ADSORPTION OF METHYL VIOLET FROM AQUEOUS SOLUTION BY USING ACTIVATED CARBON FROM MANGROVE TIMBER VIA PHYSIOCHEMICAL METHOD

NAWAL AUNI BT ABDUL RAHMAN

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by

NAWAL AUNI BT ABDUL RAHMAN

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LIST OF SYMBOLS

SYMBOL	DESCRIPTION	UNIT
C_e	Equilibrium concentration of adsorbate	mg/L
C_o	Initial concentration of adsorbate in the solution	mg/L
K_F	Freundlich isotherm constant	$(L/mg)^{1/n}.(mg/g)$
K_L	Langmuir isotherm constant	L/mg
M_1	Concentration of initial adsorbate solution	mg/L
M_2	Concentration of final adsorbate solution	mg/L
n	Freundlich heterogeneity factor	-
P/P_o	Relative pressure	-
q_e	Amount of adsorbate adsorbed at equilibrium	mg/g
q_o	Maximum adsorption capacity	mg/g
R_L	Langmuir separation factor	-
R^2	Coefficient of determination	-
S_{BET}	BET surface area	m^2/g
V	Volume of solution	L
V_1	Volume of initial adsorbate solution	L
V_2	Volume of final adsorbate solution	L
V_{micro}	Micropore volume	cm^3/g
V_{meso}	Mesopore volume	cm^3/g
V_{total}	Total pore volume	cm^3/g

LIST OF ABBREVIATIONS

AC	Activated carbon
BET	Brunuer, Emmet and Teller
CO_2	Carbon dioxide
EA	Elemental analyzer
IUPAC	International Union of Pure and Applied Chemistry
KOH	Potassium hydroxide
N_2	Nitrogen
rpm	Rotation per minute
SEM	Scanning Electron Microscope
TGA	Thermogravimetric Analyzer

PENJERAPAN METIL UNGU DARIPADA LARUTAN AKUAS MENGGUNAKAN KARBON TERAKTIF BERASASKAN KAYU BAKAU TERHASIL MELALUI KAEDAH FIZIOKIMIA

ABSTRAK

Karbon teraktif kebiasaannya digunakan untuk memerangkap toksin dan bahan kimia. Ia dibuat dari pelbagai sumber. Dalam kajian yang lalu, didapati bahawa penghasilan karbon aktif dari sisa pertanian adalah salah satu cara mesra alam yang mampu mengubah bahan buangan menjadi produk berharga. Oleh itu, matlamat projek ini adalah untuk menyediakan karbon teraktif daripada kayu bakau menggunakan kaedah fizikimia. Karbon teraktif dicirikan oleh penganalisis termogravimetrik, Brunauer-Emmett-Teller dan penganalisis unsur. Penyejatan metil ungu karbon telah dinilai. Faktor-faktor yang berbeza yang mempengaruhi penjerapan metil ungu dikaji iaitu suhu pengaktifan (650 ℃, 750 ℃ dan 850 ℃) dan nisbah jerap isi dengan kalium hidroksida (1, 1.5 dan 2). Penyingkiran tertinggi metil violet diperolehi oleh karbon teraktif pada suhu pengaktifan 850 ℃ dan nisbah jerap isi dengan kalium hidroksida 1. Kajian mendapati bahawa AC850(1) memberikan luas permukaan tertinggi iaitu 852.1913 m^3/g dan jumlah isipadu liang 0.44 cm^3/g. Peratusan penyingkiran maksimum ditentukan pada kepekatan awal metil ungu 100 mg/L adalah 87.81%. Penjerapan metil ungu pada karbon teraktif berasaskan kayu bakau telah didapati mengikuti garis sesuhu Freundlich dan model kinetik pseudo tertib kedua. Hasil kajian penjerapan menunjukkan bahawa karbon teraktif yang disediakan dari kayu bakau adalah penjerap yang sesuai bagi penyingkiran metil violet daripada larutan akuas.

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ABSTRACT

Activated carbon is commonly used to trap toxins and chemicals. It is made from a variety of sources. In the past studies, it has been found that the production of activated carbon from agriculture waste is one of the most environment-friendly which transform waste into a valuable product. Thus, the objective of this project was to prepare activated carbons from mangrove timber using physiochemical method. The activated carbon were characterized by Thermogravimetric Analyzer, Brunauer-Emmett-Teller and Elemental Analyzer. The methyl violet adsorption of the prepared carbons were evaluated. The different factors affecting adsorption of methyl violet (MV) were studied which are the activation temperature (650℃, 750℃ and 850℃) and KOH impregnation ratio (1, 1.5 and 2). The highest methyl violet removal was obtained at activated carbon with parameter 850℃ of activation temperature and 1.0 of KOH impregnation ratio. It was observed that AC850(1) gives the highest surface area of 852.1913 m^3/g and total volume pore of 0.44 cm^3/g. The maximum removal percentage were determined at 100 mg/L initial methyl violet concentration at 87.81 %. The adsorption of methyl violet on mangrove based activated carbon was found to follow the Freundlich adsorption isotherm and pseudo second order kinetic model. The result of adsorption study showed that the activated carbon prepared from mangrove timber is a suitable adsorbent for methyl violet removal from aqueous solution.

CHAPTER ONE

INTRODUCTION

1.1   Textile Industry effluent and its problem

Textile industry is the third largest foreign exchange earner after the electronic and palm oil industries which contributing total earnings of RM 18.0 million (US$ 5.4 million) from manufactured exports in 2007 (Malaysian Textile Manufacturers Association, 2008). In Malaysia, there are about 1500 textile factories which operates as backyard or cottage industries producing the local 'batik'. Batik processing utilizes wax as a physical resistant and consumes a large amount of water during dyeing, fixing and washing process (Rashidi et al., 2015).

Colours or dyes in the waste water effluent is take into account based on the quality standards for the discharge of industrial effluents in Malaysia.   Under the Environmental Quality (Industrial Effluents) Regulations, 2009, the limits of colour for discharge of effluents according to standards A and B are 100 and 200 Platinum–Cobalt (PtCo) units respectively (Department of Environment, 2010). The discharge of coloured wastes into receiving streams not only affects the aesthetic nature but also interferes with transmission of sunlight into streams and therefore reduces photosynthetic activity (Namasivayam et al., 2001). Textile wastewater is characterized by strong colour, high salinity, high temperature, variable pH and high chemical oxygen demand (COD) (Mantzavinos & Psillakis, 2004). According to (Kiran et al., 2006), dyes usually have complex aromatic structures which make them stable and difficult to decompose. Due to their good solubility, the coloured waste water affects aesthetics, water transparency and gas solubility in water bodies and can be toxic to aquatic flora and fauna, and this causes severe environmental problems worldwide (Vandevivere et al., August 1998). Moreover,

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most synthetic azo dyes and their metabolites are toxic, carcinogenic and mutagenic, posing a potential hazard to human health (Nilsson et. al, 1993).

The treatment of textile effluent involves mainly physical and chemical methods. Several studies has been done using biological methods for the wastewater treatment for textile effluents especially in colour removal. Other methods for dyes removal are also been studied, including membrane separation, flocculation, sonolysis, oxidative destruction via UV/ozone treatment, photocatalytic degradation which have certain efficiency but their initial and operational cost are too high (Crini, 2006; Ramesh et al., 2007; Zaharia et al., 2007). Adsorption has been discovered to be superior to other techniques for wastewater treatment in terms of initial cost, simplicity of design and ease of operation (Garg et al., 2004; Jumasiah et al., 2006). Nowadays, most commercial systems are using activated carbon as an adsorbent to remove dyes in wastewater by reason of its excellent adsorption power (Keyhanian et al., 2016).

There are several industrially important dyes such as bromophenol blue, alizarine red-S, methyl blue, methylene blue, eriochrome black-T, malachite green, phenol red and methyl violet (Iqbal & Ashiq, 2007). Different type of dyes will give different adsorption rate on activated carbon. Methyl violet was chosen as adsorbate because it is an acidic dye which has the potential of carcinogenic activity. Hence, it has to be removed from industrial wastewater before it is being discharged.

1.2   Mangrove waste and problem disposal

Mangroves are salt-tolerant trees or shrubs found along low-energy, tidal shorelines latitudes in tropical and sub-tropical areas (Gilbert & Janssen, 1998). They colonise newly formed tidal flats in the wind and wave shadows of promontories and islands and behind wave-absorbing sand bars and sea grass beds (Carter, 1992).

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Mangroves provide the basis for complex and extensive ecosystems at interface of terrestrial, freshwater and marine ecosystems (Robert et al., 1992). In Malaysia, mangrove ecosystems are found largely on the West Coast of Peninsular Malaysia, the Southern Coast of Sarawak and the Eastern Coast of Sabah. Mangrove resources are exploited by humans for coastal protection, forestry products, fisheries, wildlife, urban and industrial development and ecotourism (Chong, 2006).

Mangrove trees have unique characteristics such as tough root systems, special bark and have unique adaptations in harsh conditions since it has induced unique morphological and physiological features (Vannucci, 2001). Mangrove trees are impressively tall and can grow to large sizes. One of the common usage of mangrove timber is for heavy construction, pilling and buildings since it has good decay resistance.

The mangrove piles are widely used in Peninsular Malaysia for low-rise building (Lie, 2000). Although the use of mangrove piles is not recognized by other countries, Malaysia contractors and developers are very confident that mangrove piles can actually being used for piling in the low-rise buildings due to the mangrove wood nature density and strength. The mangrove piles are not only cheap, but also easy to be handled in pilling work. According to Lie (2000), the buildings using the mangrove piles as foundation can at least stand for 10 years and the mangrove piles are very easy to be cleared off when other type foundation is to be used. However, mangrove piles may be damaged if they are not fully submerged under the water table level.

The mangrove pilling is done by cutting one of the ends of the mangrove pile like cone shape with a sharp point head to make the pilling work easier. The minimum length of the mangrove piles use is only 6.0 mm and they can be joint with a pile joint which is made by a steel box (Lie, 2000). The remaining parts of the mangrove pile which is the

removal parts are waste leftovers after the construction completed. The wastes can be used to manufacture charcoal for other purpose.

1.3 Activated carbon

Activated carbon (AC) is an amorphous form of carbon that is specially treated to produce a highly developed internal pore structure and a large surface area thus, producing reasonably cheap and excellent adsorbent (Alhamed, 2006). Activated carbon has a highly developed porosity, a large surface which can reach 3000 mm^2/g^{-1}, variable surface chemistry characteristic and a high degree of surface reactivity, therefore it is considered a very effective adsorbent for the removal of a wide variety of organic and inorganic pollutants dissolved in aqueous media (Kumar et al., 2014) or form gaseous environments (Dias et al., 2007). Nowadays, approximately 275000 tons of AC are consumed annually worldwide (Sainz-Diaz & Griffiths, 2000). The materials used to prepare AC are primarily mineral carbons and lignocellulosics from biomass, wood and some types of agriculture waste (Nasri et al., 2014).

Generally, two methods are used for the production of AC which are chemical activation and physical activation. The methods used to produce AC are further discussed later in Chapter 2. Figure 1.1 below shows the process flow for preparation of activated carbon from coconut shell obtained from Wen County Hongtai Water Treatment Materials Factory which located in China. Specifically, it is produced through a series of technical process of carbonization, activation, superheated steam and screening. Table 1.1 summarizes some of local activated carbon producers in Malaysia.
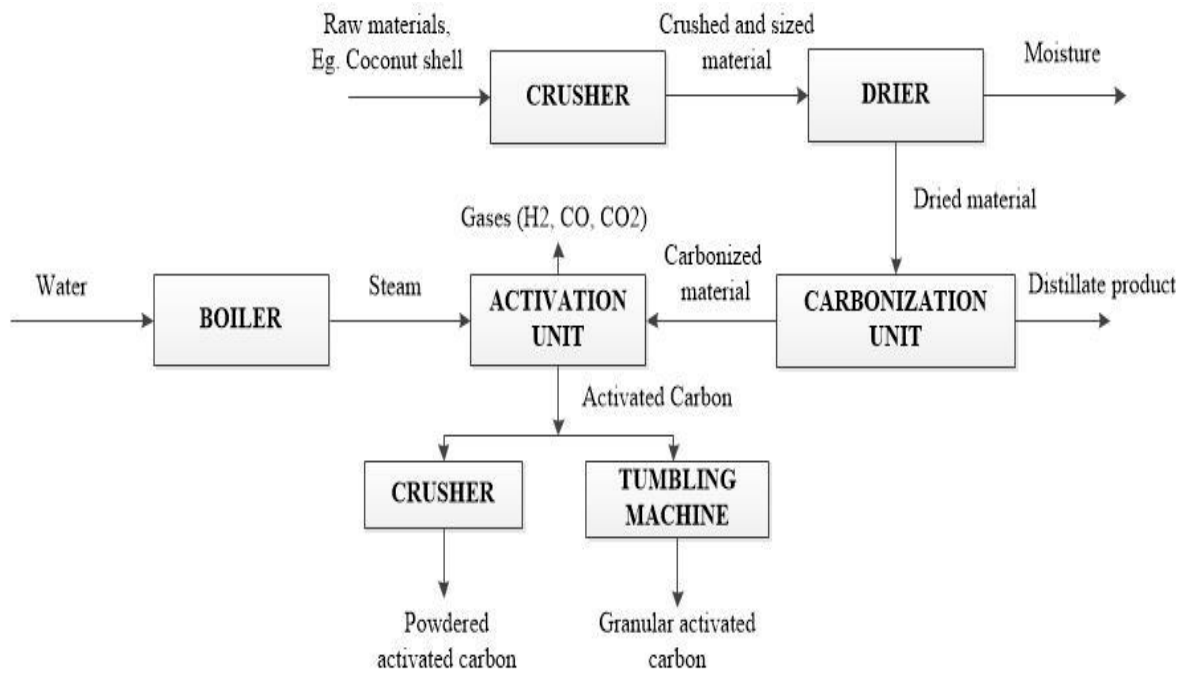
Figure 1. 1: The process flow of powdered activated carbon (Wen County Hongtai Water Treatment Materials, 2005).

Table 1. 1: List of local producer commercial activated carbons in Malaysia.

Name of producer	Raw material used	Type of activated carbon	Surface area (m^2/g)
Tan Meng Keong (TMK) Sdn. Bhd., Perak	Wood char	Powdered form	Less than 2100
Century Chemical Works, Penang	Sawdust char	Powdered form	Range 800-1000
EnviroCarbon Sdn. Bhd, Kuala Lumpur	Palm shell char	Powdered form	-

1.4   Problem statement

One of the major concern of textile wastewater is coloured effluent and disposal of these wastes into receiving waters. Though they are not particularly toxic, dyes have an adverse aesthetic effect because they are visible pollutants (Jusoh et al., 2004). The

presence of colour will affect photosynthetic activity in aquatic life due to reduced light penetration. One approach to overcome this problem is by reducing the amount of coloured effluents via adsorption process using activated carbon.

Many years ago, numerous studies have been reported on the production of activated carbon from pyrolysis of various type of agriculture waste using conventional method which are physical and chemical activation. From the literatures, it was found that this method is highly desirable as it can produce high quality activated carbon with larger surface area (Mohd Din et al., 2009).

In this paper, mangrove timber has been chosen as the agriculture waste since it is commonly used by the communities for housing construction in Malaysia. The leftover parts from the construction site can be reused and recycled to produce activated carbon. Despite of being leftover, it can be used to produce activated carbon. Since there is no research have been done yet using physiochemical activation method in production of activated carbon from mangrove timber, this study was carried out to investigate the performance of the prepared activated carbon using this method.

1.5   Objectives

1.   To prepare and characterize activated carbon from mangrove timber using physiochemical activation method.

2.   To investigate the effect of activation temperature and potassium hydroxide (KOH) impregnation ratio used towards the existence of porous of activated carbon production from mangrove timber.

3.   To study the equilibrium, isotherm and kinetics of methyl violet adsorption on the prepared activated carbon.

1.6   Scope of study

In this study, mangrove timber was used as the raw material in the preparation of activated carbon adsorbent using two-step physiochemical activation method. The experiments were conducted in a tubular furnace which can be heated up until 1000 ℃. The chemical agent used in the impregnation procedure was potassium hydroxide, KOH whereas the activating agent used in the activation process was carbon dioxide gas, CO_2. Potassium hydroxide is used instead of other chemical agents ($ZnCl_2$ and H_3PO_4) because it was found to produce highly porous activated carbon which having BET surface area and total (meso + micro) pore volume as high as 3100 m^2/g and 1.5 cm^3/g respectively (Fierro et al., 2007).

The effects of various activation condition which are activation temperature (650 ℃, 750 ℃, 850 ℃) and impregnation ratio of KOH/char (1, 1.5, 2) was studied in order to establish the optimum condition for producing high surface area activated carbon using mangrove timber that suitable for methyl violet removal. The carbonization and activation was fixed at 1 hour. The size of mangrove timber is 500 μm.

The prepared activated carbon was also characterized by using Micrometrics ASAP 2000, Scanning Electron Microscope (SEM), Thermogravimetric Analyzer (TGA) and Elemental Analyzer (EA) to determine the physical characteristics and surface chemistry of the prepared activated carbon. Methyl violet is used as the adsorbate in the adsorption studies in order to determine the performance of activated carbon adsorbent. The initial concentration of adsorbate were varied between 100 mg/l to 500 mg/l. The experimental data is important to determine the adsorption isotherm of the samples using Langmuir and Freundlich adsorption isotherm model. Adsorption kinetic was also studied by testing with two types of model which are pseudo first order and pseudo second order.

1.7   Thesis organization

Chapter one includes a brief introduction on mangrove disposal problem and utilization of mangrove timber using pyrolysis process to produce the activated carbon. The problem statement of the research is stated to give clear objectives of the present study. The scope of the study covers the research work done to meet these objectives.

Chapter two covers the utilization of activated carbon for waste water removal and type of wood used to produce activated carbon. In addition, this chapter also gives a brief explanation on the physical and chemical properties of activated carbon obtained from the characterization study. Finally the last details about adsorption study including the adsorption isotherm and kinetic study used in this present study.

Chapter three provides list of materials and chemicals reagents used in the present research work. It also gives the general description of the equipment used in the activated carbon preparation system. It continues with the explanation on the methods and analysis required on preparation of activated carbon followed by adsorption studies. The description of equipment used for characterization of activated carbon is also included in this chapter.

Chapter four presents the result obtained from experiments in the preparation of activated carbon, characterization of activated carbon and adsorption studies. Each of the results will be followed by discussion and comparison between the present results and the results obtained by other researchers. This explanation clearly describes the performances of activated carbon from present study.

Chapter five gives the conclusions of the results obtained in the present study. Some recommendations for the future studies are also included in this chapter.

CHAPTER TWO

LITERATURE REVIEW

2.1   Activated carbon

Activated carbon is basically tasteless, amorphous, microcrystalline, non-graphite form of carbon and a black solid substance which resembles granular or powdered charcoal. The term activated carbon is basically referred as carbonaceous materials with high porosity, high physicochemical stability, high adsorptive capacity, high mechanical strength, high degree of surface reactivity with immense surface area which can be differentiated from elemental carbon by the oxidation of the carbon atoms that found at the outer and inner surfaces (Yahya et al., 2015).

The most precursors used for the production of activated carbons are organic materials that are rich in carbon (Prahas et al., 2008). The organic materials can be obtained from agricultural wastes. On the other hand, agriculture wastes can be considered as one of the important feed stock for activated carbon preparation because there are renewable sources and low-cost materials. For the past few years, many research have been done and it was found that agricultural waste such as corn cob, coconut shell, palm shell, grain sorghum, pistachio nut shell, olive stone and walnut shell, cherry stone and oil palm shell have been found to be suitable precursors owing to their high carbon and low ash contents (Tongpoothorn et al., 2011).

Activated carbon are the most versatile and commonly used adsorbents because of their extremely high surface areas micropore volumes, large adsorption capacities, fast adsorption kinetics and relative ease of regeneration (Tongpoothorn et al., 2011). In addition, the adsorption process is influenced by the nature of the adsorbate and its substituent group (Wang et al., 2005). The presence and concentration of surface

functional groups plays an important role in the adsorption capacity and removal mechanism of the adsorbates (Yenisoy-Karakaş et al., 2004). Thus, activated carbon is used as an efficient and versatile adsorbent for purification of water, air and many chemical and natural products.

2.1.1 Activated carbon adsorbents for waste water removal

Activated carbons have been used for a long time as adsorbents in many applications in which impurities in low concentration are removed. Adsorption is the ideal method because it is non-specific and the adequate activated carbon must exhibit a high volume of micropores of a variety of pore size to be able to adsorb a wide range of molecules, coupled with an adequate proportion of mesopores and macropores to facilitate the access to the micropores (Molina-Sabio & Rodríguez-Reinoso, 2004). However, commercially available activated carbon is very expensive. Extensive research activity has been done in past years to emphasis the preparation of activated carbon from several agricultural by-products. The activated carbon produced from agriculture waste has grown many interest since it is low cost from renewable source and copious especially for application concerning treatment of wastewater.

Generally, activated carbon is used for tertiary treatment of many industry effluents. Activated carbon filtration is commonly used technology based on the adsorption of contaminants onto the surface of a filter. This method is effective in removing certain organics pollutants and some heavy metals presence in wastewater. The discharge of industrial wastes which is generated in chemical industry activities and the leaching from agricultural and forest land are the main sources of organic pollution in several water streams (Dias et al., 2007).

The main sources of wastes containing heavy metals are from industrial activities (mining, painting, car manufacturing, metal plating and tanneries) and agricultural activities (when fertilizers and fungicidal sprays are extensively used) (Dias et al., 2007).

Cellulose and many cellulose products are harmless to the environment because they safely return to the natural carbon cycle by a simple decay process in the presence of decomposers. Cellulose shows characteristic properties such as hydrophobicity, potential as a sorbent, non-toxicity, good mechanical properties and safe disposability after use (Klemm et al., 2005). Since mangrove timber is a cellulose-based, it is possible to produce activated carbon with high capacity adsorption. Cellulose is one of the basic constituents of lignocellulosic materials which are widely used as adsorbents. Table 2.1 below shows the compostion in cellulose, lignin, hemicellulose and ash of lignocellulosic materials.

2.1.2 Type of activated carbon

Activated carbon is available in different forms and shapes to suit special industry applications. The activated carbon which is available in the current market are powder, granular and pellet. Powdered activated carbon (PAC) has different size from 5 to 150 mm. They are finer grade particles and widely popular in market. The main advantages of PAC include processing costs, flexible operations and excellent quality parameters. The amount or dosage of PAC can be quickly increased or decreased as per project needs or demands. They can be used either for liquid phase adsorption or gas absorption. They are used in batch process and can be reused whenever necessary (Khatri, 2015).

Table 2. 1: The composition in cellulose, lignin, hemicellulose and ash of lignocellulosic materials (Suhas et al., 2016).

Reference	Raw Material	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Ash (%)
Tiryaki et al. (2014)	Almond shell	21.7	27.7	36.1	6.8
Figueiredo et. al (2010)	Bagasse	40	30	-	-
Phan et. Al (2006)	Coconut fibres	64	-	22	0.7
Daud and Ali (2004)	Coconut shell	19.8	68.7	30.1	-
Lv and Wu (2012)	Corn stalk	42.4	29.6	21.7	5.1
Figueiredo et. al (2010)	Corn stalk	35	25	-	-
Perepelkin (2004)	Cotton as natural fibre	97-98	-	-	-
Abdolali et al. (2014)	Cotton waste	80-95	5-20	-	< 1
Daud and Ali (2004)	Palm shell	38	21	27	-
Perepelkin (2004)	Wood (coniferous)	80-90	-	1-3	-

Granular activated carbon (GAC) is irregular shaped particle that are manufactured by the process of sieving and milling. They can be available in various sizes from 0.2 mm to 5.0 mm. They have long lasting features, hard in nature and more preferable type than powdered activated carbon (PAC). They can be produced in large volume and easy to clean and handle. The consistent quality of GAC makes them preferable over other type of activated carbon. Plus, it can be used multiple times for both gas and liquid based applications for fixed and moving systems (Khatri, 2015).

Last popular type of activated carbon is the extruded carbon whose diameter range from 1 mm to 5 mm. This is hard metal that is pretty much suitable for heavy duty

applications. This is popular for gas based due to their low pressure drop, ability to bear high stock resistance and low dust content (Khatri, 2015).

2.2   Activated carbon preparation

As mentioned earlier, the most precursors used for the production of activated carbons are organic materials that are rich in carbon. Currently, approximately 275000 tons of activated carbon are consumed annually worldwide (Nabais et al., 2011; Sainz-Diaz & Griffiths, 2000). There are two methods that can be used for the preparation of activated carbon which are one-pyrolysis and two-step pyrolysis. One-step pyrolysis is applied in the preparation of activated carbon using chemical activation method. For two-step pyrolysis is applied in the preparation of activated carbon which the carbonization and activation occurs separately. The product quality of two step pyrolysis is better compared to the one-step pyrolysis.

2.2.1   Carbonization

Carbonization process is a phase to enrich carbon content in carbonaceous material by eliminating non-carbon species using thermal decomposition in an inert atmosphere. The initial porosity of char even though still comparatively low, it could be developed in this stage before undergoes further development in the activation process (Mohamad Nor et al., 2013). Normally, higher carbonization temperatures (600-700℃) result in reduced yield of char while increasing the liquid and gases release rate (Ioannidou & Zabaniotou, 2007). Higher temperature will also increase ash and fixed carbon content and lower amount of volatile matter (Ioannidou & Zabaniotou, 2007; Lua

et al., 2006). This is due to the primary decomposition of biomass at higher temperature and also secondary decomposition of char residue (Ioannidou & Zabaniotou, 2007).

2.2.2 Activation

The objective of activation process is to enhance the pore volume, enlarge the diameter of pores and increase the porosity of activated carbon. Activation process can be performed by three different methods. They are named physical activation, chemical activation and physiochemical activation (a combination of physical and chemical activation). Several studies have been done using different type of activation on different materials as it can be summarized in Table 2.2.

2.2.2 (a) Physical activation

Physical activation is two-step process. It involves carbonization of carbonaceous material followed by the activation of the resulting char at elevated temperature in the presence of suitable oxidizing agents such as carbon dioxide, steam, air or their mixtures. The activation gas is usually CO_2 since it is clean, easy to handle and it facilitates control of the activation process due to slow reaction rate at temperatures around 800℃ (Zhang et al., 2004). For the carbonization, the temperature range is between 400 and 850 ℃ and sometimes reaches 1000 ℃ while for the activation temperature range is between 600 and 900 ℃. Table 2.3 shows the summary of the previous works of preparation of activated carbon produced by different raw materials by using physical activation with respect to their conditions.

Table 2. 2: Types of activation.

Activation	Steps of process	Material	References
Physical	One-step	Olive, straw, birch, bagasse, miscanthus, peanut hulls, corn stover, apricot stones, cherry stones, grape seeds, nutshells, almond shells, oat hulls	(El-Hendawy et al., 2001; Fan et al., 2004; Girgis et al., 2002,; Minkova et al., 2000; Minkova et al., 2001; Savova et al., 2001)
Chemical	One-step	Corn cob, olive seed, rice husks, rice straw, cassava peel, pecan shells, Macadamia nutshells, hazelnut shells, peanut hulls, apricot stones, almond shells	(Ahmadpour & Do, 1997; Aygün et al., 2003; Girgis et al., 2002; Tsai et al., 1997)
Physiochemical	Two-steps	Pistachio-nutshells, sunflower shells, pinecone, rapeseed, cotton residues, olive residues, peanut hulls, almond shells, oak, corn hulls, corn stover, rice straw, rice husk, rice hulls, pecan shells, sugarcane bagasse, olive-waste cakes	(Ahmedna et al., 2000; El-Hendawy et al., 2001; Haykiri-Acma et al., 2006; Marcilla et al., 2000; Yang & Lua, 2003)

2.2.2 (b) Chemical activation

In the chemical activation process the two steps are carried out simultaneously, with the precursors being mixed with chemical activating agents, as dehydrating agents and oxidants. Chemical activation offers several advantages since it is carried out in a

single step, combining carbonization and activation, performed at lower temperatures and therefore resulting in the development of a better porous structure, although the environmental concerns of using chemical agents for activation could be developed (Ioannidou & Zabaniotou, 2007). However, there are also some disadvantages of chemical activation process such as corrosiveness of the process and the washing stage (Teng & Lin, 1998). The most common chemical agents are $ZnCl_2$, KOH, H_3PO_4 and less K_2CO_3. Table 2.4 shows the summary of previous works of preparation of activated carbon produced by different raw materials by using chemical activation with respect to their conditions.

Table 2. 3: Summary of the previous works of preparation of activated carbon produced by different raw materials by using physical activation.

Raw material	Particle size	Carbonization (°C/h)	Activation (°C/h)	Oxidizing agent	References
Apricot stones/product	0.2-1 mm	800/1 h	800/1 h	Steam	(Savova et al., 2001)
Nutshells/ product	0.2-1 mm	800/1 h	800/1 h	Steam	(Savova et al., 2001)
Pistachio-nut shells	2.0-2.8 mm	500/2 h	900/30 min	CO_2	(Lua et al., 2004)
Peanut hulls	n.a	500/2 h	700-900/1 h	CO_2	(Girgis et al., 2002)
Almond shells	0.2-1 mm	800/1 h	800/1 h	Steam	(Savova et al., 2001)

2.2.2   (c) Physiochemical activation

Activation can be done either physically, chemically or combination of both known as physiochemical activation. In spite of higher cost and longer preparation time,

physiochemical activation is highly desirable as it can produce high quality activated carbon with larger surface area (Mohd Din et al., 2009). Physiochemical activation mainly happened at higher temperature ranging from 600 to 850℃ in the presence of dehydrating agent (potassium hydroxide, zinc chloride or phosphoric acid) and oxidizing agent such as carbon dioxide or steam for further gasification effect (Hameed et al., 2007; Hu et al., 2001).

In this type of activation, the chemical impregnation happened after carbonization stage. Chemical impregnation on char is recommended because it may: (i) increases the chance of carbon atom to react with the chemical thus promoting a better formation of cross-linked structures; (ii) decrease the complex reactions between the chemical and impurities; and (iii) lower the formation of viscous slurry (Mohd Din et al., 2009). Table 2.5 shows the summary of previous works of preparation of activated carbon produced by different raw materials using physiochemical activation with respect to their conditions.

2.3   Characterization of activated carbon

The physical and chemical properties of the activated carbon can be determined by carrying out characterization studies and tests. The performance and quality of prepared activated carbon in this work was based on the physical and chemical properties and adsorption capacity against methyl violet.

Table 2. 4: Summary of previous works of preparation of activated carbon produced by different raw materials by using chemical activation.

Raw materials	Particle size	Activation (°C/*h*)	Chemical agents	References
Macadamia nutshells	212-300 μm	500/1 h	$ZnCl_2$	(Ahmadpour and Do, 1997)
Hazelnut shell	1-1.25 mm	750/10 h	$ZnCl_2$	(Aygün et al., 2003)
Almond shell	1-1.25 mm	750/10 h	$ZnCl_2$	(Aygün et al., 2003)
Pecan shell	n.a	450/1 h	H_3PO_4	(Ahmedna et al., 2000)
Cassava peel	n.a	750/1 h	KOH	(Sudaryanto et al., 2006)
Corncob	0.5-2 mm	500/2 h	H_3PO_4	(El-Hendawy et al., 2001)

Table 2. 5: Summary of previous works of preparation of activated carbon produced by different raw materials using physiochemical activation.

Raw material	Particle size	Activating agent	Carbonization (°C)/*h*	Activation (°C)/*h*	References
Peach stones	2.8-3.5 mm	H_3PO_4/CO_2	450/4 h	850/3-7 h	(Molina-Sabio et al., 1996)
Fir wood	0.83-1.65 mm	KOH/CO_2	450/1.5 h	780/1 h	(Wu and Tseng, 2006)
Pistachio shells	0.83-1.65 mm	KOH/steam	450/1.5 h	780/1 h	(Hu et al., 2007)
Olive-mill waste	1-1.4 mm	KOH/CO_2	350/1 h	800/2 h	(Moreno-Castilla et al., 2001)

2.3.1 Yield

Yield is related to the economics of activated carbon manufacture. According to Putun et al. (2005), increased temperature leads to a decreased yield of solid and an increased yield of liquid and gases. As the temperature is raised, there is a rise in ash and fixed carbon percentage and there is a decrease in volatile matter. Consequently, higher temperature yields charcoals of greater quality. Other than that, by adding chemical agents to the char, the weight loss is also decreased (Rodríguez-Reinoso & Molina-Sabio, 1992). In addition, Teng et al. (2000) also reported that the yield of activated carbon decreased with the increasing chemical ratio and activation time. Yields of activated carbon can be calculated using Equation 2.1.

$$Yield\ of\ activated\ carbon, \% = \frac{w_f}{w_i}\ x\ 100 \qquad \text{(Equation 2.1)}$$

Where,

W_f = weight of precursor at initial stage, g

W_i = weight of activated carbon after activation process, g

2.3.2 Surface area and pore volume

Surface area is one of the key indicators attributed to the adsorptive properties of porous materials. Surface area provides the total surface area available for the adsorption properties. Surface area of an adsorbent is measured by adsorbing gaseous nitrogen, using well-accepted Brunaeur, Emmett and Teller (BET) in terms of m^2/g. Typically, the BET apparatus operates at the normal boiling point of N_2 (-195.8℃) by measuring the equilibrium volume of pure N_2 physically adsorbed on several grams of activated carbon at different values of total pressure in vacuum (Seader et al., 2011). The model was applied to the N_2 adsorption data at a relative pressure of 0.05 to 0.2 where the monolayer

coverage of nitrogen molecule is assumed to be completed. In order to conduct calculations using BET model, it was assumed that the surface area is related to the monolayer capacity by simple equation $A = n_m a_m L$, where a_m is the average area occupied by a molecule of the adsorbate in the completed monolayer and L is the Avogadro constant, taking 0.162 nm^2 as the cross-sectional area of the nitrogen molecule (Khalili et al., 2000). The adsorption isotherm is plotted and straight is obtained in which the slope and the intercept give the amount of gas required to form a monolayer.

According to the IUPAC system, there are six classified shapes of isotherms which are type I, II, III, IV, V and VI as shown in Figure 2.1. The typical type of isotherm of activated carbon is Type I. For this type of isotherm, the characteristic of adsorbents showed microporous structure and occur due to enhanced adsorbent-adsorbate interactions in micropores of molecular dimensions (Williams & Reed, 2006). Type II isotherm usually represents the completion of the monolayer and the beginning of the formation of multilayer. This type of isotherm indicates the formation of an adsorbed layer thickness continually increases with increasing relative pressure. These are obtained with non-porous or macroporous adsorbates with complete reversal of the isotherms being possible (Williams & Reed, 2006). Type III isotherm is indicative of weak-adsorbent-adsorbate interactions. Type IV isotherms are closely related to the Type II but exhibits a hysteresis loop, which is usually associated with the filling and emptying of mesopores by capillary condensation. A Type V isotherm is most likely the Type III, which demonstrates weak adsorbate-adsorbent interactions, but with the hysteresis loop there is mechanism of pore filling and emptying. Last but not least, Type VI isotherms are associated with layer-by-layer adsorption on a highly uniform surface, the shape being system and temperature dependent (Williams & Reed, 2006).
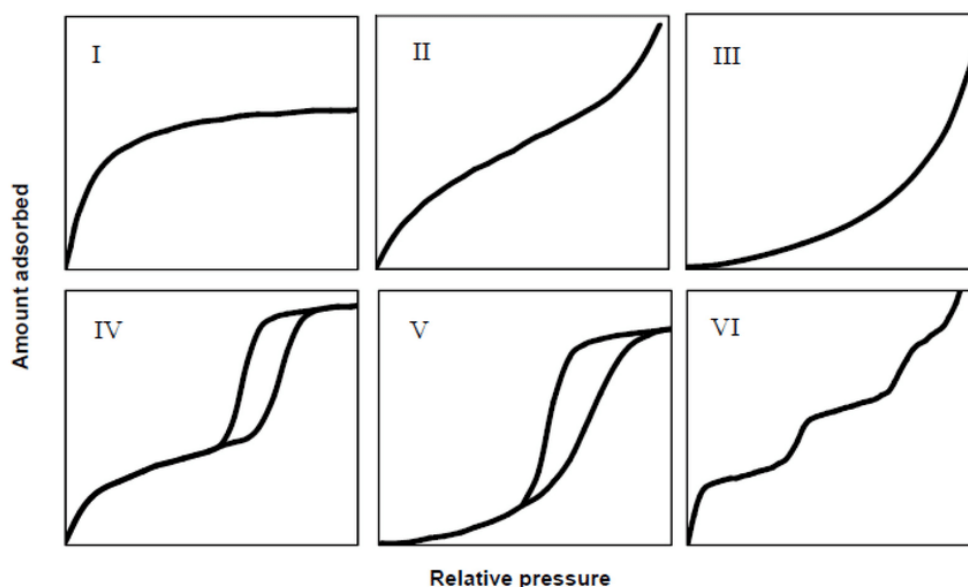
Figure 2. 1: The IUPAC classification of adsorption isotherm shapes (Williams & Reed, 2006).

The BET surface area and pore volume is decreasing not only with the increase of temperature but also with the activation time when the temperature is constant. On the contrary, according to Tsai et al. (1998), the values of total pore volume increase rapidly with increase in the activation temperature. Table 2.6 shows the surface area, pore volume and yield of different raw material.

Table 2. 6: Characteristics of activated carbon from different raw materials.

Raw material	S_{BET} (m^2/g)	V_o (cm^3/g)	Yield (%)	References
Cherry stones	875	0.28	11.2	(Savova et al., 2001)
Pistachio-nut shells	778	0.466	17.9	(Lua et al., 2004)
Almond shells	998	0.40	17.8	(Savova et al., 2001)
Corn cob	400-1410	0.19-0.70	n.a	(Tsai et al., 1997)
Corn hulls	977	0.3352	n.a	(Zhang et al., 2004)

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