

**REMOVAL OF Fe²⁺ (IRON) FROM
BATIK INDUSTRIES' EFFLUENT BY USING ACTIVATED
CARBON FROM MANGROVE TIMBER PREPARED VIA
PHYSIOCHEMICAL ACTIVATION**

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PHYSIOCHEMICAL ACTIVATION**

by

MOHAMAD ALIF BIN ABDULLAH

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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	$(L/mg)^{1/n} \cdot (mg/g)$
K_L	Langmuir isotherm constant	L/mg
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	-
S_{BET}	BET surface area	m ² /g
V	Volume of 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

AAS	Atomic Analyzer Spectrometer
BET	Brunauer–Emmett–Teller
CO ₂	Carbon dioxide
EA	Elemental Analyzer
HCL	Hydrochloric acid
KOH	Potassium Hydroxide
N ₂	Nitrogen
rpm	Rotation per minute
SEM	Scanning Electron Microscope
TGA	Thermogravimetric Analyzer

ABSTRAK

Dalam kajian ini, terdapat pelbagai jenis karbon teraktif yang dihasilkan daripada kayu bakau dengan menggunakan kalium hidroksida sebagai agent pengaktif. Karbon teraktif dicirikan dengan menggunakan *thermogravimetric analyzer*, *brunauer-emmett-teller* dan *elemental analyzer*. Penjerapan Ion Fe^{2+} diuji dengan menggunakan karbon teraktif yang dihasilkan. Terdapat pelbagai faktor yang dapat memberi kesan terhadap penyingkiran Ion Fe^{2+} dikaji dengan melalui suhu pengaktifan dan nisbah kalium hidroksida digunakan. Penyingkiran Ion Fe^{2+} optimum diperolehi dengan menggunakan karbon teraktif pada keadaan suhu pengaktifan $850\text{ }^{\circ}\text{C}$ dan nisbah kalium hidroksida digunakan adalah 1.5. Keputusan maksima sebanyak 57.86 % untuk penyingkiran Ion Fe^{2+} didapati dengan menggunakan kepekatan asal pada 50 mg/L. Penjerapan Ion Fe^{2+} pada karbon teraktif berasaskan kayu bakau didapati sesuai dengan penjerapan isotema *Langmuir* dan pseudo kinetik model kedua. Hasil kajian ini menunjukkan bahawa karbon teraktif yang disediakan daripada kayu bakau merupakan penjerap yang sesuai untuk menjerap Ion Fe^{2+} daripada larutan akueus.

ABSTRACT

In the present study, different activated carbons were prepared from carbonized mangrove timber by potassium hydroxide activation agent. The activated carbons were characterized by thermogravimetric analyzer, brunauer-emmett-teller and elemental analyzer. The Fe^{2+} ions adsorption of the prepared carbons was evaluated. The different factors affecting Fe^{2+} ions removal were studied which are the activation temperature and ratio of KOH impregnation. The optimum Fe^{2+} ions removal was obtained at activated carbon with parameter 850 °C of activation temperature and 1.5 of KOH impregnation ratio. The maximum removal percentage were determined at 50 mg/L initial Fe^{2+} concentration at 57.86 %. The adsorption of Fe^{2+} ions on mangrove based activated carbon was found to follow the Langmuir 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 Fe^{2+} ions removal from aqueous solution.

CHAPTER ONE

INTRODUCTION

1.1 Batik Industries

Textile industries such as batik industries was one of source of income for some country. Batik is a very popular traditional handmade craft in Malaysia. In Malaysia, batik industries has been existed starting from year of 1921 until present (Wan Hashim, 1996). The increases in the demand for clothing and apparel had brought both positive and negative impact toward this countries. One positive result had been an improvement in the economies. In contrast, environmental pollution is a major downside of textile factories. Textile industries have been dubbed as the worst offenders of pollution as they use more than 2,000 types of chemicals and over 7,000 types of dyes (Halimoon and Yin., 2010). They also produce heat, which is released with effluent, and increase water pH as well as saturate water with dyes. Besides dyes, heavy metal constituents in effluent also have negative ecological impacts on the water body and environment and can cause deterioration in human health (Syuhadah et al., 2015).

Heavy metals enter the environment mainly via three routes: (i) deposition of atmospheric particulates, (ii) disposal of metal-enriched sewage sludge and sewage effluents and (iii) release of by-products from metal mining processes (Begum et al., 2009). These heavy metals which are transmitted to the environment are extremely toxic and can accumulate in the human body, aquatic life, and natural water-bodies and are possibly trapped in the soil (Mathur et al., 2005). Heavy metals are present as impurities in dyes or a part of the dye molecule. In metal complex dyes, the metal forms chemical bond with the organic dye molecule and governs the speed at which materials absorb the

colours; thus, heavy metals are an indispensable constituent of the dye (Syuhadah et al., 2015).

In Malaysia, especially in the state of Kelantan and Terengganu which are located in East Coast of Peninsular Malaysia, batik is generally produced by cottage industries. It is known that textile industries, such as batik, consume an enormous amount of water especially during the dyeing process. Commonly, the batik entrepreneurs in Kelantan use traditional methods for batik production. Thus, discharge the untreated toxic effluents that contain dyes, waxes, and heavy metals, and also have a high chemical oxygen demand (COD) and total suspended solid (TSS) contents directly to the water sources (Syuhadah et al., 2015).

Some of the batik factories were built alongside the river or even at the back of an owner's house. Batik industries involve the use of mostly azo dyes that normally contain high concentrations of pollutants such as high colour pigments, carcinogenic dyes and toxic heavy metals (Ministry of Natural Resources and Environmet., 1979). Batik factories usually continuously discharge wastes into a special vessel or directly in to a river or drainage system. Wastes from these dyes were the main sources of pollution in the river, land or the drainage system. These discharges make the colour of the soil, the water in the river and in the drainage around the factory darker and malodorous. With time, there is an obvious effect on water quality and also other aspects of the environment. The stage of the pollution can be determined from the colour of water and soil, the decrease in biotic life and the quality of water.

1.2 Mangrove Pile

In Malaysia, mangrove trees have been covered approximately around of 577 558 hectare in total area (Chong, 2006) as shown in Table 1.1, it grow abundantly in saline soil and brackish water which is along the coasts and river mouths. According to Food and Agriculture Organization of the United Organization (2005), mangrove trees have specific and unique characteristics such as tough root systems, special bark and other unique adaptations which enable them to survive in harsh conditions. Under favourable conditions, mangrove trees can grow to large sizes. Due to their optimistic characteristics, mangroves timber has been used for various usages. It's resistance to decay and usually used for heavy construction, piling and buildings. There is an established demand for mangrove piling poles used in land reclamation and the construction industry in Singapore, Hong Kong and Malaysia (FAO., 2000).

The mangrove piles are widely used in peninsular Malaysia for low-rise building. Malaysia contractors and developers are very confident that the mangrove piles can actually being used for piling in the low-rise buildings due to the mangrove wood nature density and strength. There are few advantages in the use of mangrove piling. The mangrove piles are cheap and it is easy to be obtained in Malaysia. Besides, it is easy to handle in pilling work. The buildings that are built using the mangrove piles as foundation can stand for a very long period. In addition, the mangrove piles are easy to be cleared off when the other type of foundation is to be used and replaced. Mangrove piling is usually done by cutting one of the ends of the mangrove pile in a cone shape with a sharp point head to ease the piling work in the ground while the other end was flatted. The removed parts of the mangrove timber are waste leftovers after the construction finishes. The waste is either used in the manufacture of charcoal or dumped to a landfill site.

1.3 Utilization of mangrove waste as activated carbon

Commonly, activated carbon being produced from biomass waste that contain organic materials with sufficiently high amount of carbon content via appropriate activation technique. This is highly beneficial to the environment and human. By manufacturing activated carbon from biomass waste, it can enhance the reduction of the waste load on landfill field. The substitution of power and energy used for these waste materials can make some raw materials such as coal becomes available for other purposes (Daniel and Irene., 2010). In addition, the end product of this waste which is activated carbon with highly porous material that can be beneficial in many ways. It can act as an excellent adsorbent, filter bed and biological support media for contaminant removal.

1.4 Problem Statement

From 2010 to 2015, batik manufacturing had rose significantly due to the high demand in the market. The batik exportation from Indonesia to America was estimated to keep increase until 2019 (Tempo.co, 2015). Results from the Indonesia demand can be used as estimation of increment of batik demand in Malaysia because of neighboring countries. As the demand of batik increase, the manufacturer will also increasing their production of batik. This issue will probably cause a lot of water usage and it will be released to the landform. The water may contain high contamination of dye and heavy metal if it is not being treated carefully. Water that are contaminated can be treated by using an activated carbon. Usually, activated carbon are manufactured by using high carbon content in the organic waste (Williams and Reed, 2006). For several years has a

group of researcher had covered some studies on production of activated carbon from mangrove timber (Zulkarnain et al., 1993). Fundamentally, mangrove timber was used by the communities for construction of houses due to its strength. From the construction site, there are certain parts of the mangrove that are not being used and considered as a waste. Usually, mangrove timber leftover from construction site can be recycled and used in manufacturing of charcoal but most of the developers will directly dispose the waste due to its low market value and may only present in small quantity. By producing the activated carbon from the mangrove timber leftovers, it can reduce the waste of the mangrove timber leftovers and enhance the performance of activated carbon by removing heavy metal from batik effluent.

1.5 Research Objectives

The objectives of this present study are:

1. To prepare activated carbon from mangrove pile by using physiochemical activation method.
2. To investigate the effect of activation temperature and KOH impregnation ratio used toward the existence of porous of activated carbon production from mangrove timber.
3. To study the equilibrium, isotherm and kinetics of Fe adsorption on the prepared activated carbon.
4. To determine the optimum ability of activated carbon mangrove based for Fe removal.

1.5 Scope of Research

The aim of this study was to treat heavy metal concentrations in batik industries effluent by using activated carbon prepared by biomass which are produced from mangrove timber. Typically, there are several type of heavy metal that commonly contained in the batik wastewater effluent such as cadmium (Cd), Lead (Pb), Zinc (Zn), Copper (Cu), Chromium (Cr) and Iron (Fe) (Noor Syuhadah et al., 2015). But only Iron, Fe element that will be covered for this studies.

This studies was carried out by using mangrove timber as a raw material in the activated carbon production with physiochemical activation. The experiments were carried out in a furnace which can be heated up to a temperature of 1000 °C. The activation agent used in the activation process was carbon dioxide, CO₂ gas and potassium hydroxide, KOH.

The effects of various activation condition which are activation temperature (750 °C, 800 °C, 850 °C) and impregnation ratio with KOH (0.5, 1.0, 1.5) was covered in this studies in order to establish the optimum conditions for producing high surface area activated carbon using mangrove timber that suitable for Fe removal. The carbonization and activation time was fixed to 60 min.

The optimal activated carbon were characterized by using BET to determine the physical characteristics and surface chemistry of the prepared activated carbon. Adsorption studies were also carried out using nine different adsorbates to determine the performance of the activated carbon adsorbent. The experimental data was used to determine the adsorption isotherm model which are Langmuir and Freundlich Isotherm. Adsorption kinetic were covered by testing with two types of model which are Pseudo first order and Pseudo second order model.

Table 1.1: Mangrove forest area in Malaysia, (Chong, 2006)

Region	State	Total Length Of Coastline (Km)	Gazetted Forest Reserve (Ha)	Stateland (Ha)	Total (Ha)	Density (Ha Km ⁻²)
Peninsular Malaysia	Perlis	20	0	20	20	1.0
	Kedah	148	7,248	400	7,648	51.7
	Penang	152	451	500	951	6.3
	Perak	230	43,500	150	43,650	189.8
	Selangor	213	15,090	450	19,590	92.0
	Negeri Sembilan	58	454	200	654	11.3
	Melaka	73	166	100	266	3.6
	Johor	492	17,832	6,500	24,332	49.5
	Pahang	271	2,675	2,000	4,675	17.3
	Terangganu	244	1,295	1,000	2,295	9.4
	Kelantan	71	0	100	100	1.4
East Malaysia	Sarawak	1035	73,000	59,000	132,000	127.5
	Sabah	1743	328,658	12,719	341,377	195.9
	Labuan	59	0	0	0	0.0
	Total	4,809	490,369	87,189	577,558	120.1

CHAPTER TWO

LITERATURE REVIEW

2.1 Activated Carbon

Markedly, activated carbon appeared as a black solid substance resembling granular or powdered charcoal. It is a processed carbon material with a highly developed porous structure and a large internal specific surface area (Abdullah et al., 2001). Activated carbon is also described as carbon-based materials which contains well developed internal pore structure. It can be produced from a variety of carbonaceous rich materials such as wood, coal, lignite and coconut shells (Bhatnagar et al., 2013). The primary raw material used for the production of activated carbon can be any sources of organic material with a high amount of carbon content.

Carbonaceous adsorbents have been found to be particularly useful due to its good kinetic properties, high surface area, and large porosity, in the same way as well developed internal pore structure which consists of micropores, mesopores and macropores (Bhatnagar et al., 2013). Thus, activated carbon can adsorb different sort of pollutants from gaseous and liquid streams causes it to be used extensively in industrial sector for adsorption (Srinivasakannan and Abu bakar., 2004) . In addition, activated carbons are also widely used in many other fields such as water and air purification, separation of industrial gases and pharmaceuticals industry (Martinez et al., 2003).

2.1.1 Type of Activated Carbon

These days, activated carbon are commercially available in the market comes in different forms, according to its particle sizes and shape. The activated carbon which is available in the current market are powder, granular and pellet. Each type of activated carbon has its specific application and usage.

Powdered activated carbon is generally produced from wood in the form of sawdust. It is made up of crushed or ground carbon particles such that 95 - 100% of it will pass through a designated sieve of 0.297 mm in accordance to American Water Works Association Standard. The average size of powdered activated carbon is in the range of 15 - 25 μm . Thus, they present as a large internal surface with small diffusion distance. Therefore, powdered activated carbon finds wide application in the treatment of both drinking water and wastewater. It may also act as a coagulant for colloidal fractions in the liquid phase (Cecen and Aktas., 2012).

Granular activated carbon is usually in the form of crushed granules of coal or shell. It has a relatively larger particle size compared to powdered activated carbon. Thus, presents a smaller external surface. The particles of granular activated carbon have sizes ranging from 0.2 - 5 mm. It is usually used in purification processes for drinking water, groundwater and wastewater as an advanced treatment step, particularly for the removal of toxic organic compounds (Cecen and Aktas., 2012).

Pellet activated carbon consists of extruded and cylindrical shaped activated carbon with diameters in the range of 4 - 7 mm and 8 - 15 mm length. It mainly used for gas phase applications because of their low pressure drop, high mechanical strength and low dust content (Cecen and Aktas., 2012).

2.2 Activated Carbon Preparation

Activated carbon can be produced from any of organic material waste as long as it contain sufficient amount of carbon content. In current studies, there are two methods that can be used for the preparation of activated carbon which are one-step pyrolysis and two-step pyrolysis. One-step pyrolysis is when the carbonization and activation occurs simultaneously meanwhile for two-step pyrolysis the carbonization and activation was done separately in two stages. One-step pyrolysis is usually applied in preparation of activated carbon using chemical activation method. While the conventional preparation of activated carbon using physical activation method was based on two step pyrolysis.

2.2.1 Carbonization

This process carried out by pyrolysis of the precursors in an inert atmosphere to produce char which will enhance the carbon content from the organic substances. The term carbonization means to convert organic matter to elemental carbon at high temperatures in the absence of oxygen. The carbonization process is divided in four main stages as summarized in Table 2.1, based on the temperature reached (Wereko-Brobby and Takacs, 1996). Usually, some researcher use lower temperature at this stage like paper from Khezami et al., (2005), for the carbonization stage temperature of 300 °C was used. It is still in the range of the results stated by Wereko-Brobby and Takacs, (1996) which is the suitable range for the carbonization process is from 300 to 600 °C.

2.2.2 Activation

This process is to enhance the porosity of the precursor by burning the deposited of tars during carbonization process (Turmuzi et al., 2004). This process consist three types of method that can be used which are physical, chemical or physiochemical activation. During this step, the precursor will be exposed at atmospheric pressure in presence of activating agent gasses, where it can be called as oxidizing gas which carbon dioxide, oxygen or steam (Roop and Meenakshi., 2005).

Table 2.1: Steps and ranges of temperatures (Roop and Meenakshi., 2005)

Stage	Temperature, (°C)	Type of Reaction	Remarks
1	< 200	endothermic	Initial drying of precursor.
2	170 - 300	endothermic	Pre-carbonization stage.
3	250 - 300	exothermic	Greater proportion of the light tars and pyroligneous acids produced in second stage are released steadily from precursors to produce charcoal.
4	300 - 600	-	Increasing the carbon content of the charcoal by driving off the remaining volatile components of the charcoal.

2.2.2.a Physical activation

One of the oldest method for the activated carbon manufacturing. This method comprising the two-step process which is carbonization and activation in single processes. During carbonization step, moisture and volatile matters were removed from the raw material. After the carbonization of carbonaceous materials, the produced char is activated in the presence of activating agent. The main purpose of gasification is to expand the pores, resulting in meso porosity inside the carbon structure. Usually, the activation temperatures for this method in range 800 °C – 1000 °C (Mui and Mckay, 2004). Table 2.2 shows the summary of previous works of preparation of activated carbon produced by different raw materials by using physical activation.

2.2.2.b Chemical activation

Same as physical activation, chemical activation is one-step process for the production of activated carbon. This method, the carbonaceous precursors are firstly impregnated with an impregnation ratio of chemical activating agents for dehydrating purposes. Chemical agents can be used whether lewis acid ($ZnCl_2$ or H_3PO_4) or strong base (NaOH or KOH) (Ahmadpour and Do, 1997). These chemical agents act as dehydrating and stabilizing agents that enhance the development of porous structure in activated carbon. Normally for this method, the activation temperature is conducted at lower temperature compared to physical activation. Table 2.3 shows the summary of previous works of preparation of activated carbon produced by different raw materials by using chemical activation.

2.2.2.c Physiochemical activation

These days, majority of the research conducted used either physical or chemical activation method alone which yielded activated carbons either having low surface area or mainly microporous in nature (Daud and Ali, 2004). At the same time as physiochemical activation method derived from both physical and chemical activation process which the physical and chemical activations are performed simultaneously after carbonization of the precursors. The combination of the chemical and physical activation processes leads to the production of activated carbon with specific surface properties (Khalili et al., 2000). Separate and sequential application of chemical activation and physical activation were used to produce microporous carbons. Based on (Tseng et al., 2006), chemical activation alone only can produce a microporous type activated carbon. However, the process of KOH impregnation along with CO₂ gasification had produced higher ratio of macropores and mesopores. This improves mass transfer within the activated carbon matrix. Thus, the combination of both physical and chemical activation helps to obtain high surface area, granular, mesoporous activated carbon. The raw materials undergoes chemical induced activation followed by physical gasification at high temperature in the range of 600-1000 °C (Hu and Srinivasan., 2001). Based on the Khezami et al., (2005), in their studies 0.25 to 1.00 KOH impregnation ratio was tested on xylan to produce activated carbon. In this study, 0.5 to 1.5 for the KOH impregnation ratio was chosen to be tested on mangrove based activated carbon production. By varying the activation temperature of 750, 800 and 850 °C. Table 2.4 shows the summary of previous works of preparation of activated carbon produced by different raw materials by using physiochemical activation.

Table 2.2: Summary of previous works of preparation of activated carbon produced by different raw materials using physical activation

Raw Materials	Carbonization Temperature, °C	Carbonization Time, min	Activation Temperature, °C	Activation Time, min	Activating agent	Activating gas flow rate, cm ³ /min	References
Oil Bagasse	500	-	750 - 900	30,45,60	Steam	150	Demiral et al. (2011)
Used Tyre	800	60	750 - 900	60,120,180	CO ₂	100, 600	Mui et al. (2004)
Date stones	500 - 800	60	500 - 800	30,60,120, 180,360	N ₂	100	Bouchelta et al. (2008)
Corncob, Bagasse, Sawdust, Macadamia nut-shell, Rice husk fly	300 - 800	60	300 - 800	-	CO ₂	200	Aworn et al. (2008)
Sawdust	-	-	200 - 900	60,120	CO ₂	100	Matos et al. (2011)

Table 2.3: Summary of previous works of preparation of activated carbon produced by different raw materials using chemical activation

Raw Materials	Step	Impregnation Ratio, w/w	Activating Agent	Activation Temperature, °C	Activation Time, min	References
Coal and other precursors	2	3 : 1	NaOH, KOH	650,750,850	60	Lillo-Ródenas et al. (2007)
Biomass waste	2	-	ZnCl ₂	450,550,650	-	Williams, P. and Reed, A., (2006)
Tyre	2	-	KOH	700,800	-	Teng et al. (2000)

Table 2.4: Summary of previous works of preparation of activated carbon produced by different raw materials using physiochemical activation

Raw material	Carbonization Temperature, °C	Carbonization Time, min	Activating Agent	Activation Temperature, °C	Activation Time, min	References
Corncob	450	90	KOH/CO ₂	780	60	Tseng et al. (2006)
Coconut shel	500	180	ZnCl ₂ /Steam	900	30	Hameed et al. (2007)
Fir Wood	450	90	KOH/CO ₂	780	60	Wu and Tseng, (2006)
Xylan	300	60	KOH/N ₂	700	60	Khezami et al. (2005)

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.

2.3.1 Yield

Yield is one of the important factor that really need to be considered in the manufacturing of activated carbon in term of economics spectacular. The effects of products yield depending on conditions set have been reported by many different researchers. Regarding from Demiral et al. (2011), the yield will decrease with either increase in activation time or temperature. Low activation time as well as temperature result in incomplete burn-off resulting in higher yield. Similar observation was found by Zhang et al. (2004). Yields of activated carbon were calculated according to equation 2.1 below.

$$\text{Yield of activated carbon, \%} = \frac{W_f}{W_i} \times 100 \quad (2.1)$$

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 important key indicators attributed to the adsorptive properties of porous materials such as activated carbon. Surface area defines as the total surface area available for the adsorption properties. It is measured in terms of m²/g by using Brunauer, Emmett and Teller method (BET method) which is a method that works based on the adsorption of nitrogen gas at low temperatures. The adsorption isotherm is used in order to determine the surface area

and pore volume of the porous materials. According to International Union of Pure and Applied Chemistry, IUPAC, adsorption isotherms are classified into six shapes which are I, II, III, IV, V and VI. Figure 2.1 shows classification of adsorption isotherm with addition of types Ib, IIb and IVb (Rouquerol et al., 2014).

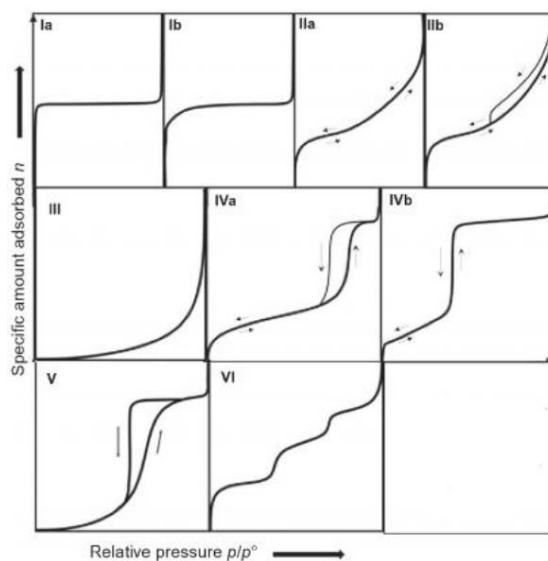


Figure 2.1: Classification of adsorption isotherms shapes (Rouquerol et al., 2014)

Type I isotherms are obtained with microporous adsorbent. It occurs due to enhanced adsorbate-adsorbate interactions in micropores of molecular dimensions (Williams and Reed, 2006). Type I isotherm is shown by activated carbon which has micropores. Type II isotherm usually represents the completion of the monomolecular layer and the beginning of the formation of multilayer. It is obtained with a non-porous or a macroporous adsorbent which allows unrestricted multilayer adsorption to occur. Type III and Type V isotherms are uncommon and are found in cases where the adsorbate-adsorbate interaction is weak. Lastly, Type VI isotherms are also rare. Type IV isotherms is closely related to Type II isotherms but exhibits a hysteresis loop, which is usually associated with filling and emptying of mesopores by capillary condensation. It is associated with layer-by layer adsorption on a highly uniform surface such as graphitised carbon,

the shape being system and temperature dependent (Rouquerol et al., 2014). Table 2.5 presents the result on surface area and pore volume properties of activated carbon prepared from various precursors by physiochemical activation. From the varies types of raw material that being summarized in Table 2.5, the most important parameter that affecting the S_{BET} and V_{total} is activation temperature compared to activation time. Based on result from Khezami et al. (2005), xylan based activated carbon being activated at temperature of 700 °C with time duration of 60 min give better result compared to date stones based activated carbon from Bouchelta et al. (2008) with duration of 180 min.

2.3.3 Pore Size Distribution

Activated carbon has been mainly be focused on the development of pores especially micropores and mesopores, in which it will present an ability and capacity of the activated carbon to absorb large amounts and various type of chemical compound within gas or liquid form. Pores in different sizes are important to the overall capacity of adsorbent in adsorption proses. According to IUPAC, pores can be categorized into:

- i. Micropores with a radius of less than 1 nm (small pores)
- ii. Mesopores with a radius of 1 - 25 nm (medium pores)
- iii. Macropores with a radius of larger than 25 nm (large pores)

The varieties of activation method will give different result of the pore structures of the activated carbon. Granular activated carbon have mesopores which allow rapid access to the meso- and micropores, where the adsorption take place. In powdered activated carbon, macropores are absent and access is not a problem due to its small size. Some research founded that the powder

type of activated carbon sample exhibits greater surface area and micropore volume compared to granular sample (Bouchelta et al., 2008). This is because the resistance to mass and heat transfers is lower when the particles have a small size. Figure 2.2 shows different type of pores present in activated carbon (Liu, 2016).

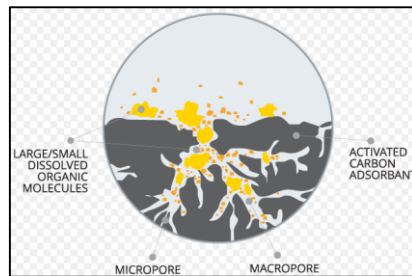


Figure 2.2: Different type of pores present in the activated carbon

2.3.4 Surface Morphology

Scanning electron microscope (SEM) is a type of electron microscope which is capable of producing high-resolution images of the activated carbon surface. It has a three-dimensional appearance. In addition, it is useful for judging the surface structure of the activated carbon produced. Figure 2.3 shows the SEM image of activated carbon after activation from sawdust of African beech wood with activation at 780°C for 60 min respectively Abdel-Ghani et al. (2016).

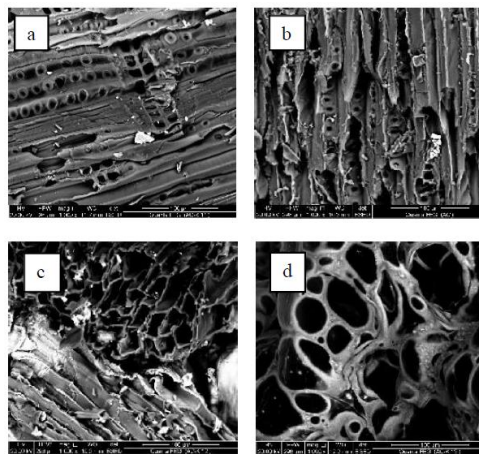


Figure 2.3: SEM image of activated carbon by Abdel-Ghani et al. (2016)

2.3.5 Adsorption Capacity

Adsorption capacity is an important characteristic which depend on the accessibility of the organic molecules to the inner surface of the adsorbent depending on their sizes. It is normally measured by adsorption of various adsorbates such as methylene blue, phenol and iodine. The adsorption capacity is affected not only by the precursors used, method of preparation and activation conditions. The adsorption capacity depends on the accessibility of the adsorbate to the inner surface of adsorbent.

2.3.6 Chemical Composition

Chemical composition of mangrove pile timber and activated carbon is defined in terms of its proximate and ultimate analysis. The proximate analysis provides the content of moisture, ash, fixed carbon and volatile matter on dry basis as well as moisture on wet basis while ultimate analysis determines the elemental content such as carbon, hydrogen, nitrogen, sulphur and oxygen. Based on Demiral et al. (2011) stated that the high carbon content and low as content makes olive bagasse a good starting material for the production of porous activated carbon. Related work was found in Lillo-Ródenas et al. (2007) where the raw material was analyzed before the activation process and was compared with the activated carbon produced. By increasing the activation temperature of activated carbon prepared from the oil-palm shells, the hydrogen (H) and oxygen (O) elements of that particular material will decreased due to the continual release of volatile matter which had decreased from 23.2% to 2.6%, leaving a high carbon content (Lua and Guo., 2001). From the studies, it is found that the activated carbon is expected to have high content of carbon and fixed carbon than its precursor.

Table 2.5: Surface area and pore volume properties of activated carbon from various precursors reported in previous works

Precursor	Activation Temperature, °C	Activation Time, min	S _{BET} , m ² /g	V _{total} , cm ³ /g	Reference
Oak	800	120	985	0.6403	Zhang et al. (2004)
Corn Hulls	800	60	1010	0.8341	
Corn Stover	800	60	712	0.5494	
Oil Bagasse	900	45	1106	0.6067	Demiral et al. (2011)
Sawdust	800	60	1167	-	Matos et al. (2011)
Date Stones	700	180	635	0.716	Bouchelta et al. (2008)
African beech wood	780	60	1553	1.325	Abdel-Ghani et al. (2016)
Xylan	700	60	926	0.443	Khezami et al. (2005)

2.4 Adsorption

Adsorption occurs whenever a solid surface is exposed to a gas or a liquid. It is defined as a process where molecules (as of gases, solutes or liquids) diffuse from the bulk area to the surface of a solid and held onto the surface through the porous site by mean forces. Generally, the material adsorbed at the surface of a phase is called as ‘adsorbate’ and the adsorbing phase is ‘adsorbent’. Figure 2.4 showed the overview of the process.

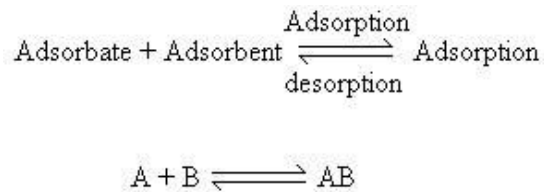


Figure 2.4: Overview of the adsorption process

2.4.1 Type of adsorption

Adsorption can be categorized into two type which are physical adsorption (physisorption) and chemical adsorption (chemisorption). Physical adsorption is mainly cause by Van der Waals forces and London dispersion forces, in where during this process the adsorbates are held on the surface of the pore walls by weak force of attraction (Liu, 2016). It is responsible for the condensation of vapours and deviations from ideal gas behaviour. On the other hand, chemical adsorption occurs between the solid and adsorbed solute. The reaction is usually irreversible such as the formation of chemical compounds (Rouquerol et al., 2014). Table 2.6 shows the comparison between physical and chemical adsorption.

2.4.2 Adsorption on Heavy Metal

Many researcher using methylene blue as their adsorbate, due to its strong adsorption onto solids, methylene blue dye serves as a model compound for adsorption of organic contaminant from aqueous solutions (Ahmad et al., 2007). At present time, some of researcher have interested in studies on heavy metal removal from the industrial waste. It's because, heavy metal have become an issues toward environment problem that can bring harm to flora and fauna cause by it toxicity.

Adsorption of heavy metal depends on both the pore structure and surface chemical properties of carbon of the activated carbon. Heavy metal, Fe^{3+} adsorption tests which helps to determine the capacity of carbon to adsorb molecules of a particular size. Fe^{3+} ions atom has a minimum molecular cross section of 0.126 nm. The minimum pore diameter is 1.3 nm. Thus, it can only enter the larger micropores but most likely to be adsorbed in mesopores. According to Malaysia Sewage and Industrial Effluent Discharge Standard, the limit for the Fe^{3+} in the effluent after the treatment with standard A of 1 ppm and standard B of 5 ppm.

Table 2.6: Comparison between physical and chemical adsorption

Physical adsorption	Chemical adsorption
<ul style="list-style-type: none">• Reversible• Non specific• Monolayer or Multilayer• Fast process• Only significant at low temperature• No dissociation of adsorbed species• Low heat adsorption (<40kJ/mol)	<ul style="list-style-type: none">• Irreversible• Specific• Monolayer• Slow process• Possible over wide range of temperature• May involve dissociation• High heat adsorption (>40kJ/mol)

2.5 Adsorption Isotherm

Adsorption isotherms indicate how adsorption molecules distribute between the liquid phase and solid phase when the process reaches an equilibrium state (Hameed et al., 2007). The equilibrium adsorption isotherm is important in the design of adsorption systems. Figure 2.5 shows the prediction of adsorption at the saturation pressure P_s , the adsorption does not occur anymore. This can be explained by the fact that there are limited numbers of vacancies on the surface of the adsorbent. At high pressure a stage is reached when all the sites are occupied and further increase in pressure does not cause any difference in adsorption process. At high pressure, Adsorption is independent of pressure. Langmuir and Freundlich are the most frequently employed models. Both models were used to describe the relationship between the amount of heavy metal adsorbed and its equilibrium concentration.

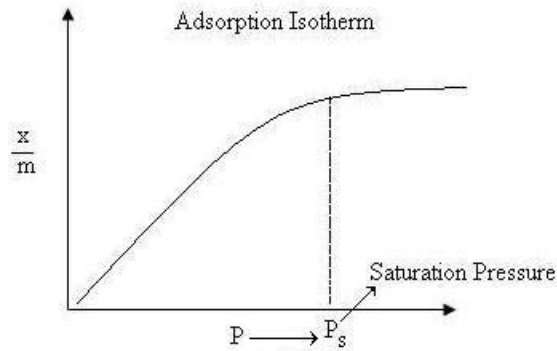


Figure 2.5: Basic Adsorption Isotherm