for the adsorption kinetics study for five phenol solutions of 54.6 mg/l, 102.0 mg/l, 144.2 mg/l, 239.5 mg/l and 350.6 mg/l are shown in Fig. 5-4.

Figure 5-4 Batch kinetic experiments for various initial phenol concentration

The steep initial drop of the solute concentration is to be expected as the adsorption rate is high for an unloaded adsorbent. The data from these five experimental tests were regressed using the proposed concentration dependent branched pore kinetic model in a nonlinear least squares routine and the theoretical curves were also plotted in Fig. 5-4. The agreement between the experimental data and the model is good. The fitted parameters using the proposed model and the conditions of the activated carbon-phenol adsorption system are given in Table 5-2. The average correlation coefficient of 0.98 as given in Table 5-2 further indicates the good agreement between the model and the experimental results.

Table 5-2 Fitted parameters and correlation results of the CDBPKM

C_0 (mg/l)	N (rpm)	K_f (cm/s)	$D_{eff,0}$ (cm ² /s)	K_b (s ⁻¹)	f	k	Correlation coefficient
350.6	150	$1.38e^{-1}$	$3.96e^{-7}$	$2.42e^{-7}$	0.36	0.23	0.98
239.5	150	$1.34e^{-1}$	$3.54e^{-7}$	$2.13e^{-7}$	0.36	0.23	0.98
144.2	150	$1.29e^{-1}$	$3.02e^{-7}$	$2.50e^{-7}$	0.36	0.32	0.98
102.0	150	$1.38e^{-1}$	$3.46e^{-7}$	$1.89e^{-7}$	0.36	0.25	0.99
54.6	150	$1.41e^{-1}$	$2.63e^{-7}$	$1.11e^{-7}$	0.37	0.37	0.98

The good agreement between the kinetic simulations and the experimental results verifies that the proposed model is accurate for predicting the adsorption kinetics in aqueous solutions and the lumped parameter approach for the micropore transport appears to be quite effective for describing the adsorptive behaviour. The calculated values of $D_{eff,0}$ and K_b given in Table 5-2 are less than that for K_f ; this indicates that the rate controlling factor is the effective diffusion within the pore structure of the adsorbent particle. The values of the parameter k are not negligible and therefore show that the surface diffusion coefficient is dependent on the solid phase adsorbate concentration. An understanding of the relative importance of each parameter can be seen from the sensitivity analyses presented in the following section.

5.5.2.1 The physical description of parameters in the model

Effect of each kinetic parameter on the aqueous phase concentration decay curve can provide the basis or principle of the mechanism involved in the adsorption kinetics. These effects can be examined from the physical properties of the parameters.

The external (film) mass transfer coefficient K_f

The external mass transfer coefficient K_f is a function of the thickness of the boundary layer surrounding the adsorbent and the hydrodynamic flow field. For the adsorption tests in this study, K_f should be fairly constant because of the constant agitation speed used in the water bath and the relatively narrow range of adsorbent sizes used. The small variation in the K_f values presented in Table 5-2 was probably due to the slight changes in the adsorbent mass used in the tests. The K_f value was evaluated from the initial bulk concentration data when the intra-particle diffusion resistance was negligible and subsequently adjusted during the optimization process. In a well-agitated reactor, adsorbent mixing in the liquid phase is rapid. Hence, the concentration of adsorbate in the liquid is nearly uniform throughout the vessel. The method for external mass transfer coefficient determination can be applied. The change in concentration with respect to time is related to the fluid-particle mass transfer coefficient by the equations.

$$V_f \frac{dc}{dt} = -K_f S_s (c - c_s) \quad (5.44)$$

with

$$c = c_0 \quad (t = 0) \quad (5.45)$$

The solution of the equation can be used to evaluate K_f . Since c_s approaches zero and c approaches c_0 , as $t \rightarrow 0$, the above equation shows that

$$\left[\frac{d(c/c_0)}{dt} \right]_{t=0} = -\frac{K_f S_s}{V_f} \quad (5.46)$$

Therefore the slope at $t=0$ of a plot of c/c_0 vs. t is equal to $-\frac{K_f S_s}{V_f}$. Subsequently, external mass transfer coefficient can be obtained. These values provide initial values for the model. The exact values need to be obtained through an optimizing sub-routine that fits the experimental data to the model.

The effective diffusion coefficient $D_{\text{eff},0}$

The effective diffusion coefficient $D_{\text{eff},0}$ in the adsorbent particle depends on the diffusion coefficient in the bulk phase and the detailed pore structure. The effective diffusion coefficient in the particle can be considered to be proportional to the diffusion coefficient in the bulk phase. So, the initial estimated effective diffusion coefficient can be obtained by the following expression:

$$D_{\text{eff},0} = \varepsilon_p^2 D_m \quad (5.47)$$

In the dilute aqueous solution, the Wilke-Chiang equation can be utilized for the estimation of the value of molecular diffusion coefficient D_m .

$$D_m = 7.4 \times 10^{-8} (aM)_2^{1/2} T / (\eta_2 V_1^{0.6}) \quad (5.48)$$

where a represents the association coefficient given as 2.6 for water, 1.9 for methanol, 1.6 for ethanol and 1.0 for non-associative solvent such as benzene, M is the molecular weight of solvent, T is the absolute temperature, η_2 is the viscosity of solution in centipoises, V_1 is mole volume of solute at normal boiling point. The above equation gives a rough estimation of D_m . From the equation, diffusion coefficient of organic molecules of low molecular weight

in water is in the range of 10^{-6} to 1.5×10^{-5} cm^2/s while it can be smaller with increasing molecular weight.

The parameter k

The present model provides a means to determine the mechanism of intra-particle diffusion in the adsorption process. There are two general diffusion mechanisms in the intra-particle diffusion, pore diffusion and surface diffusion. In surface diffusion, an adsorbed molecule can hop along the surface when it attains sufficient activation energy and when an adjacent adsorption site is available. In pore diffusion, the adsorbate diffuses into the pores in the fluid phase and is taken up by adsorption on the wall of the pores. The molecule cannot diffuse along the walls of the pores in the adsorbed state but can migrate by desorbing first. A comparison between the activation energy and the heat of adsorption can be used to discriminate the two intra-particle diffusions.

The micro-pore rate coefficient K_b :

The micropore rate coefficient K_b is highly dependent on the pore radius within the micropore structure of the adsorbent. Decreasing pore radius in the micropore increases the energy barrier in the surface migration process, thereby greatly reducing its rate of diffusion. Also, the rate of micropore diffusion is a strong function of the solute diameter/pore diameter ratio. The initial value of K_b was assumed to be of the same magnitude of the effective diffusion coefficient, $D_{\text{eff},0}$.

Fraction of total adsorptive capacity in nonmicro-pores f

The fraction of total adsorption in non-micropore f depends on the properties of both the adsorbate and the adsorbent, even though it may seem to be a structural property. In the study, the fraction of the non-micropore surface area to the total pore surface area of the activated carbon is 0.3, which is smaller than the estimated value of f by the model. The difference may be due to some of the smaller micropores may not be accessible to the larger molecular size of phenol (the molecular diameter of phenol is 6.2 Å.) as compared to the molecular size of N_2 (the molecular diameter of nitrogen is 3.64 Å.) which is used in obtaining the adsorption isotherms for the determination of the pore surface area of the activated carbons. Another possibility is the pore surface chemistry may vary within the activated carbon particle, giving rise to varying density of phenol adsorption capacity within the particle and hence this will have an effect on the value of f . The initial value of f used was based on the fraction of non-micropore surface area to the BET surface area of the activated carbon.

5.5.2.2 Parameter Sensitivity Analysis

The present model can be utilized to study the influence of individual parameter on the overall adsorption process. The relative importance of each of the five parameters (i.e., K_f , $D_{eff,0}$, K_b , f and k) can be assessed by the sensitivity analyses. For each parameter, the average value was obtained from the values given in Table 5-2 and used in the analyses. Varying one parameter at a time, the effect of each parameter on the adsorption kinetics using the present model can be demonstrated. For each particular parameter under study, three values were used: the average value, half and twice this average value. The remaining four parameters were held constant; based on their average value.

Parameter sensitivity analysis provides an indication of the relative importance of each parameter defined in the present model. The five kinetic parameters for the phenol adsorption process have been used in the simulations to obtain the aqueous phase concentration decay curves. Figure 5-5 shows that the aqueous phase concentration is a function of the external aqueous film mass transfer coefficient K_f and the duration of adsorption, if the other parameters are fixed. It shows that a lower K_f inevitably will result in a longer time to achieve a final equilibrium aqueous phase concentration. For values of $K_f = 0.68 \times 10^{-1}$, 1.36×10^{-1} and $2.72 \times 10^{-1} \text{ cm s}^{-1}$, the times required to attain equilibrium concentration are about 5.5, 3.5 and 2 h, respectively. This shows that doubling K_f does not halve the equilibrium time.

Figure 5-5 Sensitivity analysis: K_f parameter

($D_{\text{eff},0} = 3.32 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$, $K_b = 2.01 \times 10^{-7} \text{ s}^{-1}$, $f = 0.36$, $k = 0.28$).

Figure 5-6 shows that varying non-micropore diffusion coefficient, $D_{\text{eff},0}$, has limited effect on the initial uptake period and thereafter there is small variability in the three concentration

decay curves. This is expected because the adsorption in the non-micropore takes place first and once these sites are filled, the effect of $D_{\text{eff},0}$ diminishes. Figure 5-7 shows the effect of the micropore rate coefficient K_b on the aqueous bulk concentration decay curves. Varying K_b values only impact the later part of the uptake period as the micropores will be last to be filled. Increasing K_b increases adsorption and therefore results in decreasing aqueous equilibrium concentration. The effect of the fraction of non-micropore, f , in Fig. 5-8, has the greatest impact on the aqueous bulk concentration amongst the five kinetic parameters, thus demonstrating that aqueous adsorption takes place substantially in the non-micropores. Increasing f reduces the aqueous bulk concentration as more non-micropore are available for adsorption. Varying k values have insignificant effect on the aqueous bulk concentration decay curves as shown in Fig. 5-9. It is to be expected as k shows the mode of diffusions; surface or pore diffusion in the non-micropores.

Figure 5-6 Sensitivity analysis: $D_{\text{eff},0}$ parameter.

($K_f=1.36 \times 10^{-1} \text{ cm s}^{-1}$, $K_b=2.01 \times 10^{-7} \text{ s}^{-1}$, $f=0.36$, $k=0.28$)

Figure 5-7 Sensitivity analysis: K_b parameter

($K_f=1.36 \times 10^{-1} \text{ cm s}^{-1}$, $D_{\text{eff},0}=3.32 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$, $f=0.36$, $k=0.28$)

Figure 5-8 Sensitivity analysis: f parameter

($K_f=1.36 \times 10^{-1} \text{ cm s}^{-1}$, $D_{\text{eff},0}=3.32 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$, $K_b=2.01 \times 10^{-7} \text{ s}^{-1}$, $k=0.28$).

Figure 5-9 Sensitivity analysis: k parameter

($K_f=1.36 \times 10^{-1} \text{ cm s}^{-1}$, $D_{\text{eff},0}=3.32 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$, $K_b=2.01 \times 10^{-7} \text{ s}^{-1}$, $f=0.36$).

5.5.2.3 Effect of physical characteristics or operating parameters

Physical characteristics of the adsorbent or operating parameters like temperature affect the adsorption capacity; other parameters such as aqueous phase solution concentration or the mass of adsorbent influence the process of the adsorption. These parameters are important to the design of adsorption processes. For instance, the degree of adsorption is a function of the initial aqueous phase solution concentration. Similarly, the mass of adsorbent utilized for completing the adsorption is one of the most important parameters for the separation. Tests were carried out to study the effect of adsorbent mass on the bulk concentration of phenol. From these tests, the effect of different masses of activated carbons on the validity of the model was determined and therefore the prediction of the model for varying adsorbent mass was evaluated. The adsorption tests were carried out in a water bath held at 30°C and the

samples were agitated at a speed of 150 rpm. The initial concentration of the phenol solution was 259.5 mg/l.

Figure 5-10 Application of the CDBPKM to the activated carbon-phenol adsorption system with different masses of adsorbent

Figure 5-10 shows that increasing adsorbent mass increases the adsorption capacity of phenol and therefore the bulk concentration or the aqueous phase concentration decreases. This is expected because with the increase of the mass of adsorbent, the available adsorptive surfaces increase, the amount of adsorbate transferring from the solution to the surface of the adsorbent increases. The agreement between the experimental data and the model is good. The fitted parameters arising from the model simulations are: the external film mass transfer coefficient K_f is 1.36×10^{-1} cm/s, the effective diffusion coefficient $D_{\text{eff},0}$ is as 3.32×10^{-7} cm²/s, the micropore rate mass transfer coefficient K_b is 2.01×10^{-7} s⁻¹, the fractional of total adsorptive capacity in macro-pores f is 0.36, and the parameter k is 0.28.

In addition to simulating the solution concentration decay curve, the model can also generate the concentration profile within the activated carbon during the adsorption process.

Figure 5-11 Concentration profile in the nonmicropore region of adsorbent

Figure 5-11 shows the adsorbed phenol concentration development and profile within the adsorbent particle. The simulation parameters for the concentration profile were as above, i.e., $K_f = 1.36 \times 10^{-1} \text{ cm/s}$, $D_{\text{eff},0} = 3.32 \times 10^{-7} \text{ cm}^2/\text{s}$, $K_b = 2.01 \times 10^{-7} \text{ s}^{-1}$, $f = 0.36$, and $k = 0.28$. The temperature for adsorption is 30°C and the aqueous solution concentration is 259.5 mg/l . It is observed that the concentration on the surface is the highest point in the particle at all time intervals.

CHAPTER 6 FIXED BED ADSORPTION FOR AQUEOUS PHASE

6.1 Introduction

In liquid phase adsorption applications, a fixed bed is the typical operation unit. Figure 6.1 shows typical pilot scale adsorption columns in the water treatment industry.

Figure 6-1 Pilot scale carbon columns at a water treatment plant

In a fixed bed, adsorbent particles are packed in a column and fluid that contains one or more components of adsorbates flows through the bed. A nearly solute-free liquid or gas effluent is obtained until the adsorbent in the bed approaches saturation. Adsorption takes place from the inlet of the column and proceeds to the exit. In the course of adsorption, a saturated zone is formed near the inlet of the column and a zone with increasing concentrations is observed at

the frontal part. Mass transfer from the fluid to the adsorbent occurs in this region, which is known as the “mass transfer zone”. If concentrations in the effluent stream are measured continuously, seepage of the adsorbable components are observed when the mass transfer zone approaches the exit of the bed and the so-called “breakthrough curve” will be obtained.

In this study, the oil-palm-shell activated carbons will be used to adsorb phenol using a fixed-bed adsorption system. The effects of the feed volume flow rate, the initial phenol concentration in the feed and the height of the fixed bed on the adsorption capacity of the fixed bed would be studied. Further, modeling on the adsorption dynamics of the fixed bed would be carried out and finally correlation between the model and the experimental data would be carried out.

6.2 Model development

Comparative studies between the dynamic models of liquid phase adsorption by activated carbons and experimental results have been reported in the literature such as Chern and Chien (2002) and Pan *et al.* (2005). Pan *et al.* (2005) combined the constant-pattern wave approach theory and adsorption isotherm to determine the breakthrough curve of a fixed bed adsorption system. They carried out dynamic experiments at different conditions for phenol, *p*-nitrophenol and macro reticular polymeric resin adsorbent systems. The breakthrough curves predicted by the model and those of the experimental runs were in satisfactory agreement. The performance of the adsorption of *p*-nitrophenol onto granular activated carbon in 25°C aqueous solution for a dynamic process was investigated by Chern and Chien (2002). A series of column tests were performed to determine the breakthrough curves with varying bed depths and water flow rates. They applied the constant-pattern wave approach using the

Freundlich isotherm model to fit the experimental breakthrough curves. In their study, a correlation was proposed to predict the volumetric mass-transfer coefficient in the liquid phase.

Simulations are used to determine the time duration and mechanics of the occurrence of breakthroughs. The relevant breakthrough curves provided information for designing a specified fixed bed adsorption process. For nonlinear isotherm systems, explicit equations for the breakthrough curves of the fixed-bed adsorption processes with adsorption isotherms are developed by the constant-pattern wave approach using a constant driving force model in the liquid phase. “Control volume” is a scheme applied to obtain macroscopic conservation equations for the fixed bed adsorption system (Tien 1994). In a fixed bed adsorption system, the control volume is taken to be a small element of a fixed bed bounded by an upper and lower surface with a distance of Δz between the surfaces. In the control volume, certain material entities and a mass balance are applied. The flow is assumed to be one-dimensional in the z direction, along the direction of the axis of the bed only. Based on a unit cross-sectional area, the terms in the conservation balance equation can be derived. Figure 6.2 illustrates the schematic diagram of the control volume in the fixed bed adsorption model. The rate of accumulation of adsorbate mass can be expressed as: $\Delta z \cdot \varepsilon_b \cdot (\Delta c / \Delta t)$, where ε_b is the bed porosity, c is the adsorbate concentration and t is the time. The rate of net adsorbate input associated with mass flow is: $(u_s c)_z - (u_s c)_{z+\Delta z}$, where u_s is the superficial velocity. The adsorbate in the control volume composes of two parts, one is the axial dispersion and the other is the uptake by the pellet: $-\left(E_z \varepsilon_b \frac{\partial c}{\partial z}\right)_{z+\Delta z} + \left(E_z \varepsilon_b \frac{\partial c}{\partial z}\right)_z$ and $(\Delta z) \frac{(1-\varepsilon_b)}{(4/3)\pi R^3} N$ when the shape of pellet was taken as sphere. E_z is the eddy diffusion coefficient or axial dispersion coefficient, N is the adsorbate update rate per pellet or number of adsorbate species, and R is the pellet radius.

Figure 6-2 Mass balance in the fixed bed control volume

The conservation equation is:

$$-E_z \varepsilon_b \frac{\partial^2 c}{\partial z^2} + \frac{\partial}{\partial z}(u_s c) + \varepsilon_b \frac{\partial c}{\partial t} + (1 - \varepsilon_b) \frac{3N}{4\pi R^3} = 0 \quad (6.1)$$

The removal of the adsorbate from the fluid stream by adsorption does not affect the superficial velocity significantly. The value of the superficial velocity can be calculated from the volumetric flow rate of the fluid and the cross sectional area of the bed. The initial and boundary conditions are:

$$\begin{aligned} c &= c_0, & 0 \leq z \leq L, t > 0 \\ -E_z \varepsilon_b \frac{\partial c}{\partial z} &= u_s (c_0 - c), & z=0, t \geq 0 \\ \frac{\partial c}{\partial z} &= 0, & z=L, t \geq 0 \end{aligned} \quad (6.2)$$

where c_0 is the inlet value of c , i.e., the adsorbate concentration of the influent.

Equation (6.1) gives the concentration of the solute in the bulk fluid as a function of time and location in the bed. Together with the conservation equations of the adsorbate species in the adsorbent pellet, these two equations can be coupled together by the continuity condition at the particle surface by

$$D_{eff} \left(\frac{\partial c}{\partial r} \right)_R = K_f (c - c_s) \quad (6.3)$$

where K_f is the external mass-transfer coefficient and D_{eff} is the effective diffusivity in the particle. With fixed bed adsorption expression, governing equations can be solved for concentration as a function of z and t by analytical or numerical methods. For a quick estimation of the breakthrough behaviour of an adsorption column, simplified treatments can be utilized with reasonable assumptions. With these assumptions, analytical solutions to nonlinear isotherm systems can be obtained.

6.2.1 Linear driving force model

In the linear driving force model, the uptake rate of adsorbate by a pellet is postulated as linearly proportional to a driving force. The driving force can be defined as the difference between the surface concentration and the average adsorbed-phase concentration. Simple models include two-phase exchange models like LDFC (linear driving force model based on concentration difference), LDFQ model or the LDF series model. In the LDFC model, the mass transfer rate is expressed by using the overall mass transfer coefficient, K_F , based on the fluid phase concentration difference as the driving force. The model is:

$$\rho_b dq / dt = K_F (c - c^*) \quad (6.4)$$

where ρ_b is the bed bulk density, q is the average amount adsorbed, c^* is an equilibrium concentration with q . Obviously, this model is suitable for those cases where fluid-particle mass transfer is a dominant mass transfer resistance. In such cases, K_F can be replaced by fluid-to-particle mass transfer coefficient, K_f .

The LDFQ model is similar to the LDFC model except that the mass transfer is expressed on the basis of particle phase concentration difference. The model is:

$$\rho_b dq / dt = K_s (q^* - q) \quad (6.5)$$

where q^* is the equilibrium concentration defined in LDF model. The LDFC and LDFQ models are identical when the adsorption isotherm is linear, by setting $K_s = K_F / K$. For nonlinear equilibrium systems, however, the two models indicate individual behaviour, that is, considerably different concentration profiles, especially when nonlinearity is large. Compared with a more rigorous model, this model gives better approximation when intraparticle diffusion plays a dominant role in mass transfer. When intraparticle diffusion is the only rate determining step of mass transfer, K_s can be replaced by particle phase mass transfer coefficient, k_s , which is related to the intra-particle diffusion parameters (Suzuki 1990) as:

$$k_s = \rho_b \cdot 15 \phi_s D_s / R^2 \quad (6.6)$$

or

$$k_s = \frac{15 \phi_s D_p / R^2}{q_0 / c_0} \quad (6.7)$$

where ϕ_s is correlation parameter defined in equations, D_p is pore diffusion coefficient ($\text{cm}^2 \cdot \text{s}^{-1}$), D_s is surface diffusion coefficient ($\text{cm}^2 \cdot \text{s}^{-1}$), c_0 is initial aqueous solution concentration ($\text{mg} \cdot \text{l}^{-1}$), q_0 is solid phase concentration in equilibrium with c_0 ($\text{mg} \cdot \text{g}^{-1}$). Selection of the above equations depends on the dominant mechanism of intraparticle diffusion. When surface diffusion kinetics are controlling, Eq (6.6) is used. Eq. (6.7) should be used for dominant pore diffusion kinetics.

Better approximation is possible by considering that the LDFC model and the LDFQ model are valid, respectively, at fluid-to-particle mass transfer and at intra-particle diffusion. In this

case, adsorption equilibrium is considered to hold at the particle surface as $q_s = q_s(c_s)$. The basic equations for mass transfer rate expression are as follows

$$\rho_b dq / dt = K_f (c - c_s) = k_s (q_s - q) \quad (6.8)$$

6.2.2 Constant pattern front

Constant pattern front (CPF) was first described by Bohart and Adams (1920) for irreversible adsorption. For favourable isotherm relation such as that of the Langmuir or Freundlich type where $n > 1$, concentration profile moving along the column can be explained as follows. The steepness of the breakthrough curve determines the extent to which the capacity of an adsorbent bed can be utilized. Therefore, the shape of the curve is important in determining the length of an adsorption bed. As the width of the breakthrough curve and the corresponding width of the MTZ for the concentration profiles increase, less and less of the bed capacity can be utilized. Depending on the shape of the adsorption isotherm, the steepness of the concentration profiles increase or decreases with time. The derivation regarding the effect of the shape of the isotherm on the sharpness of the concentration wave front is given below.

With the assumption of a plug flow of the fluid through the bed at a constant actual (interstitial) velocity u , instantaneous equilibrium of the solute in the bulk fluid with the adsorbate; no axial dispersion, and at isothermal conditions, the fixed bed modelling equations can be simplified to a mass balance on the solute for the flow of fluid through a differential adsorption-bed length dz over a differential time duration dt .

$$\varepsilon_b u A_b c \Big|_z = \varepsilon_b u A_b c \Big|_{z+\Delta z} + \varepsilon_b A_b \Delta z \frac{\partial c}{\partial t} + (1 - \varepsilon_b) A_b \Delta z \frac{\partial q}{\partial t} \quad (6.9)$$

Dividing by Δz and taking the limit as $\Delta z \rightarrow 0$, equation (6.9) leads to

$$\frac{\partial c}{\partial t} + u \frac{\partial c}{\partial z} + \frac{(1 - \varepsilon_b)}{\varepsilon_b} \frac{\partial q}{\partial t} = 0 \quad (6.10)$$

where q is the adsorption loading/unit volume of adsorbent particles and is to given by an appropriate isotherm. In the mass conservation equation, c is a function of z and t , i.e., $c=f(z,t)$. Therefore, the velocity of the concentration wave front, $\partial z / \partial t$ at constant c can be expressed by the rules of implicit partial differentiation:

$$u_c = \left(\frac{\partial z}{\partial t} \right)_c = - \frac{\left(\frac{\partial c}{\partial t} \right)}{\left(\frac{\partial c}{\partial z} \right)} \quad (6.11)$$

The superficial fluid velocity is $\varepsilon_b u$. Combining (6.10) and (6.11), the velocity of the concentration wave front can be expressed as:

$$u_c = \frac{u}{1 + \left(\frac{1 - \varepsilon_b}{\varepsilon_b} \right) \frac{dq}{dc}} \quad (6.12)$$

So the equation gives the velocity of the concentration wave front for the solute in terms of the interstitial fluid velocity and the slope, dq/dc , of the adsorption isotherm.

As equation (6.12) indicates, the concentration wave front moves through the bed at a velocity, u_c , that is less than the interstitial fluid velocity. For a linear isotherm, the width of the MTZ and the wave pattern remain constant. If adsorption isotherm is curved, regions of the wave front at a higher concentration move at a velocity different from regions at a lower concentration. For a favourable isotherm of the Freundlich or Langmuir type, high concentration regions move faster than low concentration regions, and the wave front steeps with time until a constant pattern front (CPF) is developed. In this case, the wave front broadening diminishes and an asymptotic or constant pattern front is developed. For such a

front, the mass transfer zone is constant and curves of c/c^* and $\bar{q}/q^*$ become coincident (c^* is equilibrium concentration defined in LDF model). So the condition of the constant pattern can be derived. When the constant pattern profile is established, the speed of movement of the point on the mass transfer zone is constant regardless of concentration. The condition of the constant pattern can be derived from equation (6.10).

As the constant pattern wave moving at a constant value, the aqueous phase concentration can be expressed as a function of the adjusted time defined as:

$$\tau = t - \frac{z}{u_c} \quad (6.13)$$

where t is time, z is distance from the inlet of aqueous phase, u_c refers to the concentration wave velocity, and τ is the adjusted time. Substituting (6.13) into (6.10) on the basis of substituting $c(t, z)$ with $c(\tau)$:

$$\left(1 - \frac{u_0}{u_c}\right) \frac{dc}{d\tau} + \frac{\rho_b}{\varepsilon_b} \frac{dq}{d\tau} = 0 \quad (6.14)$$

which can be integrated as

$$\int_0^c \left(1 - \frac{u_0}{u_c}\right) dc + \int_0^q \frac{\rho_b}{\varepsilon_b} dq = 0 \quad (6.15)$$

or

$$\left(1 - \frac{u_0}{u_c}\right) c + \frac{\rho_b}{\varepsilon_b} q = 0 \quad (6.16)$$

From the boundary conditions at $c = c_0$, $q = q_0$, the following equation can be derived

$$\left(1 - \frac{u_0}{u_c}\right) c_0 + \frac{\rho_b}{\varepsilon_b} q_0 = 0 \quad (6.17)$$

When the constant pattern profile is established, the velocity of concentration wave front is constant regardless of concentration. Combining Eqs. (6.16) and (6.17), the following equation is derived as a condition of the constant pattern:

$$\frac{q}{q_0} = \frac{c}{c_0} \quad (6.18)$$

where c_0 is the feed adsorbate concentration in the aqueous phase, q_0 is the adsorbate concentration in the solid phase equilibrium with c_0 , c and q are the adsorbate concentrations in the aqueous and solid phases respectively. As the constant pattern front approaches can be determined, and then the breakthrough curves of the fixed bed adsorption process can be derived and predicted.

6.2.3 Analytical solution of the LDF series model

Using the constant pattern condition (6.18), equation (6.8) can be transformed into the dimensionless form:

$$\frac{1}{1+\zeta} \cdot \frac{d\bar{y}}{d\theta} = x - x_s = (1/\zeta)(y_s - y) \quad (6.19)$$

where

$$\zeta = \left(\frac{K_f}{k_s} \right) \left(\frac{c_0}{q_0} \right) \quad (6.20)$$

$$\theta = \frac{t - \varepsilon_b z / u}{\frac{1}{K_f} + \frac{1}{k_s (q_0 / c_0)}} \quad (6.21)$$

where $x = c / c_0$ and $y = q / q_0$

The adsorption equilibrium results in chapter 5 indicated that the Langmuir isotherm equation could describe the adsorption of phenol onto the oil-palm-shell activated carbon fairly well. Therefore, the Langmuir isotherm equation will be used to model the fixed bed adsorption process. From the original expression of the Langmuir isotherm, equation (5.1) can be rewritten as:

Chapter 6 Fixed bed adsorption for aqueous phase

$$\frac{q_e}{Q_a^0} = \frac{b_L c_e}{1 + b_L c_e} \quad (6.22)$$

where q_e is the solid phase concentration of the solute being adsorbed, c_e is the fluid phase concentration, b_L is the Langmuir equilibrium constant, and Q_a^0 is the solid phase concentration corresponding to a condition in which all available sites are filled. The relations for saturation conditions can be expressed into a general relation, resulting in

$$\frac{q_e}{q_0} = \frac{c_e(1 + b_L c_0)}{c_0(1 + b_L c_e)} \quad (6.23)$$

where q_e is the solid-phase concentration of the solute being adsorbed at equilibrium state, b_L is the Langmuir equilibrium constant, c_e is the aqueous phase concentration and c_0 is the feed concentration. A “constant separation factor” or “equilibrium parameter,” R , is defined as

$$R = \frac{1}{1 + b_L c_0} \quad (6.24)$$

Dimensionless concentrations, $y(=q_e/q_0)$ and $x(=c_e/c_0)$, are introduced, each is bounded by the values 0 and 1. Equation (6.23) then becomes

$$y = \frac{x}{R + (1 - R)x} \quad (6.25)$$

R can be solved explicitly from equation (6.25)

$$R = \left[\frac{x(1 - y)}{y(1 - x)} \right]_e \quad (6.26)$$

As the mean concentration at any given cross section in a fixed bed is given by x and y , R represents the equilibrium characteristics of different systems. For instance, $R=0$ for an irreversible system, $0 < R < 1$ for favourable equilibrium, $R=1$ for a linear system, and $R > 1$ for unfavorable equilibrium.

Using equation (6.25), equation (6.19) can be solved and the solution is

$$\begin{aligned} \frac{K_s}{\rho_b}(t-t_0) = \frac{1}{1+\zeta} \left[\frac{1}{1-R} \ln x_s - \frac{R}{1-R} \ln(1-x_s) - \ln \{R + (1-R)x_s\} - \frac{R}{1-R} \ln R + 1 \right] \\ + \frac{\zeta}{1+\zeta} \left\{ \frac{R}{1-R} \ln x_s - \frac{R}{1-R} \ln(1-x_s) - 1 \right\} \end{aligned} \quad (6.27)$$

where

$$\frac{1}{K_s} = \frac{q_0/c_0}{K_f} + \frac{1}{k_s} \quad (6.28)$$

$$t_0 = (z/u)[\varepsilon_b + \rho_b q_0/c_0] \quad (6.29)$$

where u is the interstitial velocity of the fluid in the bed, and ε_b is the bed void fraction (Suzuki 1990). Bed void fraction is a parameter in the model that is hard to measure and can vary greatly between adsorption columns. Bed void fraction is the ratio of empty volume in a packed column to the volume of an unpacked column. This ratio can vary depending on how well the activated carbon pellets are packed into the bed. The expression of equation (6.27) is based on x_s . Knowing x_s , x is obtained as follows:

$$x = [(\zeta R + 1)x_s + \zeta(1-R)x_s] / (\zeta + 1) [R + (1-R)x_s] \quad (6.30)$$

In the case of external mass transfer controlling the rate of adsorption or intra-particle diffusion being the sole rate-determining step, the above solution can be reduced to simpler forms in equation (6.31) for the LDFC model and equation (6.32) for the LDFQ model.

$$\frac{K_f}{\rho_b q_0/c_0}(t-t_0) = 1 - \frac{R \ln(1-x) - \ln x}{1-R} \quad (6.31)$$

$$k_s / \rho_b(t-t_0) = \frac{R}{1-R} \ln x - \frac{1}{1-R} \ln(1-x) - 1 \quad (6.32)$$

where t is the contact time.

6.3 Experiment

Fixed bed adsorption was carried out in a glass column with an inside diameter of 1.1cm and a length of 30cm. Figure 6.2 shows the experimental setup. The feed phenol solution was pumped through the column by a peristaltic pump (Masterflex L/S tubing pumps, Masterflux). The inlet to the pump could also be connected to the de-ionised water through the 3-way valve.

Figure 6-3 Experimental setup for dynamic experiments

Oil-palm-shell activated carbons with a known weight were packed into the column. The bed density and the void fraction were then determined. The activated carbons were flushed with de-ionized water for 12 hours to remove fine particles. The phenol solution was fed to the top of the column at a desired flow rate by the peristaltic pump until the breakthrough occurred. Samples for the determination of phenol concentration were taken from the effluent intermittently. The phenol concentration in the samples was determined by the gas chromatograph-mass spectrometer (6890N GC-5973 MSD system, Agilent).

6.4 Results and discussion

The axial dispersion Peclet numbers for the fixed bed was determined to evaluate the longitudinal dispersion (Rodrigues et al. 2005). Axial dispersion coefficient accounts for the axial diffusion mechanism. The correlation presented by Chung and Wen (1968) was used to determine axial dispersion coefficient for liquids in fixed beds. The Peclet number was calculated using the correlation, $Pe = \frac{H}{2R\varepsilon_b} \left(0.2 + 0.011 \cdot Re_p^{0.48} \right)$, where the particle Reynolds number $Re_p = \frac{u\varepsilon_b d_p \rho}{\mu}$, H is the column height, R is the particle radius, ε_b is the bed porosity, u is the interstitial velocity, d_p is the particle diameter, ρ is density of fluids, and μ is the fluid dynamic viscosity. The operating conditions for a fixed bed run were at a temperature of 30°C, 1 ml/min feed flow rate, and 8.5 cm bed height. At these conditions, the Pe number of the bed was found to be 25.74. This value is considered large enough for ignoring the axial dispersion in the operation. In addition, low flow rates were used in the tests to ensure the local equilibrium condition in the fixed bed.

6.4.1 Breakthrough dynamics

For the LDFC model, equation (6.31) can be re-arranged as follows:

$$t = t_0 + \frac{\rho_b q_0 / c_0}{K_f} \left(1 - \frac{R \ln(1-x) - \ln x}{1-R} \right) \quad (6.33)$$

where x is the non-dimensional effluent concentration, $x = c / c_0$.

For the LDFQ model, equation (6.32) can be re-arranged as follows:

$$t = t_0 + \rho_b / k_s \left(\frac{R}{1-R} \ln x - \frac{1}{1-R} \ln(1-x) - 1 \right) \quad (6.34)$$

Using the experimental adsorption data through the fixed bed, both the LDFQ and LDFC models are predicted in Figure 6-4. The LDFQ model gives a better linear correlation than the LDFC model. The value of t_0 and the mass transfer coefficient can be determined from the intercept and the slope of the line, respectively. The experimental conditions for the fixed bed tests and the correlation results are given in Table 6-1. Subsequently, the LDFQ model was used to determine the breakthrough curves for the fixed bed.

Figure 6-4 Validity of the linear driving force models based on the Langmuir isotherm

Table 6-1 Experimental conditions and correlation results for the LDF models

Experimental conditions		Flow rate: 1.00 ml/min Influent concentration: 204 mg/l Bed length: 65mm Bed diameter: 11 mm Temperature: 303 K Bed void fraction ε_b : 0.4347 Bed density: 0.4753 g/cm ³	
		LDFC model	LDFQ model
Correlation results	Correlation coefficient	0.9655	0.9834
	t_0 (min)	3251.5	2393.9
	Slope	551.88	689.33

6.4.2 Effects of fixed bed conditions on the breakthrough

The influences of operation conditions on the breakthrough curves were investigated. These conditions were the flow rate, the influent concentration and the fixed bed height.

The effect of flow rate on the breakthrough curves is shown in Figure 6-5. Five values of flow rate were investigated. The experimental values of the non-dimensional effluent concentration versus the time were plotted. Using the LDFQ model in equation (6.34), the theoretical breakthrough curves were also plotted in Figure 6-5. The operating conditions and the adsorption parameters in the LDFQ model are given in Table 6-2.

Figure 6-5 Effect of flow rate on the breakthrough curve

In Figure 6-5, the agreement between the experimental results and the LDFQ model is good. For a low flow rate, the breakthrough curve is longer than that of a higher flow rate because it takes a longer time to reach the adsorption capacity of the activated carbons if the other

operating conditions are constant. Therefore as the flow rate increases, the breakthrough curve becomes steeper because of the shorter time required.

Table 6-2 Adsorption parameters in the LDFQ model by nonlinear regression of experimental data for different flow rates

Flow rate (ml/min)	Influent phenol concentration (mg/l)	Bed height (cm)	Adsorbent weight (g)	Mass transfer coefficient ($\text{gcm}^3\text{s}^{-1}$)	Characteristic time, t_0 (h)	Equilibrium parameter R
0.50	203	8.80	2.92	1.75e^{-4}	112.8	0.32
0.75	203	8.20	2.90	2.98e^{-4}	75.7	0.32
1.00	204	8.50	2.93	5.44e^{-4}	44.4	0.36
1.25	201	8.50	2.91	7.21e^{-4}	32.1	0.37
1.50	206	8.40	2.91	7.29e^{-4}	25.2	0.31

In Table 6-2, for increasing flow rate, i.e., increasing superficial velocity, the characteristic time decreases. This is to be expected because the column of activated carbons will reach its maximum adsorption capacity earlier. Conversely, the mass transfer coefficient must increase for increasing flow rate as the column of activated carbons must adsorb its maximum mass of adsorbate in a shorter time. This is reflected in Table 6-2 that increasing flow rate increases the mass transfer coefficient.

Figure 6-6 Effect of influent concentration on the breakthrough curve

The effect of influent concentration on the breakthrough curves is shown in Figure 6-6 for four phenol feed concentrations of 53.9, 115, 204 and 395 mg/l. the operating conditions and the adsorption parameters in the LDFQ model are similarly given in Table 6-3.

Table 6-3 Adsorption parameters in the LDFQ model by nonlinear regression of experimental data for different influent concentrations

Influent phenol concentration (ppm)	Flow rate (ml/min)	Bed height (cm)	Adsorbent weight (g)	Mass transfer coefficient ($\text{gcm}^3\text{s}^{-1}$)	Characteristic time, t_0 (h)	Equilibrium parameter R
395	1.00	8.60	2.93	6.46e^{-4}	28.6	0.31
204	1.00	8.50	2.93	5.44e^{-4}	44.4	0.36
115	1.00	8.20	2.92	4.87e^{-4}	54.0	0.37
53.9	1.00	8.50	2.91	4.69e^{-4}	60.0	0.38

For a fixed temperature, changing the influent concentration will affect the breakthrough curve characteristics in two ways. Firstly, increasing the influent concentration will reduce the time required to reach its maximum adsorption capacity. Hence, the breakthrough curve becomes steeper as the influent concentration increases. Secondly, increasing the influent concentration will increase the total adsorption capacity and may increase the breakthrough time. However, from the breakthrough curves presented in Figure 6-6, the first effect is more predominate and therefore the breakthrough time decreases for increasing influent concentration. The above trends can be seen in Table 6-3. Decreasing influent concentration decreases the mass transfer coefficient but increases the characteristics time.

The effect of bed height on the breakthrough curves is shown in Figure 6-7 for four bed heights of 5, 8.5, 13 and 17cm. The operating conditions and the adsorption parameters in the LDFQ model are given in Table 6-4.

Figure 6-7 Effect of bed height on the breakthrough curve

Table 6-4 Adsorption parameters in the LDFQ model by nonlinear regression of experimental data for different bed heights

Bed height (cm)	Influent concentration (mg/l)	Flow rate (ml/min)	Adsorbent weight (g)	Mass transfer coefficient ($\text{gcm}^{-3}\text{s}^{-1}$)	Characteristic time, t_0 (h)	Equilibrium parameter R
5.00	191	1.00	2.51	9.51e^{-4}	23.3	0.36
8.50	204	1.00	2.92	5.44e^{-4}	44.5	0.36
13.00	209	1.00	3.52	3.42e^{-4}	58.0	0.36
17.00	216	1.00	4.09	2.53e^{-4}	71.6	0.37

In Figure 6-7, increasing bed height increases the breakthrough time as expected. The mass transfer zone in a fixed bed travels from the entrance of the bed and progresses towards the exit. Hence, for the same influent phenol concentration and fixed bed conditions, an increase in the bed height results in a longer distance for the mass transfer zone to reach the exit and therefore an increase in the breakthrough time. This is correspondingly reflected in Table 6-4 in which the characteristic time increases with increasing bed height. Also, in the same table, the mass transfer coefficient increases as the bed height decreases. This implies that the adsorption or loading distribution along the bed height is the highest at the front face and

gradually decreases forwards the bed exit. In other words, the adsorption capacity per unit length decreases with increasing bed height.

CHAPTER 7 CONCLUSIONS

Oil-palm shell from Malaysia were converted into useful high quality activated carbons by pyrolysis and followed by steam activation, as well as by combined steam and chemical activation. The resulting activated carbons were characterized by nitrogen adsorption isotherms at 77 K to determine the pore surface areas and pore size distributions. Phenol adsorption studies in aqueous phase were conducted for the oil-palm-shell activated carbons for both batch process and fixed bed system. A concentration dependent branched pore kinetic model is proposed that takes into account of a concentration dependent surface diffusion coefficient within the adsorbent particle. Model simulations and experimental results from the batch process were correlated for phenol adsorption studies. A linear driving force model for fixed bed adsorption was used and compared with experimental results for phenol adsorption in a fixed bed. From the experimental and theoretical studies, the following conclusions can be drawn.

1. A systematic series of tests were carried to determine the optimum pyrolysis conditions in order to maximize the pore surface areas of the activated carbons. Two different pyrolysis environments were studied; vacuum pyrolysis and pyrolysis in nitrogen atmosphere. The pyrolysis parameters studied were i) temperature, ii) hold time, iii) heating rate, iv) nitrogen flow rate (for nitrogen pyrolysis only), and v) initial particle size of the oil-palm shell. The activation conditions for the chars were fixed

for these tests, i.e., i) temperature of 900°C, ii) hold time of 1 hour, iii) heating rate of 10°C/min, iv) steam flow rate of 22.68 g/min. Varying one pyrolysis parameter at a time whilst the rest of the pyrolysis parameters remained fixed, the local optimum values of the pyrolysis parameters could be obtained based on the highest pore surface area of the activated carbon.

2. For pyrolysis in nitrogen atmosphere, the optimum pyrolysis conditions are i) temperature of 750°C, ii) hold time of 2 hours, iii) heating rate of 10°C/min, iv) nitrogen flow rate of 150 ml/min, and v) initial particle size of 2-2.8 mm. For pyrolysis under vacuum conditions, the optimum pyrolysis conditions are i) temperature of 675°C, ii) hold time of 2 hours, iii) heating rate of 10°C/min, and iv) initial particle size of 2-2.8 mm.
3. Using an experimental optimization procedure, the local optimum conditions for producing oil-palm-shell activated carbons with the largest BET surface area and pyrolysed in nitrogen stream were as follows: raw oil-palm shell size range of 2-2.8 mm; pyrolysis conditions - temperature of 750°C, 2 hour hold time, 10°C/min heating rate, nitrogen flow rate of 150 cm³/min; and activation conditions – temperature of 950°C, 1.5 hours hold time, steam flow rate of 1.13 kg/h. This activated carbon had a BET surface area of 1432 m²/g and an adsorption capacity of 150mg of phenol per gram of activated carbon.
4. The local optimum conditions for pyrolysis under vacuum condition were as follows: raw oil-palm shell size of 2-2.8 mm; pyrolysis conditions - temperature of 675°C, 2 hour hold time, 10°C/min heating rate; and activation conditions – temperature of 950°C, 1.5 hour hold time, and steam flow rate of 1.13 kg/h. The resulting activated

carbon had a BET surface area of $1383 \text{ m}^2/\text{g}$ and an adsorption capacity of 200 mg of phenol per gram of activated carbon.

5. Although the activated carbon pyrolysed in nitrogen stream yielded a maximum BET surface area of $1432 \text{ m}^2/\text{g}$, the one pyrolysed in vacuum condition produced a larger phenol adsorption capacity of 275 mg phenol per gram of activated carbon with a lesser BET surface area of $1309 \text{ m}^2/\text{g}$. The phenol adsorption capacity of the former activated carbon was only 126 mg phenol per gram of activated carbon.
6. Combined steam and chemical activation results indicated that the catalytic effect of potassium cation in the chemical activation process played an important role on the micropore development while the thermal decomposition of carbonic anion had an effect on the nonmicropore development. The aqueous phase adsorption capacity of these activated carbons is directly proportional to their BET surface areas.
7. Systematic tests on aqueous phase phenol adsorption indicated that the experimental adsorption isotherms could be correlated by the Langmuir, Freundlich, and Langmuir-Freundlich equations. Based on the root mean square (RMS) of the normalized residuals and the RMS of non-normalized residuals (non-normalized RMS), the Langmuir and Langmuir-Freundlich isotherms showed good agreement with the experimental results. Kinetic experimental results using Langmuir isotherm confirmed that the Langmuir isotherm equation is able to depict the behaviour of single adsorbate component system. The proposed concentration dependent branched pore kinetic model fitted the experimental adsorption data well and was able to predict the performance of the activated carbon phenol adsorption system.

8. The simulations from the concentration dependent branched pore kinetic model for the batch equilibrium adsorption tests showed that the external mass transfer across the boundary layer at the solid-aqueous interface was rapid and it affected the adsorption at a very early stage. After the initial period, the intra-particle diffusion coefficients were predominant. The fraction of the adsorption capacity in nonmicropore region indicated the importance of the adsorbent characteristics to be used for a particular type of adsorption medium.
9. Fixed bed tests on phenol adsorption showed that as the flow rate increased, the breakthrough curve became steeper, resulting in decreasing breakthrough time. Also, increasing influent concentration or decreasing bed height reduces the breakthrough time as expected. A linear driving force model based on the adsorbent particle phase concentration difference was applied to the fixed bed phenol adsorption results. Model simulations and experimental results agreed well. They showed that the intra-particle diffusion was the rate-controlling step in the adsorption process.

CHAPTER 8 FUTURE WORK

Future work in this research can be considered in the following areas.

1. The present study was based on conducting experimental tests on a laboratory scale. For pilot-scale operation, the deviation of transport phenomena in reactors should be considered. A scaling study is therefore necessary to apply the present laboratory results to activated commercial production of activated carbons from oil-palm shells.
2. The operating parameters for the preparation of chars were analyzed by the resulting activated carbons produced. Direct assessment of the chars for the different pyrolysis conditions can be conducted at the char stage itself.
3. Both the simulation results of the concentration dependent branched pore kinetic model and the fixed bed linear driving force model indicated that the intra-particle diffusion as the rate control step in the activated carbon phenol adsorption process. Any improvement in the adsorption process should consider the possibility of reducing the limitation of the intra-particle diffusion dependency.
4. Although the simulation results of the LDFQ model were satisfactory, there was discrepancy between the simulated breakthrough curve and the experimental data. Improvement in the model or proposal of new model can be considered.

5. The present study on the fixed bed adsorption tests was conducted on a laboratory-scale setup. The breakthrough curves can be considered for design of plant-scale operations for industrial fixed bed adsorption columns.

6. The present study has conducted phenol adsorption tests using the oil-palm-shell activated carbons. Performance of these activated carbons for other chemicals can be considered.

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APPENDIX A SUMMARY OF EXPERIMENTAL RESULTS

Table A - 1 Equilibrium results of aqueous phase adsorption

Temperature (°C)	25	30	40	45	50
Equilibrium aqueous phase concentration (mg/l)	289.94	275.79	316.92	332.96	349.01
	119.28	115.86	142.20	149.45	156.69
	79.95	80.24	106.60	110.94	115.27
	52.80	45.03	70.23	72.99	75.76
	24.31	29.73	32.44	33.92	35.41
Equilibrium solid phase concentration (mg/g)	323.51	301.63	234.96	195.85	156.73
	254.90	234.76	184.18	164.03	143.88
	228.90	201.75	153.88	159.07	133.79
	174.29	160.44	110.77	122.89	100.89
	96.76	93.50	76.70	71.58	66.46

Table A - 2 Kinetic experimental results for different solution concentrations

Time (s)	Aqueous phase concn. (mg/l)	Time (s)	Aqueous phase concn. (mg/l)	Time (s)	Aqueous phase concn. (mg/l)	Time (s)	Aqueous phase concn. (mg/l)	Time (s)	Aqueous phase concn. (mg/l)
0	144.20	0	350.60	0	239.52	0	102.04	0	54.60
65	143.64	62	349.68	60	238.86	60	101.61	60	54.42
128	143.51	115	349.25	133	238.91	140	101.35	140	54.16
265	141.04	180	346.31	252	236.58	257	100.76	257	53.88
590	140.61	300	345.65	540	234.36	580	99.39	560	52.95
1018	139.02	850	338.37	1000	230.29	1020	97.38	1090	51.63
2260	131.67	1150	335.42	2590	221.16	2810	91.42	2660	48.24
5095	123.50	3640	323.49	4080	217.35	8995	84.68	8550	42.55
8608	123.29	6354	322.72	8010	215.33	16070	83.13	16620	40.38
17180	120.45	8480	321.84	11530	215.14	25440	83.71	27650	39.92
19950	120.38	14695	321.78	18290	215.81	33050	83.65	36270	39.98
25480	120.31	20700	321.62	27120	215.86	56060	82.63	67260	39.66
50340	120.35	40070	321.29	31540	214.82	79060	82.48	93930	39.59
75200	118.41	132850	319.61	66630	214.35	102070	82.98	120600	39.27
100060	119.15	192880	318.82	101710	213.84	125080	82.48	228300	38.54
177780	118.58	252910	317.58	136800	213.39	194310	81.25		
255490	117.30			297100	211.22	263530	80.59		

Table A - 3 Kinetic experimental results for different activated carbon masses

Time (s)	Aqueous phase concn. (mg/l)	Time (s)	Aqueous phase concn. (mg/l)	Time (s)	Aqueous phase concn. (mg/l)	Time (s)	Aqueous phase concn. (mg/l)
8.41mg		15.13mg		32.06mg		65.14mg	
0	259.52	0	259.50	0	259.60	0	259.12
60	256.18	60	258.74	60	256.77	61	249.94
120	252.64	119	257.87	122	252.35	120	235.05
240	250.75	240	256.24	241	245.64	240	218.80
480	249.23	479	253.54	480	237.02	482	208.50
960	248.05	960	249.20	960	227.19	960	190.73
2700	245.41	2700	239.45	2701	214.27	2700	172.77
4079	244.37	4200	231.27	4079	202.42	4079	151.81
8010	243.38	7999	229.12	8200	197.49	8201	142.04
10800	242.84	10800	228.90	10805	197.28	11530	141.23
18300	242.44	18500	228.79	18304	196.37	18304	139.93
27120	242.27	28119	228.52	27122	195.19	27129	139.34
31539	241.98	33540	228.70	32540	196.55	31539	141.50
66629	241.41	71229	227.50	70430	195.22	66629	137.45
108910	240.90	106310	227.51	105310	191.41	98110	137.54
136800	240.94	136800	225.59	136800	192.83	136800	132.50
180000	240.13	187200	224.86	187200	191.05	198000	130.34

Table A - 4 Physical characteristics of the activated carbon in aqueous adsorption

BET surface area (m^2g^{-1})	1183
Pore volume (cm^3g^{-1})	0.69
Non-micropore surface area (m^2g^{-1})	354
Non-micropore Volume (cm^3g^{-1})	0.38
Average pore size (nm)	2.33
Particle radius (mm)	0.78
Porosity	0.58

Table A - 5 Dynamic experimental results for different influent concentrations

Time (min)	Effluent concentration (mg/l)	Time (min)	Effluent concentration (mg/l)	Time (min)	Effluent concentration (mg/l)	Time (min)	Effluent concentration (mg/l)
395mg/l		204mg/l		115mg/l		53.90mg/l	
2.93g		2.93g		2.92g		2.91g	
0	1	0	1	0	1	0	1
5	1	5	1	6	1	5	1
12	1	10	1	10	1	10	1
16	1	16	1	15	1	16	1
25	1	23	1	28	1	25	1
45	3.95	46	1	45	1	45	1
80	5.93	84	1	80	1	80	1
120	6.13	122	1	120	1	120	1
185	4.6	187	1	185	1	185	1
245	10	247	3.18	245	1	250	1
280	10	280	3.13	280	1	280	1
335	11.81	335	1	335	1	335	1
455	17.22	455	4.44	455	2	455	1
520	24.43	522	4.89	520	2	520	1
540	28.04	543	5	540	2	540	1
605	35.25	606	5.07	605	2.26	605	1
1395	163.25	1393	20.35104	1395	7.11	1395	1
1705	217.33	1704	37.85424	1705	11.31	1705	2.01
1983	266.01	1983	55.46556	1985	18.13	1985	3.33
2805	348.94	2805	129.5686	2805	48.58	2805	9.98
3075	359.75	3076	147.084	3075	56.45	3075	14.15
3260	368.77	3259	153.1265	3260	64.85	3260	17.85
3525	375.98	3525	161.8597	3525	75.35	3525	22.52
4210	383.19	4210	183.092	4210	92.14	4210	33.59
4535	390.4	4533	184.0325	4535	96.86	4535	38.26
5260	392.71	4751	191.354	4750	99.48	4750	40.72
5383	393.62	4937	186.8191	4935	101.58	4935	42.69
		5619	202.4292	5620	105.71	5620	46.63
		5788	202.9718	5788	107.36	5790	47.36
		6065	201.1134	7082	111.76	6065	48.10
		6220	206.0237	7612	113.53	6220	48.59
				7853	114.01	7060	50.15
				7911	114.56	7620	51.58
				8269	114.19	8290	53.43
				9200	114.77	9203	53.36
				9539	114.42	9673	53.60
				10140	114.54	10141	53.74
				10735	114.77	10608	53.68
				11295	114.54	11509	53.43
						12150	53.68
						12746	53.63

Table A – 6 Dynamic experimental results for different flow rates

Time (min)	Effluent concentration (mg/l)	Time (min)	Effluent concentration (mg/l)	Time (min)	Effluent concentration (mg/l)	Time (min)	Effluent concentration (mg/l)	Time (min)	Effluent concentration (mg/l)
0.50ml/min		0.75ml/min		1.00ml/min		1.25ml/min		1.50ml/min	
2.92g		2.90g		2.93g		2.91g		2.91g	
1	1	1	1	0	1	0	1	0	1
34	1	20	1	5	1	3.75	1	5	1
65	1	38	1	10	1	7.5	2.01	10	1
116	1	66	1	16	1	10.5	2.21	16	1
246	1	135	1	23	1	27	2.41	23	1
382	1	214	1	46	1	43	2.61	46	2.08
652	1	368	1	84	1	64	2.81	84	3.11
1299	12.48	711	2.23	122	1	85	4.02	122	3.81
1683	16.19	935	8.25	187	1	157	7.6	187	4.28
2092	21.25	1170	13.19	247	3.17	220	8.23	247	4.76
2775	24.32	1528	21.21	280	3.11	306	10.46	280	4.99
3095	42.35	1715	28.87	335	1.2	377	13.21	335	5.61
3515	61.73	1985	36.96	455	4.42	391	16.42	455	10.01
4193	78.63	2358	45.71	522	4.86	420	18.32	522	8.47
4675	105.21	2609	52.58	543	4.97	522	22.47	543	10.12
5596	117.25	3101	63.33	606	5.05	543	27.25	606	12.23
5996	129.72	3695	84.24	1393	20.25	606	34.02	1393	48.28
6290	128.3	3997	95.98	1704	37.67	1393	124.8	1704	70.52
7071	128.63	4527	117.47	1983	55.19	1704	143.89	1983	99.8
7372	144.53	5089	137.41	2805	128.93	1983	165.16	2805	170.68
7780	149.16	5428	148.49	3076	146.36	2805	186.87	3076	185.87
8522	163.44	5891	158.69	3259	152.38	3076	189.4	3259	190.69
9153	169.25	6339	165.03	3525	161.06	3259	194.78	4010	199.74
9955	171.76	7083	178.78	4210	182.19	4010	198.45	4433	202.84
10692	173.37	7612.5	181	4533	183.13	4433	198.27	4851	203.12
11372	182.24	8061.5	186.3	4751	190.42	4851	198.79	5698	204.25
12077	174.04	8507	188.3	4937	185.9	5698	200.93		
12787	184.25	9203	193.82	5619	201.44	6084	198.19		
13558	181.48	9673	192.67	5788	201.98				
14217	184.7	10141	195.25	6065	200.13				
14997	183.11	10608.	195.04	6220	205.01				
15683	186.86	5	200.19						
16336	189.49	11509	201.31						
17134	199.35	12460	203.6						
18236	201.7	13390							
19528	200.32								
20134	202.2								
21124	202.6								

Table A - 7 Dynamic experimental results for different bed heights

Time (min)	Effluent concentration (mg/l)	Time (min)	Effluent concentration (mg/l)	Time (min)	Effluent concentration (mg/l)	Time (min)	Effluent concentration (mg/l)
5.00 cm		8.50cm		13.00cm		17.00cm	
2.51g		2.93g		3.52g		4.09g	
0	9.87	0	1.00	0	1.00	0	1.00
5	13.35	5	1.00	5	1.00	5	1.00
10	10.74	10	1.00	10	1.00	10	1.00
15	13.35	16	1.00	15	1.00	15	1.00
25	10.74	23	1.00	25	1.00	25	1.00
50	11.61	46	1.00	50	1.00	50	1.00
90	10.74	84	1.00	90	1.00	90	1.00
120	16.84	122	1.00	120	1.00	120	1.00
190	15.10	187	1.00	190	1.00	190	1.00
250	21.20	247	3.17	250	1.00	250	1.00
280	22.07	280	3.11	280	1.00	280	1.00
350	26.43	335	1.20	350	1.00	350	1.00
450	35.15	455	4.42	450	1.00	450	1.00
520	42.99	522	4.86	520	4.12	520	1.00
540	40.58	543	4.97	540	4.34	540	2.51
600	49.30	606	5.05	600	4.34	600	1.53
1400	119.91	1393	20.25	1400	9.11	1400	5.47
1700	137.34	1704	37.67	1700	15.79	1700	9.42
1980	153.91	1983	55.19	1980	23.42	1980	12.37
2805	172.21	2805	128.93	2805	73.02	2805	43.92
3070	178.32	3076	146.36	3070	96.87	3070	60.68
3260	173.96	3259	152.38	3260	114.04	3260	73.50
3525	179.19	3525	161.06	3525	130.26	3525	86.31
4210	186.16	4210	182.19	4210	153.15	4210	119.83
4535	188.78	4533	183.13	4535	164.60	4535	135.60
4750	187.03	4751	190.42	4750	168.41	4750	143.49
4937	190.06	4937	185.90	4937	177.00	4937	152.36
		5619	201.44	5534	184.63	5526	170.11
		5788	201.98	6192	195.12	6051	181.94
		6065	200.13	6710	198.93	6649	191.80
		6220	205.01	7322	201.80	7291	197.79
				7950	205.69	7839	204.08
				8590	206.28	8421	210.30
						9011	208.10
						9652	212.12
						10141	212.61
						10603	213.30

APPENDIX B SIMULATION CODES

(1) Equilibrium isotherm correlation

```
%+++++
% PROGRAM NAME: CFEIM (MATLAB Version 7.1)
% CORRELATION FOR EQUILIBRIUM ISOTHERM FROM EXPERIMENTS DATA
% WRITTEN BY JIA, QIPENG
%+++++
% The program makes estimations about the parameters in the equilibrium equations
% from the equilibrium experiment data and make a
% selection between equilibrium equations, which isotherm equation
% generates a less standard deviation.
% The selection of initial parameters for equilibrium isotherms is based on the
% experiment of phenol aqueous solution adsorption treatment with activated carbon.
%
% Date written: 23 October 2004
%+++++

%*****INPUT SECTION*****
s = input('Please designate the path of data file as a string: ');
A = load(s);
n = input('Please input the number of points in each group of data');
k0 = input('Please designate the initial value for parameters of langmuir isotherm, k0 = ');
g0 = input('Please designate the initial value for parameters of freundlich isotherm, g0 = ');
l0 = input('Please designate the initial value for parameters of langmuir_freundlich isotherm, l0 = ');
%*****

for group = 0:4
    datamark = ['bo';'bd';'bp';'bx';'bs'];
    z = cellstr(datamark);
    XDATA = A(n*group+1:n*(group+1),1)
    YDATA = A(n*group+1:n*(group+1),2)
    number = length(XDATA);

    Langmuir = inline('k(1).*XDATA./(1+k(2).*XDATA)','k','XDATA');
    options = optimset('MaxFunEvals',1900,'Tolfun',1e-10);
    [kfinal,RESNORM,RESIDUAL]=lsqcurvefit(Langmuir,k0,XDATA,YDATA,[],[],options);
    NRMSL = 100*sqrt(sum((RESIDUAL./YDATA).^2)/number);
    nnrmsL = sqrt(RESNORM./number);

    freundlich =inline('g(1).*XDATA.^(1./g(2))','g','XDATA');
    options = optimset('MaxFunEvals', 1900,'Tolfun',1e-10);
    [gfinal,RESNORM,RESIDUAL]=lsqcurvefit(freundlich,g0,XDATA,YDATA,[],[],options);
    NRMSf = 100*sqrt(sum((RESIDUAL./YDATA).^2)/number);
    nnrmsf = sqrt(RESNORM./number);

    Langmuir_freundlich=inline('l(1).*(l(2).*XDATA).^(1./l(3))./(1+l(2).*XDATA).^(1/l(3))','l','XDATA');
    options = optimset('MaxFunEvals', 1900,'Tolfun',1e-10);
    [lfinal,RESNORM,RESIDUAL]=lsqcurvefit(Langmuir_freundlich,l0,XDATA,YDATA,[],[],options);
    NRMSlp = 100*sqrt(sum((RESIDUAL./YDATA).^2)/number);
    nnrmslp = sqrt(RESNORM./number);

    NRMS = [NRMSL NRMSf NRMSlp]
    NNRMS = [nnrmsL nnrmsf nnrmslp]
    ascendNRMS = sort(NRMS);
    ascendNNRMS = sort(NNRMS);

    if ascendNRMS(1)~NRMSf&ascendNRMS(1)~NRMSlp
```

```

disp('The Langmuir isotherm gives the better fit')
sprintf('The expression of the equilibrium is: Q=%dXC/(1+%dXC)',kfinal)
elseif ascendNRMS(1)~=NRMStp
disp('The Freundlich isotherm gives the better fit')
sprintf('The expression of the equilibrium is: Q=%dXC.^(1/%d)',gfinal)
else
disp('The Langmuir-freundlich isotherm gives the better fit')
sprintf('The expression of the equilibrium is: Q=%dX(%dXC).^(1/%d)/(1+(%dXC).^(1/%d))',lfinal)
end

%*****OUTPUT SECTION*****
x=[min(XDATA):1:max(XDATA)];
plot(x,Langmuir(kfinal,x),'k-',x,frendlich(gfinal,x),'m-
',x,Langmuir_freundlich(lfinal,x),'k:',XDATA,YDATA,char(z(group+1)))
legend('Langmuir','frendlich','three parameter')
hold on
end
%***** THE END *****%

```

(2) Adsorption kinetics computation:

```

%+++++
% PROGRAM NAME: CDBPKM.M (MatLab Version 7.1)
% Concentration dependent branched pore kinetic model for batch
% adsorption system
% Written by Jia, Qipeng
%+++++
%The program solves the problem of adsorption kinetics in a batch
%activated carbon phenol adsorption system with langmuir isotherm
%under isothermal conditions.
%
%Ref: Chapter 5 AQUEOUS PHASE ADSORPTION IN BATCH AND KINETICS MODELING,
% eqs. (5.19-24)
%Date written: 5 December 2004
%+++++

clear all
clc
% DECLARE SOME GLOBAL VARIABLES
global n u A B C w
global f R s
global aL kL Qmus concentration
global c0 cb ci c conci cboundary
global Q0 Qmub Qmui x yB
global Qsubb Qsubi Qsub Qsat t_initial t_final tout omega omega0
global Deff0 k
global FBiot PBiot SFact rou
global number
%-----INPUT SECTION-----
s = 2;
R = 0.0782;
f = 0.36;
ci = (259.5)*1e-6/94;
cb = (259.5)*1e-6/94;
c0 = (259.5)*1e-6/94;
Kb = 1.97e-7;
Deff0 = 3.74e-7;
PBiot = Kb*R.^2./(f*Deff0);
kL = 5.22*1e3*12;
aL = 0.014*1e6*94;

```

```

Qmus      = kL/aL;
Q0        = kL*c0./(1+aL*c0);
Qsat      = f*Qmus/Q0;
Vf        = 50;
m         = 0.01513/12;
SFact     = m*Q0/Vf/c0;
Qmui      = 0;
Kf        = 1.34e-1;
rou       = 2.0;
FBiot     = (Kf*c0*R)/(f*Deff0*Q0*rou);
k         = 0.28;
t_initial = 0;
%-----COLLOCATION SECTION-----
n         = 20;
n0        = 0;
n1        = 1;
al        = 1;
be        = (s-1)/2;
nt        = n + n0 + n1;
A         = zeros(nt);
B         = zeros(nt);
C         = zeros(nt);
[dif,u]   = JCRoot(n,n0,n1,al,be);
A         = AB(n,n0,n1,1,dif,u);
B         = AB(n,n0,n1,2,dif,u);
w         = RDW(n,n0,n1,al-1,be,u,dif);
for i=1:nt;
    C(i,:) = 4.*u(i).*B(i,:)+6.*A(i,:);
end
Qsubi     = 0;
cbulk     = cb/c0;
amounti   = 0;
amountb   = Q0;
omega01   = (Qmui/Q0)*ones(1,n);
omega02   = (Qsubi/Q0)*ones(1,n);
omega0    = [omega01 omega02 cbulk]';
t_final   = 0.5393;
%-----CALL ODE SOLVER-----
options   = odeset('Reltol',1e-2,'Abstol',1e-5,'BDF','on');
[tout,omega] = ode45('DAEs',[t_initial t_final],omega0,options);
%-----SOLUTIONS: CONCENTRATION PROFILES-----
time      = tout.*R.^2./Deff0;
for i=1:length(tout)
    y1(i,1:n) = omega(i,1:n);
    conc(i)   = omega(i,2*n+1);
end
for i=1:length(tout)
    ynp1(i)   = fzero('fncn',[0,1],[y1(i,:),conc(i)])
end
y1         = [y1 ynp1]';

for i=1:length(tout)
    Qnonmicropore(i,:) = Q0.*f*y1(i,:);
end
concentration = conc.*c0;
output       = [time';concentration];
fid          = fopen('concentration decay data.txt','w');
fprintf(fid,'Condition at Kb=%g Deff0=%g Kf=%g k=%g\n',Kb,Deff0,Kf,k);
fprintf(fid,'%6.2f %12.8f\n',output);
fclose(fid);

```

```
%-----
% PLOTTING
%-----
figure(1)
plot(time,conc,'r-');
xlabel('time(sec)');
ylabel('solution concentration (nondimensional)');
title('solute concentration in aqueous solution');
grid;

figure(2)
surf(u,tout,y1);
shading interp
xlabel('nondimensional radius');
ylabel('nondimensional time');
zlabel('nondimensional adsorbate concentration in adsorbent')
grid;
%----- THIS IS THE END OF THIS PROGRAM -----
```

(3) Fixed bed computation with LDFQ:

```
%+++++
% PROGRAM NAME: LDFQ.M (MatLab Version 7.1)
% CORRELATION FOR BREAKTHROUGH CURVE FROM EXPERIMENTAL DATA
% WRITTEN BY JIA, QIPENG
%+++++
% This program will correlated out the parameters in the analytical solution
% of breakthrough curve from dynamic experiment
%
% Ref: Chapter 6 FIXED BED ADSORPTION FOR AQUEOUS PHASE, eqs. (6.32)
%
% Date written: 15 June 2005
%+++++

clear all
clc

%*****INPUT SECTION*****
s = input('Please designate the path of data file as a string: ');
A = load(s);
C0 = input('Please input the influent concentration in mg/l');
k1 = input('Please designate the initial value for parameters  $k_s / \rho_b$ , k1 = ');
k2 = input('Please designate the initial value for parameters of characteristic time, k2 = ');
k3 = input('Please designate the initial value for parameters of equilibrium parameter, k3 = ');
%*****

timedata = A(:,1); % in minutes
concentration = A(:,2); % in mg/l
concentrationdata = concentration/C0;
k0 = [k1,k2,k3];
Breakthrough = inline('(k(3)/(1-k(3))*log(concentrationdata)-1/(1-k(3))*log(1-concentrationdata)-1)/k(1)+k(2)','k','concentrationdata');
options = optimset('display','iter','MaxFunEvals',1e4,'MaxIter',1e4,'MaxFunEvals',1e5);
[kfinal,resnorm,residual]=lsqcurvefit(Breakthrough,k0,concentrationdata,timedata,[],[],options)
x = [min(concentrationdata):1e-2:max(concentrationdata)]
plot(timedata,concentrationdata,'bo',Breakthrough(kfinal,x),x,'k-')

%----- THIS IS THE END OF THIS PROGRAM -----
```