PREPARATION OF ACTIVATED CARBON FROM MANGROVE PILE LEFTOVER VIA PHYSIOCHEMICAL ACTIVATION

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by

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Symbol	Description	Unit
At	Equilibrium binding constant	L/mg
B	Constant related to the heat of adsorption	L/mg
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 methylene blue standard	mg/L
M_2	Concentration of final 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	Universal gas constant	J/ mol K
R^2	Correlation coefficient	Dimensionless
R_L	Equilibrium parameter separation factor	Dimensionless
S_{BET}	Total BET surface area	m^2/g
T	Absolute temperature	K
V	Volume of solution	L
V_1	Volume of methylene blue standard	mL
V_2	Volume of final solution	mL
V_{total}	Total pore volume	cm^3/g
w	Mass of adsorbent	g

List of Abbreviations

AC	Activated carbon
BET	Brunuer, Emmet and Teller
C	Carbon
CO_2	Carbon dioxide
H	Hydrogen
HCl	Hydrochloric acid
KOH	Potassium hydroxide
N_2	Nitrogen
O	Oxygen
rpm	Rotation per minute
SEM	Scanning Electron Microscopy
TGA	Thermogravimetric Analyzer
IUPAC	International Union of Pure and Applied Chemistry

PENYEDIAAN KARBON TERAKTIF DARIPADA KAYU BAKAU DENGAN CARA PENGAKTIFAN FIZIOKIMIA

Abstrak

Penghasilan karbon teraktif dari longgokan sisa bakau daripada tapak pembinaan adalah salah satu daripada penyelesaian masalah alam sekitar yang mesra alam dengan mengubah bahan terbuang kepada produk berharga yang mempunyai kawasan permukaan yang tinggi. Oleh itu, objektif utama kajian ini adalah untuk menyediakan karbon teraktif daripada kayu bakau menggunakan kaedah fizikal dan kimia dua langkah. Proses pengkarbonan dijalankan pada suhu 600^{o}C selama 1 jam di bawah dan kapasiti penjerapan pada pewarna biru metilena telah dikaji. Karbon teraktif optimum telah ditemui kadar aliran nitrogen 150 ml/min. Selepas proses pengkarbonan, arang dijerap dengan kalium hidroksida pada nisbah jerap isi yang berbeza (0.5, 1, 1.5). Selepas arang dijerap, arang kemudiannya ke proses pengaktifan pada suhu pengaktifan yang berbeza (750^{o}C, 800^{o}C dan 850^{o}C) selama 1 jam. Kesan pemboleh ubah penyediaan yang berbeza kepada hasil karbon teraktif pada suhu pengaktifan 750^{o}C dengan nisbah jerap isi, 0.5 dan ia dinamakan sebagai AC 750(0.5). Kapasiti penjerapan mentilena biru ialah 243.90 mg/g. Data eksperimen penjerapan itu juga digunakan dengan isoterma Temkin dengan nilai R^2 daripada 0.9909. Keputusan kajian menunjukkan bahawa penjerapan karbon teraktif disediakan daripada kayu bakau adalah penjerap sesuai untuk penyingkiran mentilena biru daripada larutan akueus.

PREPARATION OF ACTIVATED CARBON FROM MANGROVE PILE LEFTOVER VIA PHYSIOCHEMICAL ACTIVATION

Abstract

Activated production from mangrove pile leftover from solid waste from construction site is one of the most environment-friendly solutions by transforming waste to valuable product with high surface area. Thus, the main objective of this research was to prepare activated carbon from mangrove timber using two-step physiochemical activation method. The carbonization process was carried out at 600^{o}C for 1 hour under nitrogen flow rate of 150 ml/min. After the carbonization process, the char were impregnated with potassium hydroxide (KOH) at different impregnation ratios (0.5, 1, 1.5). After the char were impregnated, the char were then proceed to activation process with the different activation temperature (750^{o}C, 800^{o}C and 850^{o}C) for 1 hour.. The effect of different preparation of precursor on the activated carbon yield and adsorption capacity on methylene blue were investigated. The optimal activated carbon was found at activation temperature of 750^{o}C with impregnation ratio 0.5, namely as AC 750(0.5).The metyhlene blue adsorption capacity is 243.90 mg/g. The experimental data of adsorption is well fitted to Temkin isotherm with a R^2 value of 0.9909. The result of adsorption study showed that the activated carbon prepared from mangrove timber is suitable for methylene removal from aqueous soluti

CHAPTER ONE

INTRODUCTION

1.1 Textile industries and dye effluent

Textile industries manufacture produce a large volume of contaminated wastewater, which can causes serious problem to the ecosystem. The industrial textile effluents contain a mixture of dye molecules that can lead to a toxic effect (Manai et al., 2016). These dyes are resistant to aerobic digestion and stable to oxidation. Besides, the complex aromatic molecular structures of the dyes and synthetic origin makes them difficult to treat. In Malaysia, textile industry is one of major industry that produce large quantity of water and produce large volumes of wastewater from different steps in dyeing.

Dyes are used extensively in textile industry because of their superior dyeing properties, especially in terms of fastness. Apart from that, the characteristics of dyes are bright colour, low energy consumption and simple application techniques.

In addition, dyes produces greatest problem in textile wastewater because it is not easily biodegradable and even after extensive treatment, colours of dyes still remain in the effluent (Santhy and Selvapathy, 2006). Hence, the discharge of these wastewater can causes damage and hazardous on aquatic life and even the food chain (Tan et al., 2010)

This problem had been considered as the most challenging in the environmental fraternity and the industries for the treatment of wastewater for the past decades. This is because how to remove the dyes effluent from industries that had been faced by textile dyeing industry. Adsorption process using commercial activated carbons is very effective for removal of dyes from wastewater, but its high cost has motivated the search for alternatives and low cost adsorbent (Tan et al., 2010).

1.2 Utilization of mangrove waste as an activated carbon

Activated carbon is produce from agricultural waste where is at low cost materials and most widely used as an adsorbent in the purification and separation of liquids and gases. The advantages of using agricultural waste are it converts unwanted agricultural waste into useful waste and the adsorbents can be obtained from low cost raw material. The activated carbon can be prepared either in physical or chemical activation method. Besides, the activated carbon produced has different characteristics depends on the raw material and activation technique that been used in their production.

Mangrove waste has large availability as in charcoal industry waste. The raw material is harmless, cheaper and plentiful. The final product of activated carbon of the agricultural waste has advantages in many ways. The activated carbon can acts as an excellent adsorbent for removal of contaminant due to its high surface area and porous gain structure.

1.3 Mangrove pile

According to Food and Agriculture Organization of the United Nations reports for Mangrove of Asia (1980-2005), Malaysia have 564 971 ha covering for the mangrove trees.

There are several advantages of mangrove timber for piling. The mangrove piles are cheap and it is easily found in Malaysia. Apart from that, it is easy to handle in pilling work. Usually, the building that is built by the mangrove can stand for a very long period.

Mangrove piling is usually in the form of cone shape where a sharp point head are easy to be used in piling work in the ground and used it without the skin being removed. The removed parts of the mangrove will remain as waste leftover after the construction finishes. The waste of mangrove is used either in the manufacture of the charcoal or dumped to a landfill site.

1.4 Uses of activated carbon

The releasing of dyes into wastewater is from few industries such as, textile companies, dye manufacturing industries, paper factories, food companies and other companies that related with the usage of dyes. Textile industries is an industry that use a lot of usage of dyes for fibre colouration (Seey et al., 2012). According to Seey et al. (2012), the effluent volume and composition from textile industry is the major sources of wastewater in ASEAN countries. The process of cleaning and recycling of wastewater are difficult to perform because the wastewater contains a complex mixture of organic and inorganic chemicals. Mostly of the organic dyes are hazardous which it can affect the aquatic life and even the food chain.

The adsorption is an effective and less expensive than other technologies less than other treatment such as ozone or electrochemical oxidation and membrane separation. Therefore, the dyes removal is necessary of for the wastewater. Hence, the adsorption of activated carbon is an effective way for the adsorption (Man and Zakaria, 2008).

1.5 Problem statement

There are three traditional methods for removing dyes in effluent which are physical, chemical and biological treatment. Chemical treatment of dye wastewater with a coagulating and flocculating agent which can be used to remove colour, but this chemical treatment is not suitable for highly soluble dyes. For the biological treatment, it does not able to remove dyes from effluent on a continuous basis because to its low biodegradability of the dyes, less flexibility in design and operation and time required for decolourisation-fermentation process longer. Ion exchange, reverse osmosis, coagulation and adsorption techniques are an example for physical treatment. This physical need a lot of cost and the by-products is formed. Among the physical methods, the adsorption process is the most efficient methods.

Mangrove pile leftover is used in the construction due to its strength. Besides that, the waste of the mangrove can be recycled and used in manufacture charcoal but mostly of the developers will directly dispose to its low market value and may present in a small quantity only. Hence, in order to reduce the waste of the mangrove pile leftovers, activated carbon is prepared through this work.

1.6 Research objectives

This objectives of this research are:

i) To produce the mangrove pile timber activated carbon preparation conditions in various impregnation ratio and activation temperature.

ii) To characterize mangrove pile timber based activated carbon in terms of surface area, surface morphology, proximate content and surface chemistry.

iii) To study the effects of adsorbate initial concentration, contact time and solution temperature for dye adsorption on mangrove trunk waste based activated carbon

1.7 Scope of research

The activated carbon is produced by using mangrove pile timber as a raw material. A furnace is used in this experiment which the temperature of the furnace can be heat up to 1000^{o}C. Nitrogen gas is used in both carbonization and activation process while carbon dioxide gas is used in the activation process as activating agent.

The effects of various impregnation ratio where water: KOH: char equal to 0.5: 0.5: 1.0, 1: 1: 1 and 1.5: 1.5: 1.5 by mass, denoted as the KOH/ char ratio-= 0.5, 1 and 1.5 respectively and the effects of activation temperature (750^{o}C, 800^{o}C and 850^{o}C) was studied in order to produce the optimum activated carbon with high surface area by using mangrove pile timber.

After that, the optimal activated carbon was be characterized by using Micromeritics ASAP, SEM, and TGA in order to determine its physical characteristics and surface chemistry. Besides, adsorption studies also be carried out.

1.8 Organization of thesis

Chapter one is an introduction on a mangrove pile leftover and utilization of mangrove waste using pyrolysis process to produce the activated carbon. Besides, this chapter also brief about the application of activated carbon in wastewater treatment. The problem statement of the research is stated to give clear objectives of this study.

Chapter two is about the methods of preparation that have been done by researchers. Besides, in this chapter also gives an explanation on the physical and chemical properties of activated carbon from the characterization study. The last part in this chapter discuss about the adsorption study including the adsorption isotherm.

Chapter three discuss the list of materials and chemicals reagent used in this study. It also gives the general description of equipment used in preparation of activated carbon. A brief explanation about methods and analysis required and adsorption study is included in this chapter. The description of equipment used for characterization of activated carbon is also included in this chapter.

Chapter four discuss the results obtained from the experiments in the preparation of activated carbon, characterization and adsorption study of activated carbon.

Lastly, chapter five that gives the conclusions of the results obtained in present study and some recommendations also included for future studies.

CHAPTER TWO

LITERATURE REVIEW

2.1 Activated carbon

Activated carbon are highly porous materials that can be apply as an adsorbents, catalyst and catalyst support (Zhang et al., 2004) . Besides, it has high porosity, high surface area materials that are manufactured by carbonization and activation of carbonaceous materials. The pores of activated carbon can be classified into three group, micropores (diameter <2 mm), mesopores (diameter 2-50 mm) and macropores (diameter >50 mm). The carbonaceous materials has high surface area, large porosity and well developed internal pore structure where it consists of micropores, mesopores and macropores.

The activated carbon are made from different raw materials such as, grains, nutshells, coal and polymers (Zhang et al., 2004). Generally, high carbon content in this precursors. Besides that, agricultural waste have a low cost material that can be used to produce activated carbon (Aworn et al., 2008). Activated carbon is widely use in wastewater treatment, purification of water and gas, desulphurization and mercury removal (Man and Zakaria, 2008).

2.1.1 Type of activated carbon

Activated carbon which is commercially available in the market comes in different forms following to its sizes and shape. There are three type of activated carbon in the current market which is powder, granular and pellet. In general, the most widely used is the granule activated carbon and powder activated carbon due to their excellent adsorption capability for organic pollutants (Aworn et al., 2008). Each type of the activated carbon has its own specific applications and usage.

Generally, powdered activated carbon is produced in the form of sawdust. The size of powder activated carbon usually less than 100 um and the average size is in the range from 15-25 µm. For example, the powder activated carbon is used in the wastewater treatment.

Granular activated carbon has a larger particle size than powder activated carbon where it is usually in the form of granules of coal and shell that had been crushed. The size of the granular activated carbon is ranging from 0.5 to 4.0 mm.

Pellet activated carbon consists of extruded and cylindrical shaped carbons. The diameter range for this type of activated carbon from 4-7 mm and 8-15 mm length. This activated carbon is mainly used for gas applications due to their low pressure drop, high mechanical strength and low dust content.

2.2 Preparation of activated carbon

Activated carbon can be prepared from different carbonaceous materials. There are two different methods that can be used in the preparation of activated carbon which are one step and two step pyrolysis.

One step pyrolysis is a single stage where carbonization and activation process occurs simultaneously meanwhile two step pyrolysis consist of two stages process where carbonization has to be done first then proceeds with activation process. One step pyrolysis is mostly use due to its simplicity than two step pyrolysis and it is usually applied in the preparation of activated carbon by using chemical activation method. The two step pyrolysis is being applied in the preparation of activated carbon by using physical activation method.

2.2.1 Carbonization

Carbonization process is a process where the organic matter is convert to elemental carbon at high temperature in the absence of oxygen. Besides, this process also produce char that will gain more oxygen content from organic matters. During the carbonization, the material is pyrolyzed at temperature below 800^{o}C in an inert atmosphere so that the volatile matter is be removed (Aworn et al., 2008).

2.2.2 Activation

Activation process is a process where the activated carbon gain large surface, high surface reactivity, increase the adsorption rate and improve the mechanical strength (Aworn et al., 2008). There are three main activation process namely, physical activation, chemical activation and physiochemical activation.

a) Physical activation

Physical activation is occur out by burning off some of the raw carbon in oxidizing environment to create micropores (Zhang et al., 2004). The range of temperature for the activation from 600-1200^{o}C (Man and Zakaria, 2008). The activating temperature of the activated carbon is commonly at high temperature rather than at low temperature in order to obtain high surface area (Aworn et al., 2008). The activation gas that usually been use in commercial are steam, CO_2, air or their mixtures (Zhang et al., 2004). CO_2 gas and steam are usually commonly use as the activating agent. CO_2 gas is clean and easy to handle besides it can control of the activation process due to the slow reaction at temperature around 800^{o}C (Zhang et al., 2004). For the steam activation, it used the water-shift reaction concept with water vapour (steam) as a carrier in order to obtain the porosity of the carbon matrix hence make the activated carbon more valuable (Man and Zakaria, 2008)

Activated carbon production physical activation

Table 2.1: Summary of previous works of preparation of activated carbon produced from different raw materials by physical activatio

Raw Material	**Carbonization Temperature (ºC)**	**Carbonization Time (h)**	**Activation Temperature (ºC)**	**Activation Time (h)**	**Activating Agent**	**Activating gas flow rate (cm^3/min)**	**References**
Corncob, Bagase, Sawdust, Macademia nut-shell, Rice husk fly	300-800	1	300-800	-	CO_2	200	(Aworn et al., 2008)
Sawdust	300-500	0.5	800	1,2	Steam	300	(Man and Zakaria, 2008)
Palm shell, Coconut shell	850	1	850	1.3	CO_2	15	(Daud and Ali, 2004)
Corn hull, Corn stover, Oak	500	-	700,800	1,2	CO_2	117	(Zhang et al., 2004)
Pistachio shell	450	1.5	830	2	Steam	3	(Wu et al., 2005)
Sawdust	500	1	800	1	Steam	-	(Malik, 2004)

b) Chemical activation

Chemical activation is another process for the production of activated carbon. The carbonaceous precursors are impregnated with a certain impregnation ratio of chemical activating agent. After it has been impregnated, the activated carbon is being heated at 500-800^{o}C (Man and Zakaria, 2008). The most commonly used as activating agent in this activation are phosphoric acid, zinc chloride and alkaline metal compound (Srinivasakannan and Abu Bakar, 2004). For the lignocellulosic materials, phosphoric acid and zinc chloride are used while for the activation of the coal precursors or chars, potassium hydroxide (KOH) is used (Srinivasakannan and Abu Bakar, 2004). Besides, the activated carbon that prepared by the activation by the KOH is highly microporous than activated carbon that is activated through zinc chloride and phosphoric acid (Hui and Zaini, 2015). KOH also improves the specific surface area and the formation of –OH group on the surface of carbon (Hui and Zaini, 2015).

According to Lillo-Ródenas et al. (2007), there is several advantages for the chemical activation against physical activation, such as:

i. The heat treatment usually requires lower temperature and shorter time.
ii. Chemical activation allows to obtain high surface area activated carbon with controlled micropore size distribution and good pore development.
iii. The carbon yield for chemical activation usually higher than in physical activation

Activated carbon production chemical activation

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

Raw Materials	**Step**	**Impregnation Ratio**	**Activating Agent**	**Activation Temperature (ºC)**	**Activation Time (h)**	**References**
Pistachio shell	2	0.5, 1, 2, 3	KOH	780	1	(Wu et al., 2005)
Bamboo	2	-	KOH	300-600	4	(Evbuomwan et al., 2013)
Peach stones	2	0.22, 0.34, 0.43, 0.68	H_3PO_4	500	2	(Attia et al., 2008)
Eucalyptus wood, Coconut shell, Almond shell, Carbon fibre	2	-	KOH, NaOH	350, 850	10	(Lillo-Ródenas et al., 2007)
Tamarind seeds	2	0.5, 1, 1.0	KOH	500, 600, 700	-	(Mopoung et al., 2015)

c) Physiochemical activation

Physiochemical activation is the combination of the physical and chemical activation. The temperature for this activation is ranging from 600-900^{o}C after the char had been impregnated with a certain range of impregnation ratio in w/w ratio from 0-8 (Teng et al., 2000) . After the char has been impregnated, it is heated with the presence of activating agents such as CO_2 where it has to flow for 60 minutes during the activation (Tseng et al., 2006). After the activation process, the samples is be cooling under N_2 gas flow for 0-2 hours. The flow of N_2 gas is kept constant at 150 cm^3/ min and 10^{0}C/min.

According to, chemical activation only produce microporous activated carbon. However, the process of impregnation of chemical plus with the activation of carbon dioxide which acts as activating agent had produced higher ratio of mesopores and macropores. Hence, it improve mass transfer within the activated carbon matrix. Hence, the combination of physical and chemical activation helps to increase the surface area, granular, mesoporous activated carbon.

Activated carbon production physiochemical activation

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

Raw Materials	**Carbonization Temperature (ºC)**	**Carbonization Time (h)**	**Activating Agent**	**Activation Temperature (ºC)**	**Activating Time (h)**	**Production Step**	**References**
Waste tires	-	-	KOH/ CO_2	600-900	2	1	(Teng et al., 2000)
Pinewood, Wheat straw	550	-	KOH/ microwave	Microwave power = 600 W	0.5	1	(Mao et al., 2014)
Corncob	-	-	KOH/ CO_2	780	1	1	(Tseng et al., 2006)
Sawdust	200	0.25	H_3PO_4	400-500	0.75	2	(Srinivasakannan and Abu Bakar, 2004)

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 of activated carbon

The yield is defined as the weight ratio of final carbons to the initial dried raw materials (Tseng et al., 2006).

The yield can be calculated by using Equation 2.1

$$\text{Carbon yield } (\%) = \frac{\text{Weight of activated carbon}}{\text{Weight of raw material}} \text{ x } 100 \tag{2.1}$$

Yield of activated carbon plays an important role in order to scale up of process to be commercialized.

According to Teng et al. (2000), yield of the activated carbon is decreased when the activation temperature and the impregnation ratio is increased. By referring to the Tseng et al. (2006), it also showed that the yield of the activated carbon decreased due to the increasing amount of the impregnation ratio.

2.3.2 Surface area and pore volume

Surface area and pore volume are the main factors that attributed to the activated carbon properties. The surface area is defines as the total surface available for adsorption to take place and it is measured using Burnaeur-Emmett-Teller (BET) method in m^2/g. The total pore volumes are estimated to be the liquid volume of adsorbate (N_2) at a relative pressure, P/P_o of 0.99. According to International Union of Pure and Applied Chemistry, IUPAC, there are 6 class of adsorption isotherms which are I, II, III, IV, V, and VI. Figure 2.1 shows the types of adsorption isotherms.

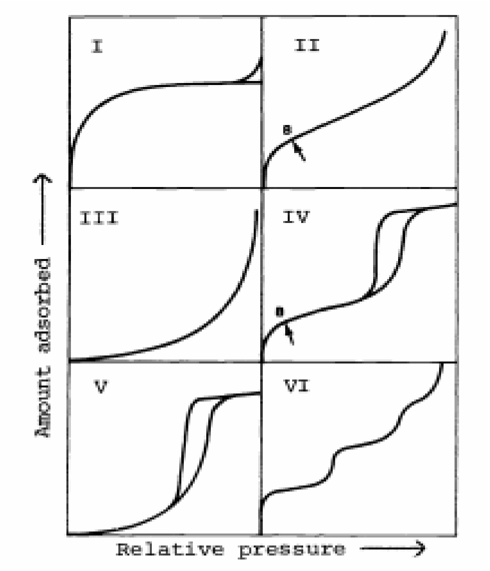

Figure 2.1: Classification of adsorption isotherms shapes (Sing, 1985)

Type I isotherm are activated carbon that has micropores and having relatively small external surface area (Aworn et al., 2008) . Besides, it also implied the near absence of mesopores and macropores inside the material. Hence, the physical adsorption of nitrogen gas usually occur in microporous structure (Lillo-Ródenas et al., 2007). For the type II isotherm represents unrestricted monolayer-multilayer adsorption for non-porous or macroporous carbon. Type IV isotherm show hysteresis loop that associated with capillary condition that occur in mesopores. Type III and V isotherms are uncommon where it has weak interaction between the adsorbent-adsorbate rather than the interactions between the adsorbate-adsorbate. For the last isotherm, type VI isotherm shows the stepwise multilayer adsorption on a uniform non-porous surface with the step-height shown the monolayer capacity for each adsorbed layer (Sing, 1985).

Table 2.4 shows the result on surface area and pore volume properties of activated carbon prepared from different precursors by physiochemical activation.

Table 2.4: Surface area and pore volume properties of activated carbon from different precursors reported in previous works

Precursors	**Activation Temperature(ºC)**	**Activation Time (h)**	**S_{BET} (m^2/g)**	**V_{total} (cm^3/g)**	**References**
Sawdust	500	0.75	1492	-	(Srinivasakannan and Bakar, 2004)
Waste tires	700	1	397	0.57	(Teng et al., 2000)
		2	285	0.57	
Corncob	780	1	2844	1.53	(Tseng et al., 2006)
Pistachio shells	830	2	821	-	(Wu et al., 2005)

2.3.3 Pore size distribution

Micropores and mesopores development is important since it allows the porous carbon to adsorb large amount and different types of chemical compound from gas and liquid steam. According to IUPAC, pores can be categorized into:

i. Micropores with a radius less than 1nm (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)

Different activation method give different structures of pores. Granular activated carbon have mesopores which allow rapid access to the meso- and micropores, where the adsorption process take place. For powdered activated carbon, macropores are absent and it can be access easily due to its small size. Powdered activated carbon exhibits greater surface area and micropore volume than granular sample (Bouchelta et al., 2008). This is because the resistance to mass and heat transfer is lower when the particles have a small size. Figure 2.2 shows different type of pores present in activated carbon.

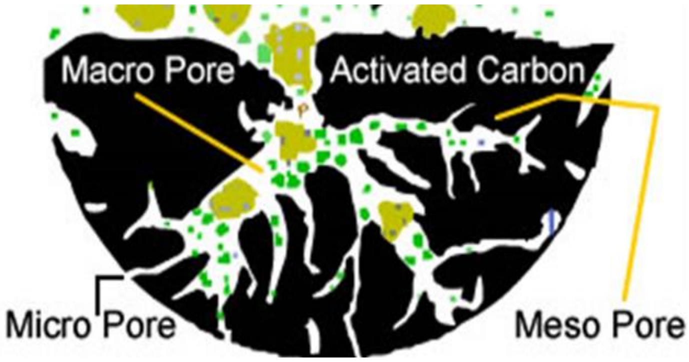

Figure 2.2: Different type of pores present in the activated carbon

2.3.4 Adsorption capacity

Adsorption study can be done by using various adsorbates such as methylene blue, iodine and phenol. During the adsorption process of the adsorbate, the migration of the adsorbate molecule through the solution of the exterior surface of activated carbon by molecule diffusion, followed by molecules pore diffusion into interior site of adsorbent and finally the molecules are adsorbed into the active site at the interior of the adsorbent. The adsorption capacity is affected by the surface charge, surface chemistry and pore structure besides the other parameters such as type of precursors, method of preparation, pyrolysis temperature and the activation time.

The capacity of adsorption of certain carbon is known to be a function of porous structure, chemical nature of the surface and pH of the aqueous solution (Wang et al., 2005). Besides, the adsorption process is influenced by the nature of the adsorbate and its constituent group. Higher adsorption occur at equilibrium due to the smaller size of adsorbent which offer large surface area (Man and Zakaria, 2008). The adsorption efficiency will be reduced if too much adsorbent is added into the dye solution, hence the transportation of dye ions to the active adsorption sites will be limited as well (Seey et al., 2012). At the beginning of the adsorption, the rate of removal of the adsorbate is higher due to the large surface area of the adsorbent available. After a certain period, the dye uptake is decreasing because only a few of the active sites of the adsorbent is available (Seey et al., 2012).

2.3.5 Chemical compositions

Chemical composition of mangrove pile leftovers and activated carbon are define by the ultimate and proximate analysis. The ultimate analysis is used to determine the elemental content such as carbon, oxygen, nitrogen and hydrogen. For the proximate analysis, it determines the content of fixed carbon, volatile matter and ash on dry basis as well as moisture on wet basis.

According to the Latiff et al. (2016), it reported the carbon content of corncob increase from 21.72% to 67.10% and 38.78% to 75.85% after the activation with the carbon dioxide gas and KOH. Besides that, according to the Mao et al. (2014), it reported that pinewood char has 12% to 20% of volatile content and for wheat straw char, it has 7.6% to 8.6% volatile content. The higher volatile content allows the formation of interconnected pores which facilitates the diffusion of KOH into the char, hence it give good result of developing of micropore structure (Tseng et al., 2006). From the studies, it is found that the activated carbon is expected to have high content of carbon and fixed carbon than its precursors.

2.4 Adsorption

Adsorption is a process where molecules (gases, solute or liquids) diffuse to the surface of a solid and held onto the surface by mean forces. The material adsorbed at the surface of a phase is named as ‘adsorbate’ and the adsorbing phase is named as ‘adsorbent’.

2.4.1 Type of adsorption

There are two types of adsorption, physical adsorption (physisorption) and chemical adsorption (chemisorption). Pysisorption is occur when there are electrostatic forces and Van der Waals forces between the adsorbates molecules and the adsorbent molecule. For the chemisorption, it is an adsorption that involves a chemical reaction between the surface and the adsorbates. The comparison between the physiorption and chemisorption is shown in Table 2.5.

Table 2.5: Comparison between physical and chemical adsorption

Physical Adsorption	Chemical Adsorption
• Low heat of adsorption	• High heat of adsorption
• Non specific	• Highly specific
• Monolayer or multilayer	• Monolayer
• Reversible	• Irreversible
• Fast, instantaneous process	• Slow process
• Relatively at low temperatures	• Relatively at high temperatures
• No dissociation of adsorbed species	• May involve dissociation

2.4.2 Adsorption of methylene blue

Dyes and pigments are important compounds that widely used in many industries especially for colouring purpose (Wu et al., 2005). Even though the discharged concentration of most dyes are controlled to be an inert and non-toxic for the receiving water, but these coloured effluents are undesirable to the water use.

Methylene blue is seen use in medical in large quantities, but it is also widely used in industrial practices such as textile and printing. Besides, it also used for the determination of removal capacity and equilibrium isotherm. Adsorption of organic depends on both the surface chemical and pore structure properties of carbon of activated carbon.

The dye, which is methylene blue is a dye adsorption tests which it help to determine the capacity of carbon to adsorb molecules of a particular size (Wang et al., 2005). Minimum molecular cross section of the methylene blue molecule is 0.8 nm and it cannot enter the pore with diameter less than 1.3 nm which means it can only enter the largest micropores but most of it is likely to be adsorbed in mesopores. Other than that, a good decolorizing carbon should fulfil at least 200 mg/g removal capacity for the dye (Attia et al., 2008).

2.5 Adsorption isotherm

Adsorption isotherm shows how the adsorption molecules distribute between the liquid phase and solid phase when the adsorption has reached the equilibrium stage. There are three types of adsorption isotherm, Langmuir, Freundlich and Temkin isotherm. The Langmuir and Freundlich equations are commonly used to describe adsorption isotherms at a constant temperature for water and wastewater treatment applications (Tan et al., 2010).

2.5.1 Langmuir isotherm

Langmuir isotherm is been use apply widely in order to describe adsorption data based on the assumption that energy of adsorption is constant and independent of surface coverage where the adsorption occurs on localized sites with no interaction between the adsorbate molecule (Malik, 2004). The maximum adsorption occur when the monolayer has covered the surface (Malik, 2004). Thus, Langmuir isotherm is expressed as:

$$q_e = \frac{q_0 K_L C_e}{1 + K_L C_e} \tag{2.2}$$

Where:

q_e = Amound of adsorbate adsorbed at equilibrium (mg/g)

C_e= Equilibrium concentration of adsorbate (mg/L)

q_o= Maximum loading corresponding to complete surface coverage (mg/g)

K_L= Langmuir isotherm constant (L/mg)

Upon linearization, the equation becomes:

$$\frac{C_e}{q_e} = \frac{1}{q_o K_L} + \frac{C_e}{q_o} \tag{2.3}$$

The linearized form of Langmuir isotherm is commonly used as a straight line can be obtained by plotting the experimental data on a graph of C_e/q_e against C^e. Hence, Langmuir model parameters, K_L and q_o can be calculated from the slope and y-intercept of the graph.

Dimensionless constant, the equilibrium parameter separation factor (R_L) is the essential features of Langmuir adsorption isotherm. R_L

$$R_L = \frac{1}{(1 + K_L C_o)} \tag{2.4}$$

Where C_o is the initial concentration of adsorbate in the solution (mg/L)

The R_L values implies the adsorption to be unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$) or irreversible ($R_L = 0$) (Man and Zakaria, 2008).

2.5.2 Freundlich isotherm

Freundlich isotherm can be used for non-ideal sorption that occurs on heterogenous surface energy system (Malik, 2004). Hence, the Freundlich isotherm is represented as:

$$q_e = K_F {C_e}^{1/n} \tag{2.5}$$

Where:

q_e= Amount of adsorbate adsorbed at equilibrium (mg/g)

C_e= Equilibrium concentration of adsorbate (mg/L)

K_F= Freundlich constant (mg/g) (L/mg)$^{1/n}$

n= Freundlich heterogeneity factor

The equation can be linearized as follows:

$$\log q_e = \log \mathrm{K}_F + \frac{1}{n} \log \mathrm{C}_e \tag{2.6}$$

By plotting the experimental data on a graph of log q_e against log C_e, Freundlich model parameters, n and K_F can be calculated from slope and y-intercept respectively. The values of n>1 represent the favourable adsorption condition. Generally, the value of K_F is increased if the adsorption capacity is increased too (Man and Zakaria, 2008).

2.5.3 Temkin isotherm

According to El Nemr et al. (2009) the Temkin isotherm assumes that the heat of adsorption decreases linearly rather than logarithmic due to the indirect interactions between adsorbate and adsorbent. Temkin model gives higher equilibrium constants compare to Langmuir parameters (Hosseini et al., 2003). Temkin model can expressed as (Thilagavathy and Santhi, 2014):

$$q_e = \left(\frac{RT}{b}\right) \ln(A_t\, C_e) \tag{2.7}$$

Which can be rearranged to:

$$q_e = B \ln C_e + B \ln A_t \tag{2.8}$$

where,

q_e = Amount of adsorbate adsorbed at equilibrium (mg/g),

R = Universal gas constant (8.314 J/mol K)

T = Absolute temperature (K)

A_t = Equilibrium binding constant (L/mg)

C_e = Equilibrium concentration of adsorbate (mg/L)

B = RT/b = Constant related to the heat of adsorption (L/mg)

Therefore, a graph of q_e versus ln C_e gives a straight line with the slope of B and intercept of $B \ln A_t$.