PREPARATION, CHARACTERIZATION AND EVALUATION OF MESOPOROUS ACTIVATED CARBONS DERIVED FROM AGRICULTURAL BY-PRODUCTS FOR ADSORPTION OF METHYLENE BLUE AND 2,4,6-TRICHLOROPHENOL

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LIST OF SYMBOLS

		Unit
A	Arrhenius factor	-
A_c	Area under breakthrough curve	-
A_i	Spectrometry absorbance	-
A_T	Constant for Temkin isotherm	L/g
a	Initial sorption rate for Elovich equation	mg/g h
B	Constant for Temkin isotherm	-
B_{DR}	Constant for Dubinin-Radushkevich isotherm	-
B_t	Constant for Boyd model	-
b	Constant for Elovich equation	g/mg
C	Solute/outlet concentration	mg/L
C_{ad}	Difference between inlet/initial and outlet/equilibrium concentration	mg/L
C_{de}	Concentration of adsorbate desorbed	mg/L
C_e	Concentration of adsorbate at equilibrium	mg/L
C_i	Constant for Intraparticle diffusion model	mg/g
C_t	Concentration of adsorbate at time, t	mg/L
C_0	Initial/inlet adsorbate concentration	mg/L
D_p	Average pore diameter	nm
E	Mean free energy	J/mol
E_a	Arrhenius activation energy of adsorption	kJ/mol
F	Fraction of solute adsorbed for Boyd model	-
K_F	Adsorption or distribution coefficient for Freundlich isotherm	mg/g $(L/mg)^{1/n}$
K_L	Rate of adsorption for Langmuir isotherm	L/mg
K_{RP}	Constant for Redlich-Peterson isotherm	L/g
k_{pi}	Adsorption rate constant for intraparticle diffusion model	mg/g $h^{1/2}$
k_1	Adsorption rate constant for pseudo-first-order kinetic model	1/h
k_2	Adsorption rate constant for pseudo-second-order kinetic model	g/mg h
N	Total number of experiments required/data point	-
n	Constant for Freundlich isotherm	-

Q	Volumetric flow rate	mL/min
Q_o	Adsorption capacity for Langmuir isotherm	mg/g
q_e	Amount of adsorbate adsorbed per unit mass of adsorbent at equilibrium	mg/g
q_{eq}	Equilibrium solute uptake in fixed-bed column	mg/g
q_s	Constant for Dubinin-Radushkevich isotherm	mg/g
q_t	Amount of adsorbate adsorbed per unit mass of adsorbent at time, t	mg/g
$q_{t,cal}$	Calculated adsorption uptake at time, t	mg/g
$q_{t,exp}$	Experimental adsorption uptake at time, t	mg/g
q_{total}	Total adsorbed solute quantity in fixed-bed column	mg/g
R	Universal gas constant	8.314 J/mol K
R_L	Separation factor	-
R^2	Correlation coefficient	-
$\mathrm{S}_{\mathrm{BET}}$	BET surface area	m^2/g
T	Transmittance	%
T	Absolute temperature	K
t	Time	h
t_{total}	Total flow time	min
V	Solution volume	L
$\mathrm{V}_{\mathrm{meso}}$	Mesopore volume	cm^3/g
V_{T}	Total pore volume	cm^3/g
W	Dry weight of adsorbent	g
w_{after}	Dry weight of activated carbon after washing	g
w_{before}	Dry weight of activated carbon before washing	g
w_C	Dry weight of prepared activated carbon	g
w_{char}	Dry weight of char.	g
w_{KOH}	Dry weight of potassium hydroxide pellets	g
w_o	Dry weight of precursor	g
x	Activated carbon preparation variable	-
Y	Predicted response	-

Greek letters

α	Constant for Redlich-Peterson isotherm	$(\mathrm{L/mg})^{\beta}$

β	Constant for Redlich-Peterson isotherm	-
ΔG^o	changes in standard free energy	kJ/mol
ΔH^o	changes in standard enthalpy	kJ/mol
Δq_t	Normalized standard deviation	%
ΔS^o	changes in standard entropy	J/mol K
ε	Constant for Dubinin-Radushkevich isotherm	-
ε_λ	Molar absorptivity coefficient of solute	-
λ	Wavelength	nm

LIST OF ABBREVIATIONS

AC	Activated carbon
ANOVA	Analysis of variance
BET	Brunauer-Emmett-Teller
BJH	Barrett-Joyner-Halenda
CCD	Central composite design
CH	Coconut husk
CR	Chemical recovery
DR	Dubinin-Radushkevich
EFB	Oil palm empty fruit bunch
EPA	Environmental Protection Agency
FTIR	Fourier Transform Infrared
GAC	Granular activated carbon
IR	Impregnation ratio
IUPAC	International Union of Pure and Applied Chemistry
LHV	Lower heating value
MB	Methylene blue
MSDS	Material Safety Data Sheet
MTZ	Mass transfer zone
PAC	Powdered activated carbon
PF	Oil palm fibre
PS	Oil palm shell
RP	Redlich-Peterson
RSM	Response surface methodology
rpm	Rotation per minute
SEM	Scanning electron microscopy
TCP	Trichlorophenol
TGA	Thermogravimetric analyzer
UK	United Kingdom
US	United States of America
2FI	Two factor interaction

PENYEDIAAN, PENCIRIAN DAN PENILAIAN KARBON TERAKTIF BERLIANG MESO YANG DIHASILKAN DARIPADA PRODUK SAMPINGAN PERTANIAN BAGI PENJERAPAN METILENA BIRU DAN 2,4,6-TRIKLOROFENOL

ABSTRAK

Penggunaan secara meluas karbon teraktif komersil dihadkan oleh kos yang tinggi disebabkan oleh penggunaan bahan mentah yang tidak dapat diperbaharui. Oleh itu, penyelidikan ini bertujuan untuk menyiasat kemungkinan bagi menghasilkan karbon teraktif berliang meso daripada produk sampingan pertanian yang banyak terdapat di Malaysia, iaitu tempurung, gentian dan tandan buah kosong kelapa sawit (PS, PF, EFB) serta sabut kelapa (CH), bagi aplikasi dalam penyingkiran metilena biru (MB) dan 2,4,6-triklorofenol (2,4,6-TCP) daripada larutan akuas. Pengaktifan fizikal kimia yang merangkumi penjerapan isi dengan kalium hidroksida (KOH) diikuti oleh penggasan karbon dioksida (CO_2) digunakan untuk menyediakan karbon teraktif. Keputusan rekabentuk ujikaji menunjukkan bahawa suhu pengaktifan CO_2, masa pengaktifan CO_2 dan nisbah jerap isi (IR) ialah faktor-faktor penting yang mempengaruhi hasil dan prestasi penjerapan MB dan 2,4,6-TCP bagi serbuk karbon teraktif. Keadaan optima yang diperoleh untuk menyediakan karbon teraktif bagi penjerapan MB daripada pelopor terpilih ialah 816-862 ^{o}C, 1.0-1.8 jam dan 2.9-3.9, masing-masing untuk suhu pengaktifan CO_2, masa pengaktifan CO_2 dan IR manakala keadaan optima yang diperoleh untuk menyediakan karbon teraktif bagi penjerapan 2,4,6-TCP ialah 750-857 ^{o}C, 1.0-2.3 jam dan 2.6-2.9, masing-masing untuk ketiga-tiga pemboleh ubah yang dikaji. Semua karbon teraktif yang disediakan adalah berliang meso dengan luas permukaan dan isipadu liang meso yang tinggi serta diameter liang purata lebih besar daripada 2.2 nm. Analisa mikroskopi elektron pengimbasan membuktikan bahawa karbon teraktif ini menunjukkan taburan saiz liang yang homogen. Analisa inframerah jelmaan Fourier memaparkan kehadiran pelbagai kumpulan berfungsi pada permukaan karbon teraktif ini. Kesan-kesan kepekatan awal bahan jerap (50-500 mg/L untuk MB dan 25-250 mg/L untuk 2,4,6-TCP), masa sentuh, suhu larutan (30-50 ^{o}C), pH larutan (2-12), garis sesuhu, kinetik dan termodinamik bagi sistem-sistem penjerapan tersebut dinilai melalui kajian penjerapan kelompok. Penjerapan MB dan 2,4,6-TCP meningkat dengan peningkatan kepekatan awal dan masa sentuh. Kecekapan penyingkiran MB dan 2,4,6-TCP adalah tertinggi pada pH 12 dan pH 2 masing-masing. Penjerapan MB pada semua karbon teraktif ini adalah terbaik dipadankan oleh model garis sesuhu Langmuir manakala penjerapan 2,4,6-TCP adalah lebih baik dipadankan oleh model Freundlich dan model Redlich-Peterson. Penjerapan MB pada CHMB, PFMB, EFBMB dan PSAC serta penjerapan 2,4,6-TCP pada CHTCP, PFTCP dan EFBTCP adalah terbaik dihuraikan oleh model kinetik pseudo tertib kedua manakala penjerapan 2,4,6-TCP pada PSAC adalah terbaik dihuraikan oleh model kinetik pseudo tertib pertama. Semua proses penjerapan ini menunjukkan tenaga pengaktifan kurang daripada 40 kJ/mol yang mewakilkan mekanisme penjerapan fizikal. Turus PSAC berprestasi dengan lebih baik dengan menggunakan kepekatan masukan dan kadar aliran suapan yang lebih rendah serta lapisan penjerap yang lebih tinggi. Nyahjerapan ethanol ialah satu teknik yang mungkin bagi penjanaan semula karbon teraktif yang telah digunakan.

PREPARATION, CHARACTERIZATION AND EVALUATION OF MESOPOROUS ACTIVATED CARBONS DERIVED FROM AGRICULTURAL BY-PRODUCTS FOR ADSORPTION OF METHYLENE BLUE AND 2,4,6-TRICHLOROPHENOL

ABSTRACT

The prolific use of commercial activated carbon is restricted by the high costs due to the use of non-renewable starting material. Therefore, this study aims to investigate the feasibility of producing mesoporous activated carbons from agricultural by-products abundantly available in Malaysia, namely oil palm shell (PS), fibre (PF) empty fruit bunch (EFB) and coconut husk (CH), for application in removing methylene blue (MB) and 2,4,6-trichlorophenol (2,4,6-TCP) from aqueous solutions. Physiochemical activation consisting of potassium hydroxide (KOH) impregnation plus carbon dioxide (CO_2) gasification was used to prepare the activated carbons. The experimental design results revealed that CO_2 activation temperature, CO_2 activation time and KOH impregnation ratio (IR) were important factors influencing the powdered activated carbon yields and adsorption performance for MB and 2,4,6-TCP. The optimum conditions obtained for preparing the activated carbons for MB adsorption from the selected precursors were 816-862 ^{o}C, 1.0-1.8 h and 2.9-3.9, respectively for CO_2 activation temperature, CO_2 activation time and IR whereas the optimum conditions obtained for preparing the activated carbons for 2,4,6-TCP adsorption were 750-857 ^{o}C, 1.0-2.3 h and 2.6-2.9, respectively for the same three variables studied. All the activated carbons prepared were mesoporous with high mesopore surface areas, mesopore volumes and average pore diameters larger than 2.2 nm. SEM analyses proved that the activated carbons demonstrated homogeneous pore size distributions. FTIR analyses revealed the presence of various functional groups on the activated carbon surfaces. The effects of adsorbate initial concentration (50-500 mg/L for MB and 25-250 mg/L for 2,4,6-TCP), contact time, solution temperature (30-50^{o}C), solution pH (2-12), isotherms, kinetics and thermodynamics of the adsorption systems were evaluated through batch adsorption tests. The MB and 2,4,6-TCP adsorption uptakes increased with increasing initial concentration and contact time. The MB and 2,4,6-TCP removal efficiency was the highest at pH 12 and pH 2, respectively. Adsorption of MB on all the activated carbons were best fitted by the Langmuir isotherm model whereas adsorption of 2,4,6-TCP were better fitted by the Freundlich and Redlich-Peterson models. Adsorption of MB on CHMB, PFMB, EFBMB and PSAC as well as adsorption of 2,4,6-TCP on CHTCP, PFTCP and EFBTCP were best described by the pseudo-second-order kinetic model whereas adsorption of 2,4,6-TCP on PSAC was best described by the pseudo-first-order model. All the adsorption processes showed activation energy lower than 40 kJ/mol which represented physisorption mechanism. The PSAC column performed better with lower adsorbate inlet concentration, lower feed flow rate and higher adsorbent bed. Ethanol desorption was a possible technique for regenerating the spent activated carbons.

CHAPTER ONE

INTRODUCTION

1.0 Research Overview

This chapter presents an overview of the research background. The scope covers the current scenario on water pollution problem in Malaysia, focusing mainly on the textile industrial effluents. The needs to find a more economical way to effectively solve the problem by applying adsorption on activated carbons derived from agricultural by-products are described. The problem statement and the objectives of this research as well as the organization of this thesis are then presented.

1.1 Water Pollution - Current Situation and Problem

Water pollution can be considered in a number of ways but in simple terms it is addition of an array of elements to the water (Forster, 2003). Industrialization and urbanization have resulted in increased water usage and the use of chemicals of increasing complexity. Water pollution is a very persistent problem and the intensive disposal of toxic substances without control constitutes a real danger. The Department of Environment, Malaysia reported that Malaysian rivers are heavily polluted with mean biochemical oxygen demand levels nearly six times the international standard (REACH, 2008).

Malaysia, like other developed and developing countries, has enjoyed remarkable growth over the last few decades, with industrialization and agriculture playing leading roles in this success story. The rapid development of industries in Malaysia has contributed to considerable pollution to many rivers in the country.

Surface water pollution by organic matter is one of the major problems in most areas. According to Malaysia Environment Quality Report 2004, 17991 water pollution point sources were recorded in 2004 comprising mainly sewage treatment plants (54%), manufacturing industries (38%), animal farms (5%) and agro-based industries (3%) (WEPA, 2004). The Department of Environment has been given the authority to monitor and enforce the laws regarding environmental issues. The most important law which directly relates to environmental pollution is the Environmental Quality Act 1974 (amended 1985) (EQA, 2002).

1.2 Textile Industrial Effluent - Source of Water Pollution

The growth of textile industry in Malaysia accelerated in the early 1970s when the country embarked on a path of export-oriented industrialization. With exports valued at RM10.6 billion, the industry was the seventh largest contributor to total earnings from manufactured exports in 2006. From the statistics obtained from the Malaysian Industrial Development Authority (MIDA), the total number of textile factories in Malaysia is approximately 1500**,** with 40% of the textile factories especially the wet processing plants being located in Batu Pahat, Johor.

According to a guideline by Hessel *et al*. (2007), the textile industry covers a wide range of activities, from preparation of the raw material to ennoblement treatment which consists of pre-treatment, dyeing, printing and finishing of textile materials. These activities are all water-consuming as well as highly chemically polluting. Water is used as the main solvent for removing impurities and applying dyes and finishing agents. The various baths are then discharged in the environment as aqueous effluents. In Malaysia, wastewaters containing dyes and phenolic compounds have been classified as scheduled wastes under Environmental Quality (Scheduled Wastes) Regulations 1989 (EQA, 2002). Therefore, the high volume of wastewaters being produced by this polluting industry needs to be properly treated before discharged into the watercourses, as it contains large amount of various dyes and phenolic compounds which will pose serious environmental problems because of their colour as well as high chemical oxygen demand and toxicity (Kumar *et al.*, 2008).

1.2.1 Dyes

Coloured dye wastewater arises as a direct result of the production of the dye and also as a consequence of its use in the textile industry (Allen and Koumanova, 2005). Dyes are chemicals which on binding with a material will give colour to the material. Dyes are ionic, aromatic organic compounds with structures including aryl rings which have delocalized electron systems. The colour of a dye is provided by the presence of a chromophore group. Over $7x10^5$ tons and approximately 10,000 different types of dyes and pigments are produced world wide annually and it is estimated that 10-15% of the dyes is lost in the effluent during the dyeing process (Senthilkumaar *et al.*, 2005).

Effluents from dyeing processes are generally highly coloured with a large amount of suspended organic solids. They are important sources of water pollution because dyes in wastewaters undergo chemical and biological changes, consume dissolved oxygen and destroy aquatic life. These coloured compounds are not only aesthetically displeasing but also inhibiting sunlight penetration into the stream and reducing the photosynthetic reaction. Colour in effluents can cause problems in several ways: dyes can have acute and /or chronic effects on exposed organisms depending on the exposure time and dye concentration; dyes are inherently highly visible where concentrations as low as 0.005 mg/L and capture the attention of both the public and the authorities (Allen and Koumanova, 2005).

Basic dyes were known from the past as synthetic dyes. By definition, basic dyes are cationic dyes with cationic properties originating from positively charged nitrogen or sulfur atoms (El Qada *et al*., 2006). The tinctorial value of basic dyes is very high; less than 1 mg/L of the dye produces an obvious coloration. Methylene blue (MB), one of the most important basic dyes, has a wide application including colouring paper, hair colourant, dyeing cottons, wools, coating for paper stock, etc. Acute exposure to MB will cause increased heart rate, vomiting, shock, Heinz body formation, cyanosis, jaundice, quadriplegia and tissue necrosis in human (Kumar and Kumaran, 2005). MB is one of the most recognized probe molecules for assessing the removal capacity of a specific adsorbent from the aqueous phase, especially for moderate size pollutant molecules with average pore size ≥ 1.5 nm (Girgis and El-Hendawy, 2002; Stavropoulos and Zabaniotou, 2005).

1.2.2 Phenolic Compounds

Phenolic compounds are common contaminants found in the water streams of textile industry. These hazardous wastes are also released by industries such as coke ovens in steel plants, petroleum refineries, petrochemical, chemical, phenolic resin as well as pharmaceutical (Gao and Wang, 2007). Phenolic derivatives belong to a group of common environmental contaminants where their presence of even low concentrations can be an obstacle to the use of water (Ioannidou and Zabaniotou, 2007). As one type of the most hazardous materials, phenolic compounds are carcinogenic, mutagenic and resistant to biodegradation, and thus have to be decomposed before discharging into receiving waters, in order to avoid the biomagnified toxicity to aquatic flora and fauna through various food chains (Wang *et al.*, 2007). The US Environmental Protection Agency calls for a maximum phenol content in wastewater of 1 mg/L. In Malaysia, the permitted limit of phenol in effluent is 0.001 and 1.0 mg/L, respectively for Standard A and Standard B, under the Environmental Quality (Sewage and Industrial Effluents) Regulations 1978 (EQA, 2002).

Chlorophenols are a group of chemicals in which chlorines (between one and five) have been added to phenol. Chlorophenols are weak acids which permeate human skin by in vitro and are readily absorbed by gastro-intestinal tract. The acute toxicity of chlorophenols includes increased respiratory rate, vomiting and nausea (Radhika and Palanivelu, 2006). Chlorophenols also create complicated problems to water bodies such as bad odour and taste in drinking water, death of aquatic life, inhibition of normal activities of microbial population in wastewater treatment plant, etc.

2,4,6-trichlorophenol (2,4,6-TCP) is one of the most commonly used chlorophenols. 2,4,6-TCP has been reported to cause adverse effects on human nervous system and respiratory problems such as chronic bronchitis, cough and altered pulmonary function (Hameed, 2007). The stable C–Cl bond and the position of chlorine atoms relative to the hydroxyl group are responsible for their toxicity and persistence in the biological environment (Tzou *et al.*, 2008). Due to its high toxicity, carcinogenic properties, structural stabilization and persistence in the environment, the removal of 2,4,6-TCP from the environment is therefore crucial. However, from the literature search, there are very limited works done on the removal of this hazardous pollutant from aqueous solutions, especially by using activated carbon adsorption technique.

1.3 Wastewater Treatment Technology

In order to remove organic pollutants and dyes from wastewaters, many physicochemical treatments have been proposed, such as coagulation, sedimentation, filtration, oxidation and adsorption. In common, the technologies for removal of these pollutants from effluents can be divided into three categories: biological, chemical and physical. However, there is no single technique which is suitable for all applications, as each of them has its own advantages and drawbacks.

Biological treatment is often the most economical alternative compared to other physical and chemical processes. Biological treatment processes are reported to be efficient in reducing organic pollutants concentration, but are ineffective in removing colour (Namane *et al*., 2005). Biodegradation methods are commonly applied to the treatment of industrial effluents because many microorganisms are able to accumulate and degrade different pollutants. However, their application is often restricted due to technical constraints as it requires a large land area, sensitivity towards diurnal variation, toxicity of some chemicals and less flexibility in design and operation. Chemical methods on the other hand are often expensive and the accumulation of concentrated sludge creates a disposal problem. Besides, it may be possible that a secondary pollution problem will arise due to excessive chemical use.

Advanced oxidation process electrochemical reduction may be efficient in the removal of dyes but their initial and operational costs are high. Although chemical methods are efficient for treatment of wastewaters, they are very costly and commercially unattractive. The high electrical energy demand in advanced oxidation and the consumption of chemical reagents in chemical processes are common problems. For physical methods, liquid phase adsorption provides an attractive alternative, especially if the adsorbent is inexpensive and does not require additional pre-treatment before its application (Crini, 2006).

The removal of colour from dye bearing effluents is one of the major problems due to the difficulty in treating such wastewaters by conventional treatment methods. Majority of the dyes used in textile industries are synthetic in nature and are usually composed of aromatic rings in their structure which makes them inert and non-biodegradable when discharged into the waste streams (Ofomaja and Ho, 2007). Crini (2006) has summarized the various technologies used to remove dyes, together with their respective advantages and disadvantages, as listed in Table 1.1.

Various treatment methods have also been applied to remove chlorophenols from aqueous solutions, such as biological treatment using anaerobic granular sludge and dead fungus as well as adsorption technology using activated clay and activated carbons. Other treatment technologies include chemical oxidation, air stripping, incineration, ion exchange and solvent extraction. Nevertheless, the efficiency of traditional biological treatment method is not satisfying due to chlorophenol’s structural stabilization and toxicity (Gao and Wang, 2007). Adsorption on activated carbon however, is one of the most effective and widely used techniques in treating high strength and low volume of phenolic wastewater (Radhika and Palanivelu, 2006; Mourão *et al.*, 2006).

Table 1.1 Principal existing processes for dye removal (Crini, 2006)

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

1.4 Activated Carbon Adsorption

According to literature, liquid phase adsorption using activated carbon has become one of the most popular methods for removal of various pollutants from wastewaters, owing to its efficiency in the removal of pollutants. Activated carbon adsorption has been cited by the US Environmental Protection Agency as one of the best available environmental control technologies (Moreno-Castilla, 2004). Activated carbon is the most popular adsorbent used in industry because of its high adsorption ability for a large number of organic compounds due to its organophilic character (Allen and Koumanova, 2005). This adsorbent has the advantage of exhibiting high adsorption capacity due to its high specific surface area, adequate pore size distribution and relatively high mechanical strength (Mohanty *et al*., 2005).

Despite their prolific use, certain problems with the high costs of commercial activated carbons have limited their applications. The high production cost is mainly due to the expensive and non-renewable starting materials such as bituminous coal, lignite and petroleum coke, which is a major economic consideration. Therefore, this has prompted a growing research interest in the production of activated carbons from abundant, renewable and low cost materials such as agricultural and industrial by-products.

1.5 Agricultural Biomass - Precursor for Activated Carbon Production

The first commercial activated carbon was prepared from wood and peat. In fact, any carbonaceous material can be employed to obtain activated carbon. Biomass is produced from organic materials, either directly from plants or indirectly from industrial, commercial, domestic or agricultural products. Biomass falls into two main categories (Biofuels and Bioenergy Information, 2007):

- Woody biomass includes forest products, untreated wood products, energy crops and short rotation coppice, which are quick-growing trees like willow.
- Non-woody biomass includes animal waste, industrial and biodegradable municipal products from food processing and high energy crops. Examples are rape, sugar cane, maize.

Agricultural biomass is considered to be very important feedstock in virtue of especially two facts: they are renewable sources and low cost materials. Besides, this biomass contains high concentration of volatiles and low ash content which is ideal for creating highly porous structures within the activated carbon matrix (Dias *et al.*, 2007). In Malaysia, agricultural by-products are the most abundant biomass resources, exceeding 70 million tonnes annually. The high production rate of biomass throughout the year is mainly due to the high sunlight intensity/time and high rainfall. As can been seen from Figure 1.1, palm oil industry is the main contributor of agricultural biomass in Malaysia, generating 94% of the total agricultural biomass (Hassan and Yacob, 2007).

One significant problem faced by the agricultural industries currently is the managing of the by-products and wastes produced. The disposal of the by-products in large quantity is difficult and expensive to the industries. At present, some agricultural by-products are being used as boiler fuel, however large portion of the wastes are either burnt using open burning or dumped aside which will cause environmental pollution as well as harboring pests and diseases. This will result not only in wastage, but also severe economic set back to the industries and the country.

Therefore in order to make better use of these abundant agricultural by-products, they need to be utilized effectively to the point that they can be considered as valuable products that will serve as raw materials to support another industry. For this purpose, it is proposed to convert the negative value agricultural by-products into valuable products such as activated carbons. The use of agricultural wastes for the production of activated carbons is very attractive from the point of view of their contribution to decrease the cost of waste disposal, hence helping in environmental protection.

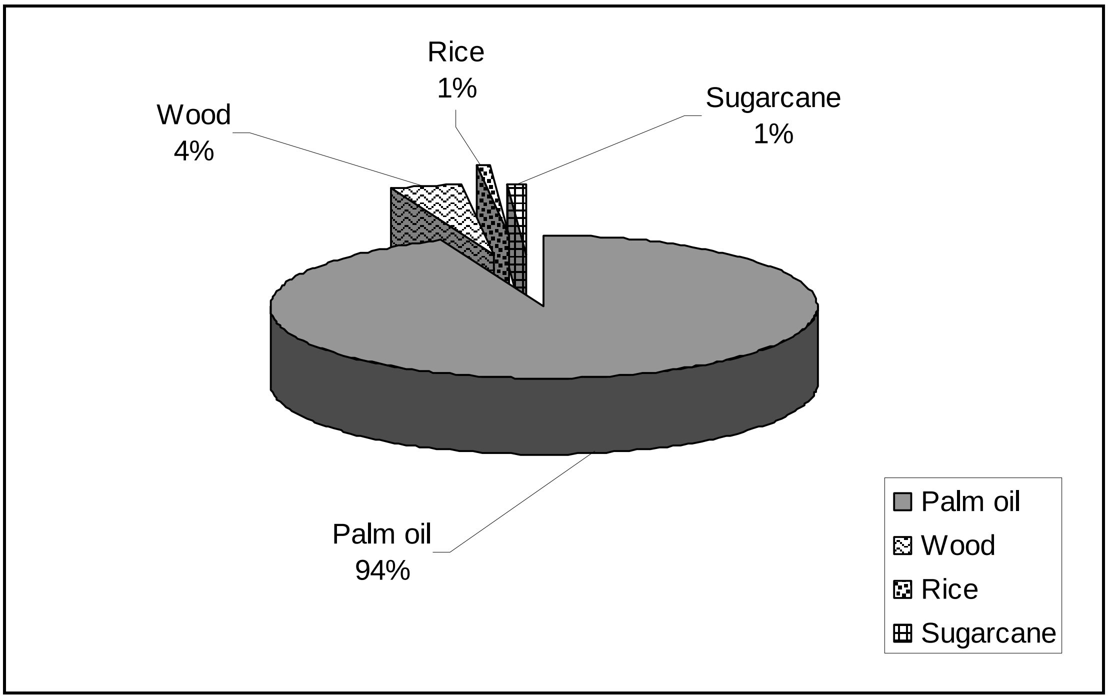

Figure 1.1 Source of agricultural by-products in Malaysia (Hassan and Yacob, 2007)

1.6 Problem Statement

Industrialization has resulted in increased water usage and the use of chemicals of increasing complexity. The rapid growth of textile industry in Malaysia has caused increasing concern about the hazardous effects of dyes and phenolic compounds which are widely found in textile industrial effluents. Activated carbon adsorption has been proved to be superior as compared to other techniques for wastewater treatment due to its simplicity of design, high efficiency and ease of operation. However, the prolific use of commercial activated carbons is restricted by the high costs due to the use of non-renewable and expensive starting materials to produce the activated carbons. Recently, special emphasis has been given on the preparation of activated carbons from renewable, abundant and low cost precursors.

Agricultural industry in Malaysia produces large amount of by-products each year, and one significant problem faced by this industry currently is the managing of the wastes produced. However, not many studies have been reported on the utilization of potential agricultural by-products abundantly available in Malaysia, such as oil palm fibre, oil palm empty fruit bunch and coconut husk, especially on converting these biomass into high value products such as activated carbons which are suitable for liquid phase adsorption. Conversion of agricultural by-products into activated carbons will turn negative-value wastes into useful, value-added products, hence solving the waste disposal problem and second, the costs of activated carbon production will be reduced. Moreover, the use of agricultural by-products represents a potential source of adsorbents which will contribute to solving the water pollution problem in Malaysia.

Activated carbon production costs can be reduced by either choosing a cheap raw material or by applying a proper production method; nevertheless, it is still a challenge to produce activated carbons with very specific characteristics which are suitable for certain applications. Therefore, it is of extreme relevance to find suitable low cost precursors that are economically attractive and at the same time able to produce activated carbons with high adsorption performance. From the literature, a few studies have been carried out on converting oil palm shell into activated carbons, however the activated carbons produced were microporous materials which were applied only for gas phase adsorption. Most of the studies carried out by previous researchers applied either physical or chemical activation method which yielded activated carbons which were either having low surface areas or mainly microporous in nature and not efficient in removing larger molecules such as dyes and phenolic compounds from aqueous solutions. Recently, combination of both physical and chemical activations has become priority as this physiochemical activation method can produce activated carbons with high surface areas and pore volumes, especially those contributed by mesopores, which are important characteristics of activated carbons applied for liquid phase adsorption. Besides, limited studies have been reported on design and optimization of activated carbon preparation conditions, which are important to produce activated carbons with high product yield and adsorption performance.

Methylene blue is one of the most commonly used dyes and it is known to cause various harmful effects on human. Besides, adsorption of methylene blue has been one of the most recognized probe molecules for assessing the removal capacity of a specific adsorbent from aqueous phase, especially for moderate size pollutant molecules with average pore size ≥1.5 nm. For this reason, methylene blue is selected to be the adsorbate in this research. 2,4,6-trichlorophenol is chosen to represent smaller size pollutant molecules due to its common use, high toxicity, structural stabilization and persistence in the environment. Besides, from the literature search, very limited studies have been reported on the removal of 2,4,6-trichlorophenol, especially using activated carbon adsorption. It is utmost important to remove these hazardous pollutants from aqueous solutions and therefore, evaluation of the adsorption performance of the activated carbons prepared on these pollutants is crucial.

This study aims to investigate the feasibility of preparing mesoporous activated carbons from agricultural by-products abundantly available in Malaysia, namely oil palm shell, oil palm fibre, oil palm empty fruit bunch and coconut husk, for application in removing methylene blue and 2,4,6-trichlorophenol from aqueous solutions.

1.7 Research Objectives

(i) To prepare mesoporous activated carbons from coconut husk, oil palm fibre, oil palm empty fruit bunch and oil palm shell using physiochemical activation method consisting of potassium hydroxide impregnation plus carbon dioxide gasification.

(ii) To optimize the operating parameters (carbon dioxide activation temperature, carbon dioxide activation time and potassium hydroxide impregnation ratio) in the preparation of powdered activated carbons from coconut husk, oil palm fibre and oil palm empty fruit bunch, using response surface methodology.

(iii) To characterize the activated carbons prepared in terms of surface area, pore volume, pore size distribution, particle size distribution, surface morphology, proximate content and surface chemistry.

(iv) To study the effects of adsorbate initial concentration, contact time, solution temperature, solution pH, isotherms, kinetics and thermodynamics for adsorption of methylene blue and 2,4,6-trichlorophenol on the activated carbons prepared using batch adsorption tests.

(v) To study the breakthrough characteristics for adsorption of methylene blue and 2,4,6-trichlorophenol on oil palm shell-based activated carbon through fixed-bed adsorption tests by varying the adsorbate inlet concentration, feed flow rate and activated carbon bed height.

1.8 Organization of the Thesis

There are altogether six chapters in this thesis. Chapter One (Introduction) presents an overview on the current scenario on water pollution problem in Malaysia and the needs to produce activated carbons from agricultural by-products abundantly available in Malaysia, in order to effectively and economically solve both the solid waste disposal and wastewater treatment problems. The research objectives of the present study and the overall content of this thesis are summarized in the last section of this chapter.

Chapter Two (Literature Review) elaborates the important information on activated carbon adsorption technology for wastewater treatment as well as various precursors and activation methods used by previous researchers for preparation of activated carbons . Information on optimization of operating conditions for activated carbon preparation and characterization of activated carbon are discussed in detail. The last section explains the adsorption isotherms, kinetics and thermodynamics for batch adsorption system as well as the breakthrough characteristics of fixed-bed adsorption system.

Chapter Three (Materials and Methods) describes in detail all the materials and equipments used in the present study, including the experimental rigs and schematic diagrams. This is followed by the experimental procedure which includes activated carbon preparation, experimental design, model fitting and statistical analysis, activated carbon characterization, batch and fixed-bed adsorption studies as well as activated carbon regeneration. This chapter is ended with the schematic flow diagram showing the experimental activities carried out in this research.

Chapter Four (Results and Discussion) presents the results obtained from the experimental design used to prepare powdered activated carbons from coconut husk, oil palm fibre and oil palm empty fruit bunch, together with their respective regression model equations developed. The optimization results based on the adsorption capacity/uptake for methylene blue and 2,4,6-trichlorophenol as well as activated carbon yield for each activated carbon prepared are also presented and discussed.

Chapter Five (Activated Carbon Characterization and Adsorption Performance) presents the results obtained from characterization and adsorption studies of the activated carbons prepared. This chapter is divided into four main sections. The first section discusses on the characterization of the activated carbons prepared. Section two covers the batch adsorption studies of methylene blue and 2,4,6-trichlorophenol on the activated carbons prepared whereas the last two sections respectively discusses on the fixed-bed adsorption studies of the same adsorbates on oil palm shell-based granular activated carbon as well as activated carbon regeneration.

Chapter Six (Conclusions and Recommendations) concludes the findings from the present research. The conclusions reflect the achievements of the listed objectives which were obtained throughout the study. Finally, recommendations for future research are listed. These recommendations are presented in view of their significance and importance related to the present research.

CHAPTER TWO

LITERATURE REVIEW

2.0 Introduction

This chapter provides the general information regarding adsorption and activated carbon, followed by the literature review on activated carbon preparation and application of activated carbons in liquid phase adsorption. An overview of various precursors and activation methods used to prepare activated carbons, characterization of activated carbons as well as the application of various adsorbents for removal of methylene blue and 2,4,6-trichlorophenol are then presented. The adsorption isotherms, kinetics and thermodynamics of various adsorbent-adsorbate systems are shown, followed by a brief description on activated carbon regeneration technologies. A short summary on this chapter is provided in the last section.

2.1 Adsorption

Adsorption is the process of capturing molecules of dissolved solids, liquids or gases on the surface of certain active solids (Paul, 1995). A solid surface in contact with a solution tends to accumulate a surface layer of solute molecules because of the unbalance of surface forces (Eckenfelder, 2000). In liquid phase adsorption, the atoms, molecules or ions in a liquid are diffused to the surface of a solid where they bond with the solid surface or are held there by weak intermolecular forces. The solid which is insoluble, is called the adsorbent whereas the components being adsorbed are called solutes when in the liquid and form the adsorbate upon adsorbed on the solid. In general, the higher the concentration of solute, the higher is the equilibrium adsorbate concentration on the adsorbent (Seader and Ernest, 1998), with the condition that the maximum adsorption capacity of the adsorbent is not exceeded. For the design of adsorption processes, it is important to know the adsorption capacity at constant temperature in relation to the adsorbate concentration.

On their surfaces adsorbents have active centers where the binding forces between the individual atoms of the solid structure are not completely saturated. At these active centers, an adsorption of foreign molecules takes place. Figure 2.1 shows the mechanism of adsorption and desorption process (Henning and Degel, 1990).

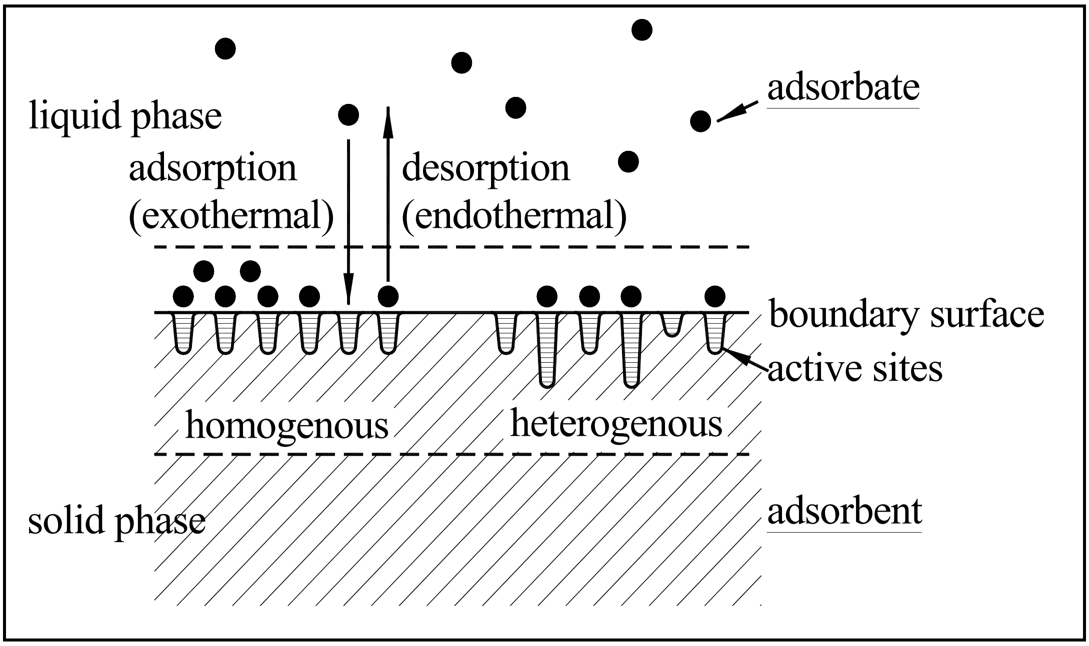

Figure 2.1 Mechanism of adsorption and desorption (Henning and Degel, 1990)

2.1.1 Classification of Adsorption

Adsorption can be classified into physical adsorption (physisorption) and chemical adsorption (chemisorption). Physical adsorption occurs when weak interpartical bonds such as Van der Waals, Hydrogen and dipole-dipole exist between the adsorbate and adsorbent whereas chemical adsorption occurs when strong interparticle bonds are present between the adsorbate and adsorbent due to an exchange of electrons (Allen and Koumanova, 2005). Physical adsorption results from molecular condensation in the capillaries of the solid which usually occurs in gas phase adsorption. There is a rapid formation of an equilibrium interfacial concentration, followed by the rate of diffusion of the solute molecules within the capillary pores of the carbon particles. The rate varies reciprocally with the square of the particle diameter, increases with increasing concentration of solute and temperature, but decreases with increasing molecular weight of the solute (Eckenfelder, 2000). Physical adsorption is a relatively weak adsorptive interaction which is assumed to proceed with zero or negligible activation energy (Mattson and Mark, 1971).

Chemical adsorption on the other hand results in the formation of a monomolecular layer of the adsorbate on the surface through forces of residual valence of the surface molecules (Eckenfelder, 2000). Such interactions are often characterized by a high degree of chemical reaction or molecular configuration, specificity between the adsorbent and the adsrobate that involve specific functional group reactions (Mattson and Mark, 1971). It is the result of chemical interaction between the solid and the solute. The strength of the chemical bond may vary considerably and identifiable chemical compounds in the usual sense may not actually form. The adhesive force is generally greater than that found in physisorption and the heat liberated during chemisorption is usually large in sequence of the order of the chemical reaction heat. Chemisorption occurs when strong interparticle bonds are present between adsorbate and adsorbent due to an exchange of electrons. Examples of such bonds are covalent and ionic bonds (Allen and Koumanova, 2005).

Adsorption is considered to be superior compared to other techniques due to its low cost, easy availability, simplicity of design, high efficiency, ease of operation, biodegradability and ability to treat pollutants in more concentrated form (Arami *et al*., 2005). Besides, adsorption does not result in the formation of harmful substances (Crini, 2006).

2.2 Activated Carbon

Activated carbon encompasses a broad range of amorphous carbon-based materials having high degrees of porosity and extensive surface areas. The use of activated carbon dates back to ancient Egypt where it was used for medicinal purposes. Later, in ancient Greece, wood chars were used to treat a host of ailments. In the 18th century, an application was found for removing foul odors from gangrene. Also in the 18th century, the phenomenon of adsorption was discovered by Scheele who conducted experiments on gases (Yehaskel, 1978). In subsequent years, the application of charcoal was used mainly as a decolorizing agent for sugar. The real thrust and rapid development of activated carbon was stimulated by World War I, when the Allies sought protection against chlorine gas, where gas masks employing activated carbons were used (Yehaskel, 1978). Following the war, new source materials were found and new processing equipments were developed. Today, many different activated carbons exist. The properties of each finished activated carbon are influenced by the starting materials used and by the conditions of activation. The result is a myriad of activated carbons, each having a specific utility.

The method most frequently used for preparation of activated carbon involves carbonization of the precursors at high temperature in an inert atmosphere followed by activation. There are mainly two different methods for activation, namely physical and chemical. Physical activation process comprises treatment of the char obtained from carbonization with some oxidizing gases, generally steam or carbon dioxide at high temperature. The porous structure is created due to the elimination of volatile matter during pyrolysis and the carbon on the char is removed during activation. The main function of gasification is to widen the pores, creating large mesoporosity. In chemical activation, a chemical agent is impregnated to the precursors prior to heat treatment in an inert atmosphere. The pores are developed by dehydration and oxidation reactions of the chemicals.

2.2.1 Application and Demand of Activated Carbon

Activated carbons find wide applications as adsorbents, catalyst or catalyst supports. Activated carbon is one of the most important adsorbents from an industrial point of view. The main application of this adsorbent is for separation and purification of gaseous and liquid phase mixtures. In general, activated carbons can be divided into two classes:

- Gas adsorbent carbons which are used for purification applications in the vapor or gas phase such as solvent recovery, gas separation or cigarette filter tips.
- Liquid-phase carbons which are used to decolorize or purify liquids, solutions and liquefiable materials.

The main distinction between gas-adsorbing and liquid-phase carbons lies in the pore size distribution. Basically, the structure of activated carbons containing pores are classified according to the International Union of Pure and Applied Chemistry (IUPAC, 1972) classification into three groups, micropores (pore size <2 nm), mesopores (pore size 2-50 nm) and macropores (pore size >50 nm) (Namane *et al*., 2005). Gas-adsorbing carbons usually have the most pore volume in the micropore and macropore ranges, whereas liquid-phase carbons have significant pore volume in the mesopore or transitional pore range, permitting ready access of liquids to the micropore structure which results in rapid attainment of adsorption equilibrium for smaller adsorbates.

Activated carbons concern many industries as diverse as food processing, pharmaceuticals, chemical, petroleum, nuclear and automobile, because of their adsorptive properties due to high available surface area which is presented in their extensive internal pore structure. The high porosity of activated carbons is a function of both the precursor as well as the scheme of activation. Activated carbons are now frequently used in environmental processes for removing toxic gases and in wastewater as well as potable water treatments (El-Hendawy, 2005).

The introduction of more stringent environmental legislation worldwide should ensure future growth in demand for activated carbons. Water treatment provides both the largest market and the main area of growth for activated carbons. In fact, it is known that around 80% of the world production of activated carbons is used in liquid phase applications (Dias *et al*., 2007). Activated carbon production capacity is now shifting from western industrialized countries to China and those in

South-East Asia, where raw material, energy and labour costs are lower (Roskill, 2007). Being the largest local activated carbon producer in Malaysia, Century Chemical Works Sdn Bhd. raised the production from 3000 tonnes per year up to 11000 tonnes per year due to upturn demand after Asian economic turmoil in late 1990's (Mohd Din, 2005). World demand for activated carbons is forecast to expand around 5% per year through 2009 to over 1.2 million metric tonnes in 2010 (World Activated Carbon Forecasts to 2010 & 2015).

2.2.2 Activated Carbon Adsorption for Wastewater Treatment

According to the review papers by Allen and Koumanova (2005) and Crini (2006) on decolourization of wastewater using various types of adsorbents, many non-conventional low cost adsorbents have been applied for dye removal, including activated carbons derived from agricultural and industrial solid wastes, as summarized in Table 2.1.

Table 2.1 Non-conventional low-cost adsorbents (Crini, 2006)

Category	Low-cost adsorbent
Waste materials from agriculture and industry	Activated carbons from solid wastes Agricultural solid wastes: sawdust, bark, pit, pith, wood chip, husk, straw Industrial by-products: metal hydroxide sludge, fly ash, red mud
Natural materials	Clays: bentonite, kaolinite, diatomite, Fuller's earth Siliceous materials: silica beads, glasses, alunite, perlite, dolomite Zeolites: clinoptilolite
Biosorbents	Chitin and chitosan Peat Biomass: white-rot fungi, microbial cultures
Miscellaneous sorbents	Starch Cyclodextrin