

CHAPTER 2

LITERATURE REVIEW

2.1 Activated Carbon

Activated carbon is a monolithic porous carbon material (Ahmad et al., 2012), which plays an important role in various areas and industries. It possess a large surface area ranging from 1000 m²/g (Marsh & Reinoso, 2006) to 2800 m²/g and may achieve 4000 m²/g (Yang, 2003) to 5000 m²/g (Marsh & Reinoso, 2006). It is best functions for the adsorption and storage applications due to its highly porous material (Alabadi et al., 2015). It has been demonstrated as an effective adsorbent to remove a various inorganic and organic contaminants (Jain et al., 2016; Lim and Aris, 2014; Alslaibi et al., 2013; Nguyen et al., 2013). The adsorptive capacity is dependable on its high activity, surface area and uniformity of its shape (Yahya et al., 2015), which make it fit for removing a variation of contaminants from air and gas streams (Jain et al., 2016; Lim & Aris, 2013; Alslaibi et al., 2013; Nguyen et al., 2013).

Although activated carbon is preferable in removal of many organic and inorganic contaminants, the treatment process is usually expensive (El-Sayed et al., 2014). Industrial players could not bear the cost for the treatment processes. They always consider cost as an important factor in choosing suitable adsorbent in need. The cost of an individual adsorbent differs subject to the methods involve and availability of the precursor.

The processes involved in preparation of activated carbon are usually costly. It is a disadvantage to the economical aspect which encouraged the attention to exploit raw materials that are cheaper and abundant in nature. When cheap precursors are used, the production cost and the disposal problem are reduced (Al-Qodah & Shawabkeh, 2009). The major challenge in activated carbon production is to yield the optimum carbons with a preferable structure and pore at low temperature (Ahmad et al., 2009).

Quality of adsorbent differs by its pore size. That is the reason for pore size as one of the criteria in selection of activated carbon for a specific application. Pore size can be described in three groups using IUPAC classification. They are: micropores (when the pore width less than 2 nm), mesopores (when pore width is between 2 nm and 50 nm) and macropores (when the pore width is greater than 50 nm) (Yahya et al., 2015).

Commercial activated carbon is commonly available in two forms: powder and granular. Powdered activated carbon is usually comes in the sizes of 15 – 25 μm and used mainly in liquid media, whereas granular form is usually used both in liquid and gas applications. Both types of activated carbons are widely used in medicine (Ilomuanya et al., 2016), pharmaceutical (Nguyen et al., 2013; Jodeh et al., 2016), wastewater treatments (Bonvin et al., 2016), air purification (Choo et al., 2013), food and beverage industry (Egwim et al., 2013), and industrial processes such as decolorizing agent (Dawood & Sen, 2014), product purification (Reay, 2013) and odor-removing agent (Opara et al., 2013).

2.2 Activated Carbon Precursors

Activated carbons are produced from carbonaceous materials. Precursors are chosen depending on several factors: available in abundant, low in cost, consistency of quality and its purity (Hidayat & Sutrisno, 2017). The materials can either be natural or synthetic resources. Natural resources like bituminous coals and forest products such as peat and wood are commonly used for activated carbons production (Demirbas, 2009).

Commercial activated carbon is widely used for adsorbing various substances in various industries. However, commercial activated carbon is expensive material, specifically in heavy metal removal in wastewater treatment. Alternatively, industries use live biological systems to encounter heavy metal contaminants at low concentrations. However, in highly contaminated areas and industrial effluents, the system shows a failure. Therefore, natural materials and certain wastes from agricultural processes come into the picture. These non-living bio-materials have potential to be used as low cost adsorbents because of their capability in lowering metal ion concentration to parts per billion (ppb) levels due to their high affinity for cationic metals (Johnson et al., 2008). Agricultural wastes can provide a renewable and cheaper precursors in the preparation of activated carbons (Hameed et al., 2009).

A numbers of agricultural bio-wastes (or by-products) have been used as activated carbon precursor such as rice husks (Ghosh & Bhattacharjee, 2013), (Hazza, 2014); cocoa shells (Ahmad et al., 2013a), (Ribas et al., 2014), (Theivarasu & Mylsamy, 2011); cocoa pod husk (Cruz et al., 2012), (Chethana, 2014); almond shells (Chayande et al., 2013); palm kernel shells (Abechi et al., 2013); oil palm (Allwar, 2012); grass (Palanichamy et al., 2013); date (Hameed et al., 2009); date palm seed (Halbus et al., 2013); olive stone (Larous & Meniai, 2016) and (Bohli et al., 2013); and mango nuts

(Kwaghger & Ibrahim, 2013). The performance of each precursor is varies to each other, but suit their objectives.

Tropical countries produce abundant of agricultural by-products and often considered them as wastes which lead to environmental problem. Conversion steps from waste materials into activated carbon not only to provide solution to handle the wastes in profitable way but also provides a potentially adsorbent for the various purposes (Altenor et al., 2009).

Cocoa is among major crops planted in Malaysia with about 6.75 % of the total crop plantations (Zafar, 2015). Although the total cultivated area for cocoa trees had decreased in 2016, and the pattern was expected to remain for years, the supplies of cocoa beans are maintained from import activities from other cocoa-planter countries (MCB, 2016). Therefore, wastes from cocoa products (shells and nibs) are still available.

Cocoa pod husks and cocoa shells have been used as precursors for activated carbon productions in various researches. Mostly, activated carbons produced from these two by-products are designed for wastewater treatments and dye removals activities. Table 2.1 shows the applications of cocoa-based activated carbon. The proposed cycle in producing cocoa nib-based activated carbon is as in Figure 2.1.

Table 2.1 Cocoa-based Activated Carbon and Its Applications

Activated Carbon	Applications	Reference
Cocoa Pod Activated Carbon	Removal of Zn (II) in aqueous solution	Njoku, 2014
	Textile industrial wastewater color removal	Chethana, 2014
	Removal of methylene blue in aqueous solution	Pua et al., 2013
	Removal of arsenic in aqueous solution	Cruz et al., 2012
	Wastewater treatment	Odubiyi et al., 2012
Cocoa Shells Activated Carbon	Removal of Remazol Black B reactive dye from aqueous solution	Bello & Ahmad, 2011
	Adsorption of Cu (II) ions from aqueous solution	Ajifack et al., 2014;
	Removal of Reactive Violet 5 Dye	Ribas et al., 2014
	Adsorption of Ni(II) ion from an aqueous solution	Kalaivani et al., 2014
	Removing of Cationic dye from aqueous solution	Ahmad et al, 2012

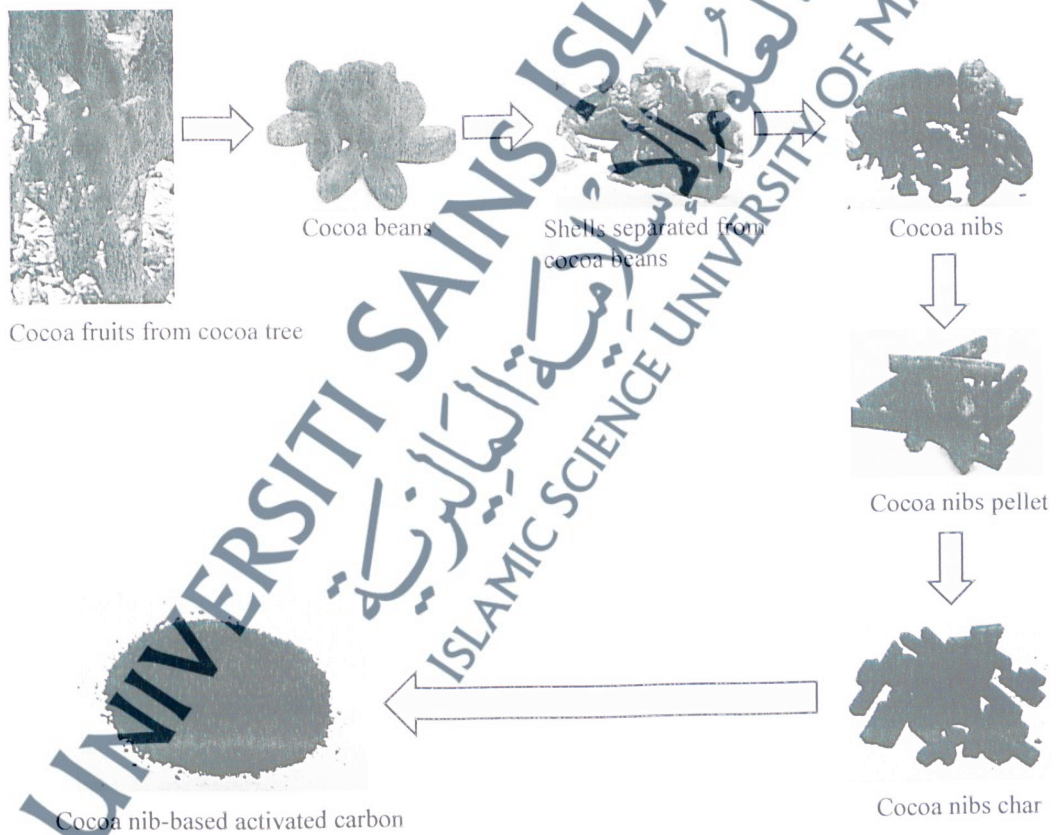


Figure 2.1 A simplified schematic diagram on production of activated carbon: from cocoa tree to cocoa nib-based activated carbon.

2.3 Preparation of Activated Carbon

By principal, the two main steps in the preparation of activated carbons are the carbonization of the raw material or precursor and the activation of the char using either physical or chemical activation (Alslaibi et al., 2012).

2.3.1 Carbonization

Correia et al., (2017) defined carbonization as a process to convert organic material to fundamental carbon at a set temperature without oxygen to be present. During this process, the volatile compounds are eliminated and char is formed. The produced char usually has poor adsorption capacity due to the poor porous structure. The reactions were generally complex and occurred simultaneously at varying rates depending on type of organic materials (precursors), carbonization time and temperature involves.

In carbonization process, moisture content was decreased to residual values below than 3.6 %. Variabilities of the moisture content among the different biochars can result from the availability of low boiling point components formed during hemicellulose and cellulose decomposition. The components were trapped in the biochar structure and were released gradually during the moisture content determination. This moisture reduction is important to improve the combustion efficiency. However, thermal decompositions cause structure rearrangement, which reduce the number of hydroxyl groups in the biochar surface that becomes more hydrophobic (Correia et al., 2017).

During carbonization, the temperature attacks the organic matters that caused cracking, surface changes, rearrangement of dimension, decrease in volume due to shrinkage and mass loss (Sebbahi et al., 2014). At the same time, devolatilization and

depolimerization took place (Wang et al., 2016). Pyrolysis temperature is the critical parameter in pyrolysis followed by heating rate, inert gas flow rate and the holding time. Generally, increase in carbonization temperature shall reduce the carbon yields (Ioannidou & Zabaniotou, 2007).

The process of carbonization can be divided into six stages. The remarks for each stage are summarized in Table 2.2.

Table 2.2 Carbonization process

Stage	Temperature (°C)	Reaction	Remark
1	20 – 110*	Endothermic	Drying process where precursor is release its moisture as water vapor.
2	110 – 270*	Endothermic	Final traces of water are eliminated and the organic matter starts to decompose by releasing carbon monoxide, carbon dioxide, acetic acid and methanol.
3	270 – 290*	Exothermic	Decomposition continues as heat is evolved. Gases and vapors continue to be released together with some tar.
4	290 – 400*	Exothermic	Decomposition of the structure continues and the combustible gases are released (carbon monoxide, hydrogen, methane and carbon dioxide gas) together with the condensable vapors (water, acetate, methanol, acetone and tars).
5	400 – 500*	Not available	The transformation to carbon is practically complete. Tar is still trap in the structure. Further heating until 500 °C is needed to eliminate more tar and increase the fixed carbon content to about 75 %. The carbonization stage is completed.
6	500**	Not available	Loss of hydrogen and reordering of the structural units

*Beaumont (1985)

**Gonzalez et al. (1997)

In general, the optimum carbonization temperature is in the range of 500 to 900 °C. The products of carbonization are chars, gas and tar (Rozhan & Purwanto, 2015).

Flash pyrolysis will generate high volumes of liquid (bio oils). Meanwhile, carbonization or slow heating pyrolysis will produce high yield of char (Wang et al., 2016).

2.3.2 Activation Step

Activation step is applied to the produced char to improve the porosity by increase the pore diameter and develop new pores (Alslaibi, 2012). Moreover, Chandra et al. (2009) presented the idea that porosity of activated carbon is influence by the nature of the precursor used and the process of activation applied.

Generally, there are two methods to activate the carbon: physical and chemical activations or treatments. These methods are widely applied in commercial activated carbons production (Alslaibi, 2012). As an alternative to cater for high quality activated carbons needs, the physiochemical activation is applied as activation method to provide very promising activated carbon (Yahya et al., 2015).

2.3.2.1 Physical Activation

Physical activation is a two-step process to transform a precursor into activated carbon. The first step is carbonization of the precursor to form non-porous or less-porous char by pyrolysis at a range of temperatures (400 to 1000 °C) depending on the suitability of the process, in an inert atmosphere (usually under nitrogen gas flows) (Adegoke & Bello, 2015). It is follows by activation step which involves the contact of the char with steam, oxidizing gas such as carbon dioxide (CO₂), air or their mixtures without the presence of a catalyst (Alslaibi, 2012).

Usually, in physical activation, the carbonization temperature ranges between 400 and 850 °C is applies and it can reach to 1000 °C (Guo et al., 2009). In between the

process, rearrangement of carbon atoms into graphite-like structure happens (Yahya et al., 2015). Aromatic sheets and strips will produce a rigid carbon skeleton. This is due to the elimination of non-carbon elements such as hydrogen, oxygen, and nitrogen from polymeric cellulose or lignin. The porosity constitutes by the gaps between these basic graphitic crystallites (Kwagheger & Ibrahim, 2013).

The activation temperature applied is between 600 to 900 °C (Guo et al., 2009). Commonly, the activation involves two stages of pore formation. The first stage is the removal of disorganized carbon and exposition of aromatic sheets to introduce microporosity. The second stage is the widening the existing pores or formation of larger-sized pores (Ozaki, 2013).

CO₂ is commonly used as activating gas in physical activation process. It is a clean gas which is easy to handle and is able to facilitate control of the activation process because at 800 °C of activation temperature, the reaction rate is slow (Taer et al., 2018). Physical activation produces activated carbons which lack of satisfactory characteristics as adsorbents or as filters (Adegoke & Bello, 2015).

In a study conducted by Ahmad et al. (2013a), they reported the significant effect of physical activation method using CO₂ on cocoa shell waste to produce porous structures of activated carbons. They found that the char was highly microporous with a narrow pore size distribution when carbonized at temperature below 600 °C. Char produced at 600 °C recorded higher uptake of CO₂ compared with char carbonized at 400 and 500 °C. Char produced at temperature above 600 °C was found to decrease in CO₂ uptake, an indication of low surface area. A similar findings was reported by Guo et al. (2009) when they studied the influence of CO₂ on the porous structure of activated carbon prepared from coconut shell. They found that while the yield and average pore diameter of the prepared activated carbons decreased; the surface area and pore volume

increased with increasing activation temperature from 750 to 900 °C. This is due to a combination of liberating the volatiles from the char and char oxidation with carbon dioxide.

Activating temperature in each study runs on agricultural wastes to produce activated carbon varies. Some were using high activating temperature (800 °C) while others experimenting with low temperature (300 to 500 °C). The optimum condition to activate carbon from agricultural wastes is much depended on raw material itself. Selection of activation temperature and activation agent use is also important (Aworn et al., 2008). Table 2.3 shows previous studies on production of activated carbon using physical activation process.

Table 2.3 A list of activated carbon produced from agricultural waste using physical activation method.

Raw Material	Activating Agent	Activation Temperature (°C)	Reference
Coconut shell	CO ₂	900	Rashidi et al., 2014
Cocoa shells	CO ₂	850	Ahmad et al., 2013a
Palm shell	Steam	900	Guo & Deng, 2013
Coconut shell	CO ₂	900	Ghe et al., 2009
Bean pods	Steam	700	Cabal et al., 2009
Macadamia nut-shell	Steam	800	Aworn et al., 2008
Apricot stones	Steam	850	Sentorun-Shalaby et al., 2006
Oak	CO ₂	800	Zhang et al., 2004

2.3.2.2 Chemical Activation

Al-Qodah & Shawabkah (2009) as being quoted by Yahya et al. (2015) referred chemical activation as wet oxidation which requires impregnation of activating agent into the precursor. Activated carbon is the end-product after washing procedure. In chemical activation both the carbonization and the activation step starts concurrently (Hayashi et al., 2000). Chemical activation usually performs at fairly low temperature:

300 to 700 °C, 400 to 700 °C, 400 to 800 °C or 500 to 800 °C. However, it was suggested that in preparing the activated carbon suitable for gas phase applications, the temperature use should be as low as 400 °C (Suhas et al., 2007).

Chemical activation gets its name from the usage of inorganic additives (activating agents) which play a role in degrading and dehydrating the cellulosic materials in the precursor (Yahya et al., 2015). Activating agents prevent the formation of the tar or ash (Yahya et al., 2015), develop porosity and enhance the carbon yield (Rodríguez-Reinoso & Molina-Sabio, 1992). According to Chen et al. (2011), chemical activation has been done at 400 to 900 °C.

Basically during the chemical activation process, carbonization and activation steps happen simultaneously with the aid of chemical activating agents during impregnation process (Yahya et al., 2015). Activating agents such as zinc chloride (ZnCl_2), phosphoric acid (H_3PO_4) (Suhas et al., 2007; Chen et al., 2011), potassium hydroxide (KOH), sodium hydroxide (NaOH), potassium carbonate (K_2CO_3) (Chen et al., 2011), sodium carbonate (Na_2CO_3), aluminium chloride (AlCl_3), magnesium chloride (MgCl_2), and sulphuric acid (H_2SO_4) (Karagez et al., 2008) are usually use in various studies of producing activated carbon by chemical activation. The precursors impregnated with these agents can prevent tar development and reduce the volatile matter growth (Chandra et al., 2009).

In chemical activation method, more than one chemical (activating agent/s) can be used in a single production. The activating agents assist the development of the carbon porosity through dehydration (Kumar & Jena, 2016) and degradation mechanisms (Ioannidou & Zabaniotou, 2007). The interaction between the activating agents and the carbon structure allows the application of a lower temperature compared with that of physical activation. However, prior usage of the prepared activated carbon,

the residual chemicals need to be removed from the carbon using distilled water or a mild acid (Alslaibi et al., 2012).

There are at least four main advantages of chemical activation in comparison to physical activation as listed below:

- i. The activation required lower activation temperature, therefore can minimized the cost of energy (Bashir et al., 2015).
- ii. The chemical activation produced higher carbon yield compared with the physical activation (Acharya et al., 2009),
- iii. The chemical activation required less activation time (Alslaibi et al., 2012)
- iv. The chemical activation developed high porosity carbon structure (Alslaibi et al., 2012)

It was proven that chemical activation has the ability to suppress the tar production which results in high carbon yield (Purnomo et al., 2012). Besides, a development of oxygenated groups on the surface of activated carbon can be enhanced by chemical activation (Gad & El-Sayed, 2009).

However, the application of activating agents will add a relatively high cost to the operational budget. Additional washing stage is needed to remove the chemical (Alslaibi et al., 2012, Yener et al., 2008). This process could also lead to a possible contamination and equipment corrosion caused by the chemical agents (Yener et al., 2008).

The most common chemical agents used are ZnCl_2 , KOH and H_3PO_4 . Researchers be likely to use less K_2CO_3 as activating agent (Ioannidou & Zabaniotou, 2007). However, ZnCl_2 can be harmful to human, animals and environment due to its toxicity effects (Panchalingam et al., 2016). Activated carbons impregnated with ZnCl_2 are not suitable in pharmaceutical and food industries applications due to its possibility

to contaminate products (Chandra et al., 2009). Tay et al. (2009) suggested that NaOH is efficient to activate low structural-ordered carbon materials and KOH is capable for the highly ordered carbon structures.

The two-stage chemical activation process is more practical, where the produced activated carbon is equipped with higher porosity and better surface area (Ioannidou & Zabaniotou, 2007). Impregnates a carbonized raw material would give a better result in porosity as the activating agent can get inside the pores and respond to the carbon. Activating agents have a great influence on the pore development and surface characteristics (Sahira et al., 2013). It also helps in creating a better development of cross-linked structures, as well as lessening the complicated respond among the chemical and contaminations (Mohd Din et al., 2009). Table 2.4 enlists a summary of researches on application of chemical activation technique in preparation of activated carbons using agricultural waste as precursor.

Table 2.4 A list of agricultural waste-based activated carbons prepared using chemical activation technique.

Raw Material	Activating Agent	Activation Temperature (°C)	Reference
Palm oil shells	Na ₂ CO ₃ , ZnCl ₂	700	Hussaro, 2014
Corn cobs	H ₃ PO ₄	500	Njoku & Hameed, 2011
Pistachio nut shells	KOH	600 W (microwave)	Foo & Hameed, 2011
<i>Jatropha curcas</i> shell	NaOH	70	Tongpoothorn et al., 2011
Bamboo	H ₃ PO ₄	200 W (microwave)	Liu et al., 2010
Sugar beet bagasse	ZnCl ₂	500-700	Demiral & Gündüzoğlu, 2010
Jute sticks	ZnCl ₂	400 – 700	Asadullah et al., 2010
Soybean oil cake	K ₂ CO ₃ , KOH	600 – 800	Tay et al., 2009

2.3.2.3 Physiochemical Activation

Physiochemical activation is performed by simultaneously activating the precursor with physical and chemical activation. The process is usually performed at high temperature (600 to 850 °C) in the presence of activating agent (e.g. K_2CO_3 , $ZnCl_2$ or H_3PO_4) under the flow of oxidizing agent such as CO_2 or steam (Salman & Hameed, 2010). With the combination of chemical and physical activation, physicochemical activation is highly desirable where high quality activated carbon with larger surface area can be produced. However, this type of activation is costly (Mohd Din et al., 2009).

Recently, high quality activated carbons from various precursors through CO_2 –KOH activation with different operating parameters and thermal treatment routes have been reported by several researchers. Nowicki et al. (2015) produced microporous activated carbons with surface areas ranging from 361 to 1173 m^2/g from cherry stones. Temdrara et al. (2013) succeeded to produce microporous activated carbon with relatively larger surface area (1793 m^2/g) from olive stones. Paltynowicz et al. (2015) produced a microporous activated carbon with surface area of 768 m^2/g using giant knotweed as precursor.

The interaction between KOH and CO_2 results in dehydrated to K_2O and K_2CO_3 due to the water-shift reaction. The extreme growth of the carbon material is due to the intercalation of potassium into the carbon network, which accelerates the carbon liberation (Hui & Zaini, 2015). Similar observation was reported by Huang et al. (2015) when they found that application of CO_2 in activation technique was efficient in increasing the surface area and the formation of mesopores in the activated carbon. Another study by Veksha et al. (2016) demonstrated the effect of interaction between KOH and CO_2 or steam gasification in pore opening thus leading towards well-

developed pore structure. Table 2.5 shows a summary of researches on application of physiochemical activation technique in preparation of activated carbon.

Table 2.5 A list of researches on application of physiochemical activation technique in preparation of activated carbon.

Raw Material	Activating Agent	Activation Temperature (°C)	Reference
Aspen wood	KOH/CO ₂	900	Veksha et al. (2016)
Olive stones	KOH/CO ₂	800	Temdrara et al., 2015
Giant-knotweed	KOH/CO ₂	800	Faltynowicz et al. (2015)
Cherry stones	KOH/CO ₂	800	Nowicki et al., 2015
Oil palm fronds	KOH/CO ₂	850	Salman & Hameed, 2010
Date stones	KOH/CO ₂	850	Hameed et al., 2009
Coconut shell	KOH/CO ₂	850	Mohd Din et al., 2009

2.3.3 Ash in Activated Carbon

Ash is a troublesome compound in an activated carbon which can disturb the porousness (Ahiduzzaman & Sadrul Islam, 2016). It is a form of impurity or residue that remains when the carbonaceous material is burned off. Inorganic such as silica, and other metal oxides such as calcium oxide (CaO), magnesium oxide (MgO) and potassium oxide (K₂O) present in the organic material that usually formed the ash content (Danewalia et al., 2016). However, ash can be leached out from the activated carbon using acid or alkali solutions (Ahiduzzaman & Sadrul Islam, 2016).

According to Ahmad et al., (2013b) cocoa shell-based activated carbon had recorded an increased in surface area from 367 m²/g to 1,000 m²/g after acid treatment was applied. The temperature used and the acid concentration applied during the acid treatment had affected the development of highly mesoporous structure. Acid treatment modified the surface chemistry by releasing the acidic and phenol groups linked to calcium, which increased the acidity of activated carbon (Ahmad et al., 2013b).

2.4 Characterization of Activated Carbon

The quality of an activated carbon lies on the adsorption performance, which basically reliant on its characteristics and properties. Qualitative and quantitative information of activated carbons will give a foundation for assessment and assortment of activated carbons for explicit applications. This information is also beneficial for modeling the characteristics and performance of activated carbons.

The usual measured data are surface area, average pore size, pore size distribution, pore volume, and the surface chemistry of the carbon. The most popular method to characterize activated carbons is by using surface area and porosimeter where adsorption data is measured with mathematical models such as surface area using BET model equation and pore volume using BJH model. Microscopic methods are another method of characterization which enable the examination into the micro and sub micro aspects of activated carbons. Such microscopic method is scanning electron microscopy (SEM) (Achaw, 2012).

2.4.1 Physical Properties

Physical properties or textural characteristics of activated carbons play an important role. The types of their structures (macropore, mesopore or micropore) suite them with their adsorption manner and define their porosity. Pore size is a very important element in liquid adsorption as well as the specific surface area. Another component is pore volume, where the ratio between the pore structure and the pore volume may be useful in the adsorption capacity studies.

2.4.1.1 Carbon Yield

Selection of precursor is very important in producing the properties of the end-product of the carbon. Both physical and chemical activation methods affect the carbon yield. Physical activation via thermal application produces lower carbon from the raw material and the type of pore structure is usually microporous. Chemical activation produce higher carbon material compared with that of physical activation method. Usually, raw materials with high content of volatiles are treated with chemical activation method to produce the activated carbon (Kharat, 2015).

Yield (in percentage) of activated carbon is established from the calculation of ratio of the dry weight (g) of the prepared activated carbon, w_c to the dry weight (g) of the precursor, w_o as shown in Equation 2.1 (Wu et al., 2013).

$$(2.1) \quad Yield (\%) = \frac{w_c}{w_o} \times 100$$

where w_c is the dry weight (g) of the prepared activated carbon and w_o is the dry weight (g) of the precursor. This amount was measured to investigate the efficiency of the activation process (Ahmad et al., 2011).

Higher temperature during carbonization (600 - 700 °C) can increase the release of liquid and gases but at the same time, reduce the char yield. It will also intensify fixed carbon and ash contents and decrease the volatile matter content. This is the effect of the primary decomposition of precursor and the secondary decomposition of char at high temperatures. In consequence, high carbonization temperatures provide a higher quality char but lower the yield (Zhao et al., 2017).

Commonly, the increase in pyrolysis temperature would decrease the yield of char and activated carbon that can be observed from the reduction of solid yield and the increase of liquid and gases production. However, as the temperature is elevated, the

ash and fixed carbon contents are also raised but the volatile matter is decreased (Zhao et al., 2017).

As a result, when the temperature is raised, the quality of char produce is better but the yield is decreased due to the decomposition of raw material (primary decomposition) and the decomposition of char residue (secondary decomposition) (Nor et al., 2013). The secondary decomposition of the char produces non-condensable gaseous products that adds to the increase in gas yield (Mazlan et al., 2015).

According to Yahya et al. (2015), agricultural waste and lignocellulosic material yield lower activated carbons compared with hard raw materials such as coal, anthracite or peat. However, these materials can produce a higher-quality activated carbon which is the top concern. Volatile matters contained in the raw materials is extremely important in creating activated carbon with highly porous structures (Yahya et al., 2015).

Generally, in optimizing the preparation of the activated carbon, there are important parameters that need to be considered such as the carbonization time, the carbonization temperature and the flow rate of carbon dioxide (CO₂)/steam in physical activation, the impregnation duration and impregnation ratio in chemical activation method. Both the raw material and the activation method affect the characteristics of the prepared activated carbons (Tan et al., 2008).

2.4.1.2 Activated Carbon Structure

Activated carbon is a carbon based material equipped with internally well-developed pore structure. The developed pore structure defines the surface area and porosity of the carbon which can be divided into micro-, meso- and macropores (Bhatnagar et al., 2013). Much attention was given to the effect of pyrolysis pressure in

structuring the carbon to form the chars and liberation of ash. Such effects can be observed by the occurrence of plastic deformation where particles were melted at high heating rates. This phenomenon usually correlates with carbon species which contain volatile matter (Tchapda & Pisupati, 2014). Due to carbonization, the structure of activated carbon is consists of elementary crystallites, graphitic layers and stacks of horizontal planes (Mopoung, 2008).

Figure 2.2 depicts of a porous structure of an activated carbon. The large or diffusion pores are penetrating through the entire particle. Adsorbates rapidly diffuse from the external surface into the fine pores, that branching off from large pores within the particle. The fine pores are where most of the adsorption occurs. Capillary condensation (with the formation of a meniscus of the liquid adsorbate) takes place within the mesopores (Grosman & Ortega, 2008).

Macropores are important as passages to the inner part of the pores for the adsorptive molecules but are least significant in adsorption. The difference between adsorption in micropores and that in larger pores (mesopores and macropores) lies in the adsorption mechanisms. Adsorption in micropores corresponds to the filling of volume, whereas for mesopores and macropores, adsorption consists of a gradual and multilayer adsorption process according to the Brunauer-Emmett and Teller (BET) theory (Thommes et al., 2015).

2.4.1.3 Pore and Surface Area Characteristics

The key property of an activated carbon is its adsorption performance which is associated with surface area, pore volume and pore size distributions. Variables in preparation stage such as activation temperature, activation time and chemical impregnation ratio will affect the development of pore and surface profiles of the

produced activated carbon (Guo et al., 2009). Porosity and pore size distribution for an activated carbon characterize its pore space, that portion of the carbon's volume that is not engaged by solid material (Nimmo, 2004). The pore size distribution of activated carbon is well represented in Figure 2.3.

A pore is a hole or cavity on the outer surface of an object. It has large influence on the performance of an activated carbon. The pore space is usually measured in terms of individual pores – a concept that enables quantifications of its crucial character. Porosity is the ratio of voids to solids in an activated carbon. It is the fraction of the total volume that is taken up by the pore space (Nimmo, 2004).

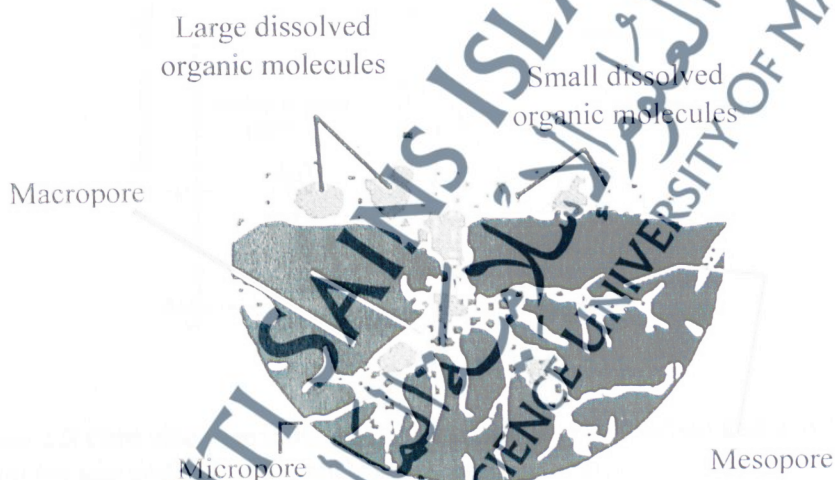


Figure 2.2 A schematic diagram explains the difference between pore structures: macropore, mesopore and micropore (Cousland, 2017).

Pore size distribution is a very important property of adsorbents which determines the fraction of the total pore volume accessible to molecules of a given size and shape. According to the classification of IUPAC-pore dimensions, the pores of adsorbents can be grouped into micropores, where the diameter, d is smaller than 2 nm,

mesopore where d is between 2 to 50 nm and macropore when d is bigger than 50 nm (Yahya et al., 2015).

The distribution of pore size describes the internal structure of solid carbon base on the assumption that the empty and vacant spaces in the carbon can be characterized by a model of same set of non-communicating and commonly shaped pores. The distribution is directly associated with equilibrium and kinetic parameters relevant to porous material. Possibly, the pore size distribution is the main player in characterizing variety of the structures of porous materials (Chandra et al., 2009).

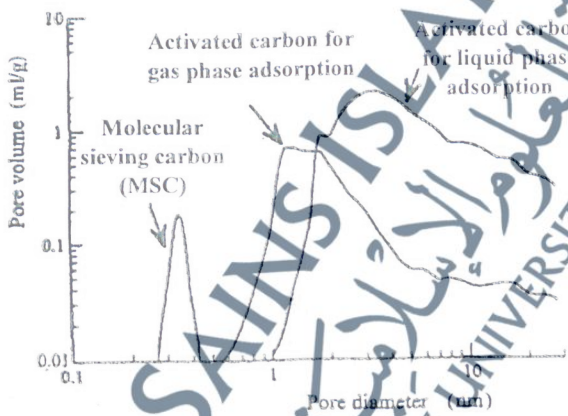


Figure 2.3 Pore size distributions of molecular sieving carbon and activated carbon for gas and liquid adsorbates (Manocha, 2003).

Hard materials like coconut shell and palm shell are preferable raw materials for production of activated carbon because of their high density, high carbon content and low ash. Hard materials are rich with lignin. High lignin content will produce the highest yield of char, activated carbon and higher activation rate during activation as lignin has a high carbon content and a molecular structure similar to bituminous coal (Suhas et al., 2007). Hard shell-based activated carbon was shown to have a major portion of its pores in the micropore range, whereas wood-based and husk-based

activated carbon contained significant amounts of mesopores and macropores (Ginsburg, 2016).

According to Yahya et al. (2015), pore size distribution of the produced activated carbon depends on the degree of initial impregnation of the catalyst used. It varies depends on the type of precursor used as well as the method applied in production of activated carbon (Ioannidou & Zabaniotou, 2007; Tan, 2008). Raw materials with a high lignin content (grape seeds, cherry stones) develop macroporous activated carbons, while precursors with a high cellulose content (apricot stones, almond shells) produce microporous activated carbon (Ioannidou & Zabaniotou, 2007).

Gas adsorption method exposes critical information about the textural properties of porous material (surface area, pore structure etc.). The method is known as physisorption (physical adsorption) (Anovitz et al., 2015). Gas adsorption is a well-recognized method to characterize the texture of porous objects and fine particles (Thommes et al., 2015). Nitrogen (N_2) is the usual gas used to characterize porosity at 77 K. Alternative gases such as krypton, argon and carbon dioxide can be used at 77 K, 87 K and 273 K, respectively (Anovitz et al., 2015).

In physical activation, the surface area of the activated carbon increases due the development of pore structure when treated with thermal treatment using carbon dioxide, steam, or partially oxidizing gases. The carbon selectivity and adsorption capacity is improved with further chemical treatment using chemicals comprising numerous functional groups. Chemicals such as sulfuric acid, nitric acid, phosphoric acid are among the usual chemical used. A mixture of acids could result in increases or decreases of the surface area of the carbon. This is due to the impact of the acids to the pore structures, where too much acid applied could damage the pore (Shawabkeh et al., 2015).

According to Shawabkeh et al. (2015), activated carbon contains mineral oxides in ash matrix which block the pores and decrease the total pore volume and the surface area. The acid treatment could leach out some of these minerals and eventually increase the porosity of the activated carbon. The acid used and the composition in acid mixtures significantly affect the porosity's increment scale.

2.4.1.4 Surface Morphology

Scanning Electron Microscope (SEM) is usually used to study the surface morphology of precursors and produced activated carbons (Yang, 2003; Wu et al., 2013; Ahmad et al., 2013a; Yahya et al., 2015; Yakout and Sharaf El-Deen, 2016). Some of them use Transmission Electron Microscope (TEM) (Nor et al., 2013). In usual practice, the pore structure, surface structure and pore arrangement of activated carbon is visualized via SEM. SEM is useful in activated carbon production due to its ability to verify the presence of porosity and pore development during carbonization and activation periods (Ahmad & Alrozi, 2010).

Wu et al. (2013) managed to appreciate the peanut shell material which has rough irregular surface with few cracks and voids but lack of porous structure. They compared the findings with the produced activated carbon where porous structure existed with a relatively smooth surface containing many craters and its pores were uniform from microporous to mesoporous structures. Ahmad et al. (2013a) presented different types of pores (small, transitional and large pores) with different shapes which were visible in micrograph images when studied the cocoa shell-based activated carbon with SEM.

Figure 2.4 shows the SEM micrographs of cocoa shell precursor and cocoa shell-based activated carbon produced (Ahmad et al., 2009). It shows that the coconut shell

activated carbon has relatively numbers of pores developed after activation process compared to char itself.

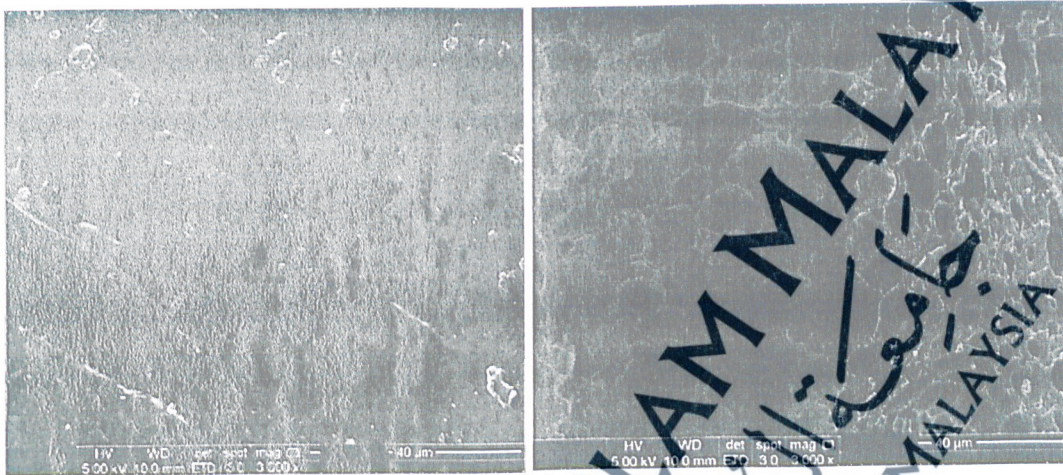


Figure 2.4 Scanning electron micrographs of (A) raw cocoa shell and (B) cocoa shell-based activated carbon (Ahmad et al., 2013a).

2.4.2 Chemical Properties

Chemical characterisation of an activated carbon is represented by proximate analysis, ultimate analysis and surface functional groups.

2.4.2.1 Proximate and Ultimate Analysis

Proximate analysis is performed to determine the moisture, ash and volatile matter content in order to calculate the fixed carbon of a precursor. Ultimate analysis or elemental analysis is carried out to determine the percentage of carbon, hydrogen, nitrogen, oxygen and sulphur present in a precursor (Wu et al., 2013). The thermal treatment applied during the production of activated carbon removes the moisture, some ashes and the volatile matter contents of the precursor to produce solid char and activated carbon with different properties than the initial material. This leads to

development of porous structure, larger surface area, variation in pore structures (micropores, mesopores and macropores) and different composition of elements and ash content (Ioannidou & Zabaniotou, 2007). The inorganic material remained in activated carbon is measured as ash content (in percentage) where allowable practical limit (the ash content) in commercial activated carbon usually in the range between 2 and 5 % (Huang et al., 2015).

Most lignocellulosic materials are composing mainly of oxygen, carbon and hydrogen. A study done on peanut shell material demonstrated that there were 48 % of oxygen, 45 % of carbon and 6 % of hydrogen. It was also shown that the ash content might be due to the presence of potassium, calcium, silicon and sodium. Mineral contents such as potassium and calcium in the precursor could encourage various reactions engaged in the production of activated carbon and could enhance for higher reactivity which support the process (Wu et al., 2013).

2.4.2.2 Surface Functional Groups

Activated carbons have a wide variety of surface functional groups which depend on the precursor and method of activation (Suhas et al., 2007). Kalijadis et al. (2011) had stated that Boehm method (as suggested by Boehm, 2002) can be used to determine the surface oxygen groups on an activated carbon with acidic (carboxyl, lactone and phenol) and basic properties. The O-containing groups are the most important surface functional group which gives features such as polarity, hydrophilic and acidic character (Li, 2012). Allwar (2012) proved that the activated carbons have oxygen functional groups consisting of carboxylic, phenol or lactonic group besides aromatic hydrocarbons ring.

Acid such as nitric acid modifies the surface functional groups of activated carbon by increase the presences of acid group. This might be due to the elimination of inorganic compounds and the left sites on the carbon were filled with oxygen by chemisorb. Additionally, the increase in intensity of C=O (carboxylic group), O-H (hydroxyl group) and C-O (phenol group) in the FTIR spectra show the presence of more oxygen functional groups on the activated carbon (Allwar, 2012). The acidic character that relates to the surface oxygen contents (carboxyl, phenolic, lactone, lactol and quinone groups) are primarily located at the edges of graphene layers that contribute to the building blocks of activated carbon (Chen et al., 2011). Figure 2.5 and 2.6 demonstrate the surface chemistry of carbon (Brennan et al., 2001) and FTIR spectrums of cocoa shell-based activated carbon (Ahmad et al., 2013a), respectively.

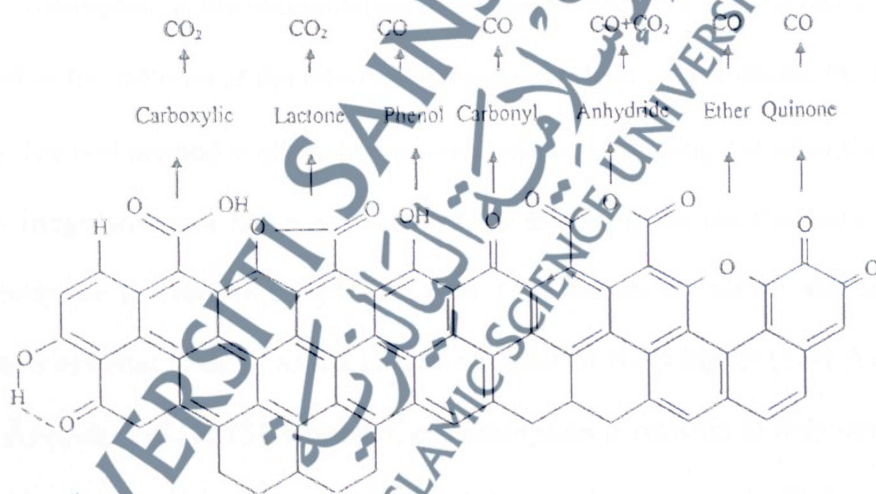


Figure 2.5 Surface oxygen containing groups on carbon (Shafeeyan et al., 2010)

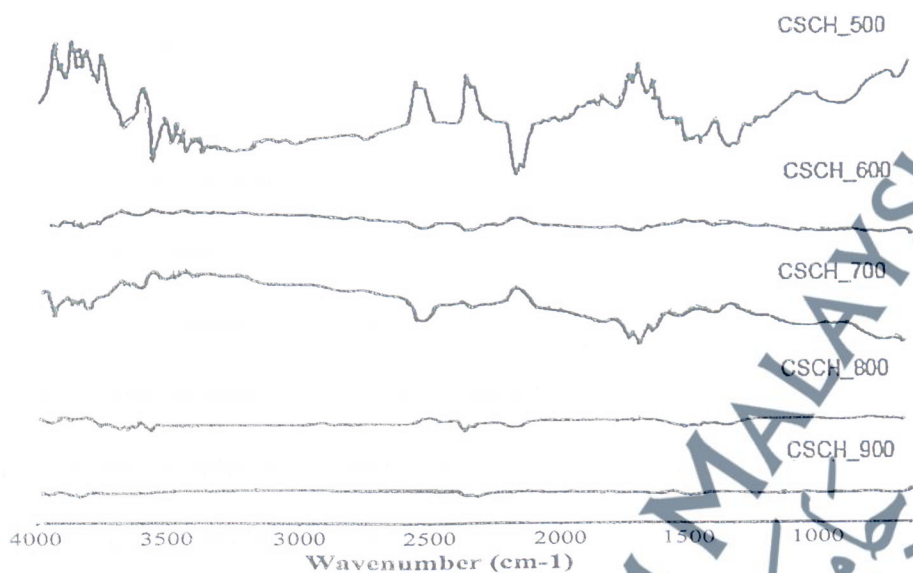


Figure 2.6 FTIR spectra of cocoa shell-based activated carbons at different carbonization temperatures (Ahmad et al., 2013a).

2.5 Adsorption Isotherm

Adsorption is the accumulation of a mass transfer process that can generally be defined as the material at the interface between solid and liquid phases (Khaled et al., 2009). The best method to characterize activated carbon is using gas adsorption because of the irregularities of the pore system. CO_2 and N_2 gases are the usual adsorbent molecules use to evaluate the pore systems. CO_2 can access narrow and small pores (micropore) better than N_2 as the kinetic diameter of N_2 is bigger (3.64 Å) than CO_2 (3.30 Å) (Sun et al., 2015). However, gas adsorption is relevant to only material with pore size less than 300 nm based on the Kelvin equation (Cao et al., 2016).

Theoretically, adsorption isotherm is important as it describes qualitative information on the nature of the solute – surface interaction. Additionally, in the practical point of view, it defines the specific relationship between the concentration of adsorbate and its degree of accumulation onto the surface of adsorbent at constant temperature (Li et al., 2009).

Most of the adsorption isotherms fit into one of the five types shown in Figure 2.7. Type I isotherm shows that the pores are microporous. Type II isotherms indicate the adsorption occurs on nonporous powders or on powders with pores diameter larger than micropores. Type III isotherms are specify the greater interaction between adsorbate and an adsorbed layer than the interaction with the adsorbent surface. Type IV isotherms occur on porous adsorbents possessing pores mainly in mesopore range. Type V isotherms exhibit the potential interaction of adsorbate-adsorbent which is similar to the Type IV isotherms (XAmplified, 2009).



Fig. 2.7 Five types of adsorption isotherms (XAmplified, 2009).

The analysis of the isotherm data by fitting them to different isotherm models is an important step to find the suitable model that can be used for design purposes (Tan et al., 2008). The parameters obtained from the different models provide important information on the sorption mechanisms, the surface properties and affinities of the sorbent (Khaled et al., 2009). Several equilibrium models are available for analysing

experimental sorption equilibrium data. From the literature, it was found that different adsorbent – adsorbate systems showed different adsorption behaviours where the adsorption data were represented by different isotherm models.

2.5.1 Langmuir Isotherm

The Langmuir isotherm was developed on the assumption that the adsorption process will only take place at specific homogeneous sites within the adsorbent surface with uniform distribution of energy level. Basically, once the adsorbate is attached on the site, no further adsorption can take place at that site; which concluded that the adsorption process is monolayer in nature (Mohd Din et al., 2009). The isotherm indicates that monolayer adsorption might occur on surface of the adsorbent as the surface was created with homogeneous adsorption patches (Ng et al., 2017).

The Langmuir equation is based on assumptions as stated by Desta & Lucia (2013):

- i) Monolayer adsorption onto a surface containing a fixed adsorption sites.
- ii) No shifting of adsorbate in the plane surface.
- iii) Sorption stops as adsorption site is filled.

The Langmuir isotherm equation is expressed by the following equation (Langmuir, 1918):

$$(2.2) \quad q_e = \frac{Q_o K_L C_e}{1 + K_L C_e}$$

The linear form of Langmuir isotherm equation is given by Equation 2.3.

$$(2.3) \quad \frac{C_e}{q_e} = \frac{1}{Q_o K_L} + \frac{1}{Q_o} C_e$$

where C_e is the equilibrium concentration of the adsorbate (mg/L) and C_o is the highest initial solute concentration, q_e is the amount of adsorbate adsorbed per unit mass of adsorbent (mg/g), Q_o is the maximum monolayer adsorption capacity of the adsorbent (mg/g) and K_L is the Langmuir adsorption constant related to the free energy adsorption (L/mg). The constant value can be evaluated from the intercept and the slope of the linear plot of experimental data of (C_e/q_e) versus C_e .

The essential characteristics of Langmuir equation can be expressed in terms of dimensionless separation factor, R_L , defined as (Dada et al., 2012):

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

where R_L value implies the adsorption to be either unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$), or irreversible ($R_L = 0$).

2.5.2 Freundlich Isotherm

The Freundlich isotherm assumes that adsorption occurs on a heterogeneous surface through a multilayer adsorption mechanism between equilibrium liquid and solid phase capacity (Kalavathy et al., 2005). The isotherm model is given by equation 2.5 (Dada et al., 2012, Bulut et al., 2008):

$$(2.5) \quad q_e = K_F C_e^{1/n}$$

where q_e is the amount of adsorbate adsorbed at equilibrium, (mg/g), C_e is the equilibrium concentration of adsorbate, (mg/L), K_F is the Freundlich constant, (mg/g)(L/mg)^{1/n} and n is the Freundlich heterogeneity factor.

The equation is conveniently used in the linear form by taking the logarithmic of both sides as equation 2.6 (Dada et al., 2012, Bulut et al., 2008):

$$(2.6) \quad \log q_e = \log K_f + \frac{1}{n} \log C_e$$

A plot of $(\log q_e)$ against $(\log C_e)$ yielding a straight line indicates the confirmation of the Freundlich isotherm for adsorption. The constant can be obtained from the slope and intercept of the linear plot of experimental data. The value of n indicates favourable adsorption when $1 < n < 10$.

2.5.3 Temkin Isotherm

Temkin isotherm explains the interaction between the adsorbent and the adsorbate. The principle of the model is to ignore the extremely small and great concentrations value, and assume that the adsorption heat of all molecules in the layer would fall linearly with coverage (Dada et al., 2012). In other word, Temkin isotherm describes a linear function of the adsorption energy to the surface coverage, which only works with ion concentrations in intermediate range (Ayawei et al., 2017).

The isotherm model is presented as in equation 2.7 and 2.8 (Dada et al., 2012):

$$(2.7) \quad q_e = \frac{RT}{b} \ln (A_T C_e)$$

$$(2.8) \quad q_e = \frac{RT}{b_t} \ln A_T + \left[\frac{RT}{b} \right] \ln C_e$$

The linear form of the model is as in equation 2.9 (Dada et al., 2012):

$$(2.9) \quad q_e = B \ln A_T + B \ln C_e$$

where, A_T is Temkin isotherm equilibrium binding constant (L/g), b_T is Temkin isotherm constant, R is universal gas constant (8.314 J/mol/K), T is temperature at 298 K and B is the constant related to heat of sorption (J/mol).

2.6 Adsorption Kinetics

The adsorption kinetics depicts the rate of adsorbate uptake on activated carbon and which regulates the equilibrium time. In order to select the optimum conditions for adsorption at full-scale batch equilibrium study, the adsorbate uptake kinetics is essential. The kinetic parameters are important to predict the adsorption rate. These parameters are: the effects of initial concentration, contact time, pH and adsorbent dosage, provides important data to design and modelling the adsorption process (Kalavathy et al., 2005). In fact, kinetic models are useful in determine the significance of diffusion mechanisms and the accuracy estimation of the diffusivities inside the adsorbent particles (Demirbas et al., 2008a). Such kinetic models for liquid-phase adsorption are pseudo first-order and pseudo second-order models (Kalavathy et al., 2005).

The approach of the adsorption process will be influenced by the physical and chemical characteristics of the adsorbent and on the system conditions (Ruíz-Baltazar & Perez, 2015). The kinetic data can be well-fitted to either the pseudo-first order or pseudo-second order kinetic models (Shahmohammadi-Kalalagh et al., 2011; Theivarasu & Mylsamy, 2010).

2.6.1. Pseudo-First-Order Kinetic Model

The pseudo-first order-kinetic model (Srihari & Das, 2008) has been widely used for the prediction of sorption kinetics. The model is defined as in equation 2.10 (Ho & McKay, 1998):

$$(2.10) \quad \frac{dq_t}{dt} = k_1 (q_e - q_t)$$

where q_e is the amount of adsorbate adsorbed at equilibrium, (mg/g), q_t is the amount of solute adsorb per unit weight of adsorbent at time, (mg/g), k_1 is the rate constant of pseudo-first order sorption (1/h).

Integrating equation 2.10 for the boundary conditions $t=0$ to t and $q_t=0$ to q_t , gives the following equation:

$$(2.11) \quad \log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t$$

Elimination of the logarithm constant as in equation 2.12, below.

$$(2.12) \quad \ln(q_e - q_t) = \ln q_e - k_1 t$$

The plot of $\ln(q_e - q_t)$ versus t gives a slope of k_1 and intercept of $\ln q_e$.

2.6.2. Pseudo-Second-Order Kinetic Model

In contrast, the pseudo-second-order equations predict the behavior over the whole range of adsorption and it is agreement with an adsorption mechanism being the rate controlling step (Bulut *et al.*, 2008). The pseudo-second-order equations based on equilibrium adsorption can be expressed as equation 2.13 (Ho & McKay, 1998):

$$(2.13) \quad \frac{dq_t}{dt} = k_2 (q_e - q_t)^2$$

where q_e is the amount of adsorbate adsorbed at equilibrium, (mg/g), q_t is the amount of solute adsorb per unit weight of adsorbent at time, (mg/g), k_1 is the rate constant of pseudo-second-order sorption (g/h.mg).

Integrating equation 2.13 for the boundary conditions $t=0$ to t and $q_t=0$ to q_t , gives the following equation:

$$(2.14) \quad \frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 t$$

which is integrated rate law for a pseudo-second-order reaction. Equation 2.14 can be rearranged to obtain linear form:

$$(2.15) \quad \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$$

The linear plot of t/q_e versus t gives $1/q_e$ the slope and $1/k_2 q_e^2$ as the intercept.

2.7 Adsorption Mechanism

The kinetics and mechanism of adsorption process can be determined using a developed kinetic model. The diffusion limitation needs to be considered as to effectively define the adsorption system (Akpomie et al., 2015). The adsorption process mechanisms (or the rate-controlling steps) can be determined using intraparticle diffusion and Boyd models.

The intraparticle diffusion and Boyd kinetics models can be expressed as in equations 2.16 (Khartikeyan et al., 2010) and 2.17 (Dada et al., 2017), respectively:

$$(2.16) \quad q_t = K_p t^{0.5} + C$$

where, where K_p ($\text{mg/g min}^{0.5}$) is the intraparticle diffusion rate constant and C is the intercept. The boundary layer thickness is described by the values of the intercept. The larger the intercept, the greater is the boundary layer effect (Ahmad et al., 2014).

$$(2.17) \quad B_t = -0.4977 - \ln(1 - F)$$

where F is the fraction of solute adsorbed at different times (t) and B_t is a mathematical function of F . F value represents the fraction of solute adsorbed at any time, t (min) and can be calculated by equation 2.18 (Okewale et al., 2015):

$$(2.18) \quad F = \frac{q_t}{q_e}$$

According to Okewale et al. (2015), there were three steps (mechanisms) in the process of an adsorption. The first one was film diffusion, where the ions of the adsorbate moved in the direction to the external surface of the activated carbon. The second step was particle diffusion, where the ions of the adsorbate moved inside the pores of the activated carbon not including an indefinite amount of adsorption that took place on the outer surface of the activated carbon. The last step was where the ions of the adsorbate adsorbed on the interior surface of the activated carbon.

2.8 Principal Component Analysis

Principal Components Analysis (PCA) is a method to identify patterns in data and use the identified patterns to highlight any similarities and differences. PCA is a powerful multivariate statistical tool for data analyzing, especially in high dimension data. Once the pattern of data is identified, the data could be compressed by reducing the number of dimension (Bartel et al., 2013).

In various literatures focusing in the characterization of prepared activated carbons, PCA was applied with the aim of highlighting the patterns, trends and groups of data and compare it with commercially available activated carbons. The idea is to avoid any inconsistency arise from undetected differences among these sorbents. This data analyzing technique allows a more specific assessment of the influence of each property assessed such as the physical structures, chemical properties and adsorption performance data (Álvarez-Uriarte et al., 2014).

As a descriptive technique, the selected variables for the PCA can be of any type. For example, x value may have a multivariate normal distribution, and the variables could be a mixture of continuous, ordinal or binary (0/1). Without taking into consideration the relevance of variances, covariances and correlations, and the linear

functions of binary and continuous variables, PCA summarizes almost every data variation from the original set of p variables using a smaller number of derived variables (Matricardi & McNally, 2014).

In order to apply the PCA properly, the mean from each of the data dimensions needs to be subtracted to get the average across each dimension. For example, the x values will give $\bar{x}$ subtracted and the y values will give $\bar{y}$ subtracted. The data set produced is having zero mean (Bartel et al., 2013).

In performing PCA, the original data is transforms linearly using mathematic procedures. The transformation into a new set of data is associates with new variable that termed as Principal Components (PCs). The PCs is identified as factor and eigenvector, and can be anticipated using variable's numerical quantity.

PC is explained as in equations below (Salleh & Hassan, 2015). As for example, the data consists of n observation on a vector of p variables:

$$(2.13) \quad X = (x_1, x_2, x_3, \dots, x_p)$$

The first PC of the data sample is defined by linear transformation as follows:

$$(2.14) \quad Z_i = a_1^T x = a_{1i} x_i$$

where $a_1 = [a_{11}, a_{21}, a_{31}, \dots, a_{p1}]$ is the chosen vector and variance $[z_i]$ is maximum. The simplified equations are as follows:

$$(2.15) \quad PC1 = a_1 x_1 + a_2 x_2 + a_3 x_3$$

$$(2.16) \quad X = \text{mean} + b_1 PC1 + b_2 PC2 + \text{Error} \dots$$

The above PCA model equation can be explained as below:

$$(2.17) \quad X = TP^T + E$$

where, X is data matrix, TP^T is the data structure and E is the residual which are left unexplained by the model.

In PC analysis, the results are commonly explained using the graphical features of component scores called Scores Plot and Loadings Plot. The Scores Plot is the values of the transformed variable equivalent to a certain data point. The Loadings Plot is the load that each coordinated original variable ought to be increased to produce the score.

From the literature reviews, there are few examples of application of PCA in evaluating the characteristics of activated carbons. For example, Eza et al. (2014) had applied PCA to investigate the relationship between the adsorption of onion odor onto two types of fabrics which were lined with different type of activated carbons. The study was to confirm a hypothesis; that an onion odor will be absorbed by fabric and the distance between the fabric and the source of odor will give a different adsorption result. However, Eza et al. (2014) used Linear Discriminant Analysis (LDA) to combine with PCA, as to get a better separation between the samples and got a distinguishable result.

In another work-related to activated carbon characterization, PCA was implemented to evaluate an adsorption process of unwanted organosulfur compounds (OSCs) from diesel fuel using activated carbon. A study performed by Al-Ghouthi & Al-Degs (2014) on the adsorption technique was to evaluate the practicability and effectiveness of the studied method in industrial scale. They used PCA to assess the adsorption performance (PC variables) onto manganese-loaded activated carbon. The assessed variables were activated carbon mass, adsorption temperature and surface functional groups and they found out that the activated carbon was significant in OSCs removal from the PCA experimental parameters.

In previous work of Al-Degs et al. (2012), PCA was used to measure the empirical relationship between the adsorption performance and the studied variables. Two data sets were made for experimental model and validation purposes which consisted with linear terms, non-linear terms and interaction term of the variables. The

performed PCA discovered the significant of linear and non-linear terms of variables for data modelling rather than the interaction term. Based on PCA, the best combination between the variables was established for maximum adsorption among the following: 7 days of shaking time, pH 12, 950 mg of mass of activated carbon, 450 mg/L as initial dye concentration, 3.0 M NaCl concentration, and 40 °C set for solution temperature.

PCA was also applied to compare the degree of accumulation of elements onto activated carbon after one year of usage with a new activated carbon. The sample data was developed from inductively coupled plasma – optical emission spectrometry (ICP-OES) experimental technique in determining the elements presented in the activated carbons (Ca, Mg, Ba, Sr, Mn, Ti, Al, Cr, Cu, Fe, Ni, K, Na, Zn, and P). Using the PCA, Dabioch et al. (2013) discriminated the activated carbons into three groups. Among these groups, the similarities were assessed to identify the differences. As a result, elements such as Ba, Al, Cr, Ni and Ti were distinguished as irregular accumulation of elements during the usage of the activated carbons.