

CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Activated carbon ^(6,7)

Activated carbon, has been in use for thousands of year. The major development of activated carbon began during World War I, when hard granular activated carbon (GAC) was manufactured for use in gas masks. In the last 50 years the technology involved in active carbon manufacture has advanced. Powdered active carbon (PAC) is extensively used in water purification processes together with granulated active carbon. PAC is associated with larger pore diameters than GAC.

Activated carbon can be defined as highly porous, carbonaceous materials. The very large porosity provides a large surface area, which results in exceptional adsorptive properties. Basically, the porosity is only a means, to provide the adsorptive properties that make activated carbon of practical use. In the industry, carbons are therefore characterised by adsorptive properties rather than pore structures.

Adsorption on activated carbon is selective favouring nonpolar over polar substances and in a homologous series, generally improving with increasing boiling point. Adsorption is also improved with increased pressure and reduced temperature. Reversal of the physical adsorptive conditions (temperature, pressure or concentration) more or less completely regenerates the carbon's activity and frequently allows recovery of both the carrier fluid and adsorbate. Compared with other commercial absorbents, activated carbon has a broad spectrum of adsorptive activity, excellent physical and chemical stability and ease of production from readily available, frequently waste materials.

2.2 Raw materials for the production of activated carbon ⁽⁸⁾

Activated carbon is manufactured from a wide variety of materials but those most frequently used on commercial scale are peat, coal, lignite, wood and coconut shell. The principal properties of manufactured activated carbon depend on the type and properties of the raw material used. Any cheap substance with a high carbon and low ash content can be used as a raw material for the production of activated carbon. Source materials that have been studied for the production of activated carbon.

Bagasse	Lampblack
Beet-sugar sludges	Leather waste
Blood	Lignin
Bones	Lignite
Carbohydrates	Molasses
Cereals	Nut shells
Coal	Oil shale
Coconut shells	Peat
Coffee beans	Petroleum acid sludge
Corncobs and corn stalks	Petroleum coke
Cottonseed hulls	Potassium ferrocyanide residue
Distillery waste	Pulp-mill waste
Fish	Rice hulls
Flue dust	Rubber waste
Fruit pits	Sawdust
Graphite	Wood

2.3 Applications for activated carbon

Activated carbon is used for gas- and liquid-phase adsorption processes. Nearly 80% of about 300000 tons per year is used for liquid-phase applications and

approximately 60000 tons per year for gas-phase applications; these figures are based on worldwide usage.⁽⁹⁾ Granulated active carbons are mainly employed for gas adsorptions and separations.

Table 2.1 Applications for activated carbon.

Vapour Phase

Industry	Description	Typical use
Solvent recovery	Recovery of organic solvents to optimise process economics and control vapour emissions	Acetate fibres(acetone),pharmaceuticals (methylene chloride), film coating and printing (ethyl acetate), magnetic tape
Carbon dioxide	Purification of carbon dioxide from fermentation processes	Asorption of alcohols, amines and mercaptans
Industrial respirators	Adsorption of organic vapours	-
Waste disposal	Disposal of domestic, chemical and clinical waste by high temperature incineration	Removal of heavy metals and dioxins from flue gas
Cigarettes	Incorporation as either powder or granule in filter tips	Extraction of some harmful elements of cigarette smoke, or taste and flavour control
Air conditioning	Heating, ventilation and air conditioning	Airports (partially combusted fuel odours), offices (motor vehicla odours), fume cupboards (solvent odours)
Composite fibres	Impregnation of powdered activated carbon into foam/fibre/ non-woven substance	Air treatment, face masks and respirators, shoe insole deoderiser and water treatment
Fridge De-oderisers	In situ filter units	Removal of general food odours

Liquid Phase

Industry	Description	Typical use
Potable water treatment	Granular activated carbon (GAC) installed rapid gravity filters	Removal of dissolved organic contaminants, control of taste and odour problems
Soft drinks	Potable water treatment, sterilization with chlorine	Chlorine removal and adsorption of dissolved organic contaminants
Brewing	potable water treatment	Removal of trihalomethanes (THM) and phenolics
Semi-conductors	Ultra high purity water	Total organic carbon (TOC) reduction
Gold recovery	Operation of carbon in leach (CIL), carbon in pulp (CIP) and heap leach circuits	Recovery of gold from "tailings" dissolved in sodium cyanide
Petrochemical	Recycling of steam condensate for boiler feed water	Removal of oil and hydrocarbon contamination
Groundwater	Industrial contamination of ground water reserves	Reduction of total organic halogens (TOX) and adsorbable organic halogens (AOX) including chloroform, tetrachloroethylene and trichloroethane
Industrial waste water	Process effluent treatment to meet environmental legislation	Reduction of total organic halogens (TOX), biological oxygen demand (BOD) and chemical oxygen demand (COD)
Swimming pools	Ozone injection for removal of organic contaminants	Removal of residual ozone and control of chloramine levels

2.4 Production of activated carbon

The most desirable method of producing activated carbon is by adjusting processing conditions to control precisely the properties of the end-product. This is more cost-effective than changing the precursor to suit changing requirements, but necessitates a consistent material. Variations occur in precursors in terms of structure and mineral matter content, associated with locality of growth, climate and cropping.

Mineral matter is often responsible for preferential gasification during the activation process resulting in meso-and macropore channelling and pitting, and not the preferred microporosity. Activated carbon is usually produced by the carbonization and activation of carbonaceous materials.

2.4.1 Carbonization (or pyrolysis) ⁽¹⁰⁾

This is one of the most important steps in the production process of activated carbon since it is in the course of carbonization that the initial porous structure is formed. During carbonization most of the non-carbon elements, hydrogen and oxygen are first removed in gaseous form by pyrolytic decomposition of the starting material, and the freed atoms of elementary carbon are grouped into organized crystallographic formations known as elementary graphitic crystallites. The mutual arrangement of the crystallites is irregular, so that free interstices remain between them and apparently as the result of deposition and decomposition of tarry substances, these become filled or at least blocked by disorganized ("amorphous") carbon. There are three clear stages in the carbonization process: (a) loss of water in the 27-197°C range; (b) primary pyrolysis in the 197-497°C range with evolution of most gases and tars with formation of the basic structure of the char; (c) consolidation of char structure at 497-847°C with a very small weight loss. The resulting carbonized product has only a very small adsorption capacity. Presumably, at least for carbonization at lower temperatures (400-600°C), part of the tar remains in the pores between the crystallites and on their surface. A carbon with a large adsorption capacity, however, can be produced only by activating the carbonized material under such conditions that the activation agent (steam, carbon dioxide, etc.) reacts with the carbon.

2.4.2 Activation

The large internal surface areas of activated carbon are the result of the activation process. Two routes are used to increase porosity: chemical and physical

activation. Generally, there are two main types of production of activated carbon:

- By carbonizing material with the addition of activating agents ($ZnCl_2$, $CaCl_2$, H_3PO_4). This method is generally known as "chemical activation".
- By allowing the inactive carbonized product (prepared by the usual methods of carbonization) to react with usually suitable gaseous substances (steam, carbon dioxide, oxygen). This method is generally known as "physical activation".

2.4.2.1 Chemical activation ⁽⁷⁾

This process involves carbonizing the parent material after impregnation with, e.g., phosphoric acid, zinc chloride, sulphuric acid, potassium sulphide, carbonates of alkali metals and metal chlorides. The common feature of these compounds is their ability to act as dehydrating agents which influence the pyrolytic decomposition and inhibit tar formation. The temperature range for chemical activation is 400-800 °C. These temperatures are lower than those needed for activation with gaseous agent (physical activation). An important factor in chemical activation is the degree (coefficient) of impregnation; this is the weight ratio of the anhydrous activation salt to the dry starting material. The effect of the degree of impregnation on the resulting product is apparent from the fact that the volume of salt in the carbonized material equals the volume of pores which are freed by its extraction. For small degree of impregnation the increase in the total pore volume of the product with increase in the degree of impregnation is due to the increase in the number of small pores. When the degree of impregnation is further raised, the number of larger-diameter pores increases and the volume of the smallest decreases.

During chemical activation the chemistry of pyrolysis is changed and a different, macromolecular network system is established with enhanced porosity. The activation agent also changes the chemical nature of the cellulose substance by dehydration, which decomposes the organic substances by the action of heat and

prevents the formation of tar.

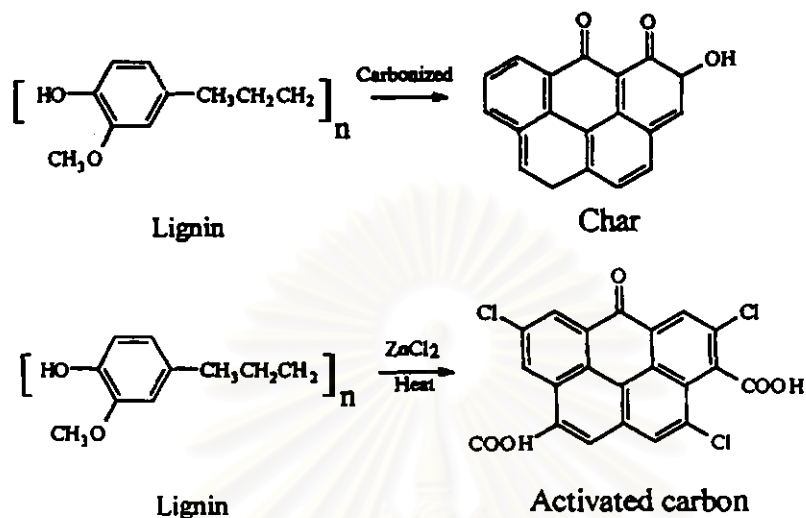


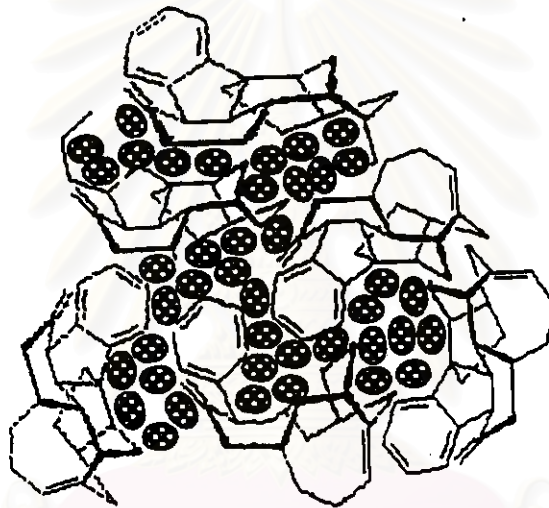
Figure 2.1 Chemical reaction of lignin with activated by ZnCl_2 ⁽¹⁰⁾.

2.4.2.2 Physical activation⁽⁷⁾

Physical activation is the development of porosity by gasification with an oxidizing gas at 700-1100 °C. Commonly used gases are carbon dioxide, steam and air. They can be used singly or in combination. Several types of oven can be used in the manufacture of activated carbon, i.e. rotary kilns, multiple hearth furnaces and fluidized beds. The type of oven used determines the properties of the activated carbon produced. In general, a decreasing mesoporosity is observed in the order: fluidized bed, multiple hearth furnace, rotary kiln⁽¹¹⁾.

To understand the process of “physical” activation it is helpful to use the model of porosity outlined above. This model states that carbons consist of networks of bonded carbon atoms, with a limited extent of ordered structural arrangements, and that porosity is the continuous, interconnected assembly of volume elements

between the carbon atoms. It would appear that the ratio of volume element space to carbon atom space is not optimized during normal carbonization procedures. Hence, if carbon atoms can be removed, extremely selectively, from within the carbon particles, then the above ratio will be enhanced (Figure 2.2). Because of structural defects and strain energy differences within the defective carbon atom networks, not all carbon atoms have the same reactivity to an oxidizing gas molecule, such as water, carbon dioxide or oxygen.



● An adsorbate molecule.

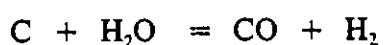
Figure 2.2 Model illustrating the process of physical activation by selective removal of carbon atoms to enhance adsorption capacity.

When gasifying conditions are optimized in terms of oxidizing gas, temperature, flowrate and pressure, an acceptable compromise exists between “selective” burn-off (oxidation) of carbon atoms and “external” burn-off, which is simply removal of carbon material without any increase in porosity. This happens with fast burn-offs, e.g. as with oxygen. Thus, the extent of development of porosity and the characteristics of this porosity are a function of:

- the structure of the initial carbon;
- the presence of catalytic inorganic impurities in the carbon;
- the oxidizing gas;
- temperature of gasification;
- pressure of the gas;
- duration of gasification;
- particle size of the carbon.

Generally, the slower the reaction the more extensive is the development of porosity within the particle. The gas molecule, e.g. carbon dioxide, must penetrate into the interior of the particle to remove a carbon atom from that position. Thus, many carbon atoms within the porous carbon are bypassed during penetration without undergoing reaction or gasification. There are at least two reasons for this: the sensitivity of carbon atom "reactivity" to relative position within the carbon network is critical; also of importance are stereoeffects, i.e. the steam, carbon dioxide or oxygen molecule needs appropriate space to orientate itself for the reaction which leads to gasification. During this process an oxygen atom has to be transferred and bonded to the carbon atom of the network, and the resultant carbon monoxide has subsequently to be "desorbed" from the network. These are extremely complicated processes and may never be understood other than in general terms. In principle, however, it is easy to appreciate how different activation conditions influence the mechanistic detail of carbon atom removal, so creating a wider range of porosities in carbons. This is where activation becomes a matter of experience as well as understanding.

The reactions of carbon with steam and carbon dioxide to remove carbon atoms from the network within solid carbon are as follows:



$$\Delta H = +117 \text{ kJ mol}^{-1}$$

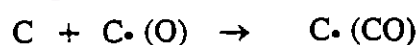
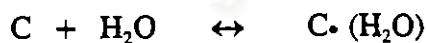


where () represents the chemisorbed state.

Steam is the preferred activation gas because the water molecule has smaller dimensions than the carbon dioxide molecule, and consequently the use of steam leads to:

- faster diffusion into the porous network;
- easier access into the micropores;
- a faster reaction rate, i.e. approximately three times faster than the carbon dioxide reaction at a temperature of 800 °C and a pressure of 10 kPa.

The steam reaction is product inhibited; hydrogen is strongly adsorbed on the active centres of the carbon surface and this reduces the reaction rate. In some way, these inhibition reactions also influence the selection of carbon atom removal.



The reaction of carbon dioxide with solid carbon is known as the Boudouard

reaction. The mechanism and kinetics of this reaction have been extensively studied. Activation with carbon dioxide is inhibited by hydrogen and carbon monoxide. The carbon monoxide acts by increasing the rate of the back reaction [$C \cdot (O) + CO = C \cdot + CO_2$]. Rand and Marsh⁽¹²⁾ showed that the addition of carbon monoxide to the reacting gas resulted in the development of a better microporous structure in addition to decreasing the rate of gasification. Carbon dioxide activation requires higher temperatures than steam activation and is generally used as a mixture of flue gas plus steam. Although pore development is dependent on temperature and concentration of reactant gas, the carbon precursor also determines the characteristics of the activated carbon produced.

2.5 Chemical nature of the surface of activated carbon ⁽¹⁰⁾

The chemical nature of activated carbon significantly influences their adsorptive, electrochemical, catalytic, acid-base, redox, hydrophilic-hydrophobic, and other properties. It is determined decisively by type, quantity and bonding of various heteroatoms, especially oxygen. Heteroatoms may be combined both with peripheral carbon atoms at the corners and edges of crystallites, and in intercrystalline spaces and even in defect zones of particular planes continuing the crystallites. Most heteroatoms are grouped at the surface of activated carbon. Apart from their different locations, the heteroatoms are strongly differentiated in terms of their chemical reactivity. Surface-bound heteroatoms are believed to adopt the character of the functional groups typical for aromatic compounds. The surface functional groups often consist of more than one type of heteroatom, e.g. oxygen and hydrogen together as -OH or -COOH.

Surface functional groups can originate from the starting material from which a particular activated carbon is produced. Substantial quantities of oxygen can be introduced during the production process itself, e.g. during activation of carbonaceous materials by oxidizing gases, such as water vapor and air. Activated

carbon used predominantly for practical purposes generally includes some percentage by weight of chemically-bound oxygen and usually much smaller quantity of hydrogen combines with surface carbon atoms either directly or through oxygen.

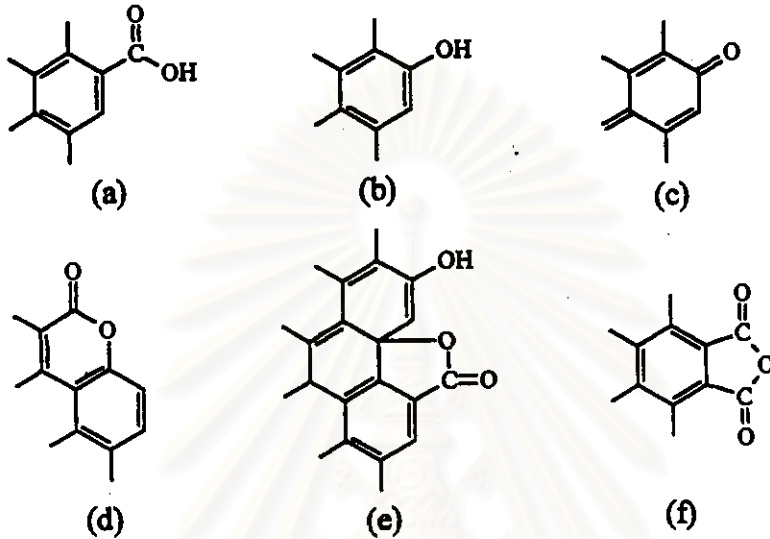


Figure 2.3 Principal types of acidic oxygen surface functional groups : (a) carboxyl, (b) phenolic, (c) quinonoid, (d) normal lactone, (e) fluorescein-type lactone, (f) anhydride originating from neighbouring carboxyl groups ⁽¹⁰⁾.

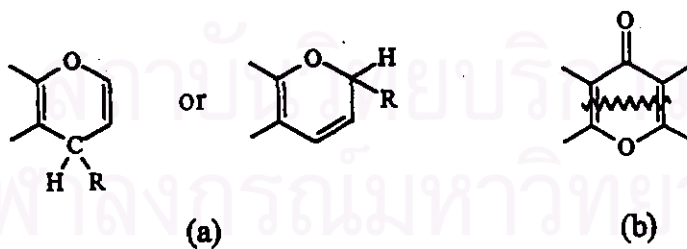


Figure 2.4 Functional groups of basic character : (a) chromene, (b) pyrone-like⁽¹⁰⁾.

Oxygen surface compounds are usually divided into two main types: functional groups of acidic nature and basic groups. The first acidic group is exemplified

schematically in Figure 2.3. The later basic group is much less well-characterized compared with the first. Usually structures corresponding to chromene or pyrone-like structures are illustrated in Figure 2.4.

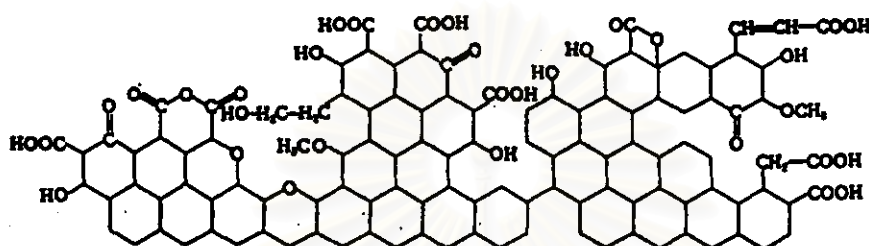


Figure 2.5 Model of fragment of an oxidized activated carbon surface⁽¹⁰⁾.

2.6 Shapes and sizes of pores in activated carbon

In any activated carbon particle, pores of different sizes are found. Pores can, by definition (IUPAC), be distinguished into:

- Micropores (radius (or half-width) below 1 nm),
- Mesopores (radius 1-25 nm), and
- Macropores (radius larger than 25 nm).

Micro- and mesopores give the carbon its adsorptive capacity. They are formed during the process of activation. Activation is basically the development of pores in a non-porous raw material, by means of chemical reactions. There are two main varieties of the activation process, historically referred to as “steam activation” and “chemical activation”. These two processes give fundamentally different pore structures.

Granular activated carbon have also macropores. They allow a rapid access (throughout the particle) to the meso- and micropores, where the actual adsorption

takes place. In powdered carbon, access is not a problem due to the small particle size, and macropores are often absent.

2.6.1 Micro- and mesopores in chemically activated carbon

The chemical activation process is different from the steam activation process, in that carbonization and activation occur at the same time, and at lower temperatures. As a result of the relatively low process temperature, graphitic basal planes are not found in chemically activated carbon. Instead, each particle can be seen as a partly aromatic, partly aliphatic organic molecule, or a highly crosslinked polymer produced from an almost infinite number of different monomers. The pore walls are thus not flat but "rough", even in the micropores, and contain a relatively large amount of hetero atoms (mostly oxygen). As a result, chemically activated carbon is somewhat less hydrophobic than steam activated carbon.

2.6.2 Micro- and mesopores in steam activated carbon

To envisage the nature of micro- and mesopores in steam activated carbon, it is easiest to start with the structure of the material just before the activation process. A step always preceding the steam activation itself, is the carbonization of the raw material (e.g. peat, lignite, coal).

Carbonized raw materials used in steam activation all consist of very small graphite-like plates, called basal planes. One such plate is shown in Figure 2.6. It consists of mostly aromatic carbon atoms, with some functional groups involving other atoms at its edges. The basal planes are flat or somewhat bent, 0.35 nm in thickness, and a few nanometres in width and length. In the carbonized material, many basal planes are packed together. Wherever a number of adjacent planes have the same orientation, they will form a graphite-like stack. In other places, orientations of plates will be fully random.

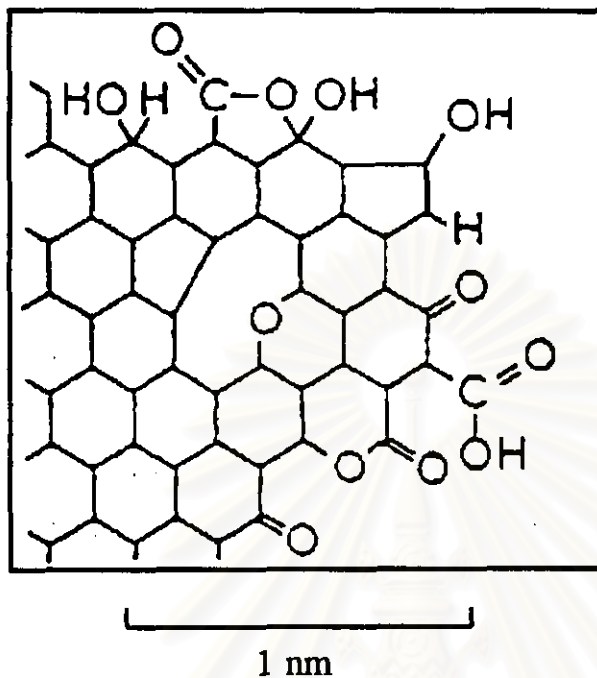


Figure 2.6 Structure of a basal plane in a steam activated carbon.

2.6.3 Macropores

In general, macropores are either of botanical origin, or formed during a shaping step near the beginning of the production process. Botanical pores are (the remnants of) botanical cell structures in the raw material. Wood and coconut shells have a clear cell structure which is fully retained during its processing into activated carbon. Relatively young fossil fuels like peat show macropore structures which can also be attributed to the living material they originate from.

Man-made macropores are found in activated carbon that have been produced through the briquetting or extrusion of a raw material. In the production of bituminous coal based carbons, finely milled coal is briquetted (compressed) at high pressures. In this process the coal powder particles deform plastically, and adhere to each other. The residual space between the coal powdered particles is seen as macropores in the final product.

2.7 Methods for measuring porosity and surface area ⁽⁷⁾

A range of techniques is available for estimating porosity and surface area. Comparisons are made between results obtained from isotherms and those from other methods.

2.7.1 Physical adsorption of gases

2.7.1.1 Adsorption isotherms

To quantify the adsorption process, extents of adsorption (mmol g^{-1}) are related to the equilibrium partial pressure p/p^0 at constant temperature to create the *isotherm*. Adsorption isotherms are studied to obtain information about the following:

- estimates of surface areas;
- estimates of pore volumes in the various porosities present, i.e. pore-size on potential energy distributions;
- assessments of the surface chemistry of the adsorbent;
- the fundamentals of adsorption processes, i.e. the nature of the adsorbed phase;
- assessments of the efficiency of industrial carbon employed in separation/purification techniques.

Interpretation of isotherms is not straightforward and this causes considerable debate among surface chemists. Adsorption processes in microporosity are the most difficult to describe accurately. The adsorption processes occurring within mesopores are more easily understood. Macroporosity behaves in the same way as an open surface to adsorption and accounts for <1% of the adsorption processes within microporous carbon.

Figure 2.7 sets out the six major classes of isotherm shape that are obtained from adsorption experiments. A knowledge of adsorption mechanisms in different sizes of porosity is necessary to explain the isotherm shapes.

Type I isotherms are typical of microporous solids in that micropore filling occurs significantly at relatively low partial pressures $< 0.1 p/p^0$, the adsorption process being complete at $\sim 0.5 p/p^0$. Examples include the adsorption of nitrogen on microporous carbon at 77 K and of ammonia on charcoal at 273 K.

Type II isotherms describe physical adsorption of gases by non-porous solids. Monolayer coverage is succeeded by multilayer adsorption at higher p/p^0 values. *Type II* isotherms can also be obtained from carbon with mixed micro- and mesoporosity.

Type III and *Type V* isotherms are convex towards the relative pressure axis. These isotherms are characteristic of weak gas-solid interaction⁽¹³⁾. *Type III* isotherms originate from both non-porous and microporous solids and *Type V* isotherms from microporous or mesoporous solids. The weakness of the adsorbent-adsorbate interactions causes the uptakes at low relative pressures to be small; however, once a molecule has become adsorbed at a primary site, the adsorbate-adsorbate forces promote further adsorption in a cooperative process, which is known as the cluster theory, e. g. the adsorption of water molecules on oxides of carbon surfaces. An example is the adsorption of water vapour on graphitized carbon black.

Type IV isotherms possess a hysteresis loop, the shape of which varies from one adsorption system to another. Hysteresis loops are associated with mesoporous solids, where capillary condensation occurs.

Type VI isotherm is a stepwise isotherm and represents complete formation of successive monomolecular layers. Halsey⁽¹⁴⁾ proposed that stepwise isotherms arise from extremely homogeneous, non-porous surfaces and the step height corresponds to monolayer capacity. An example is the adsorption of krypton on carbon black (graphitized at 3000 K) at 90 K.

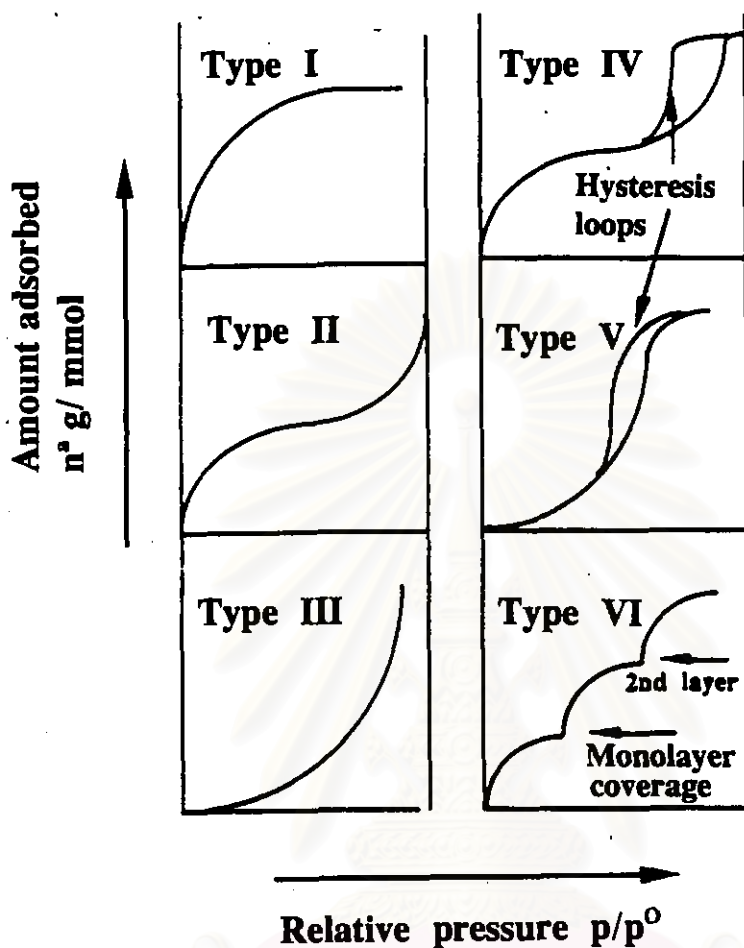


Figure 2.7 Classification of isotherm shapes into six principal classes (Gregg and Sing ⁽¹⁵⁾).

2.7.1.2 Adsorption equations

A significant literature exists describing mathematical models to interpret shapes of isotherms obtained from porous and non-porous solids. Usually these models ignore structural features of the adsorbent, except in the most general of ways, e.g. distributions of adsorption energy (microporosity) or pore width (mesoporosity). Interpretations of isotherms from non-porous materials are relatively straightforward. Information concerning effective surface areas, pore-size distributions, micropore

volumes, etc., is incorporated within the isotherm. Extracting this information is a matter for debate as direct experimental evidence is limited. Hence all equations are based on assumptions placed into models and then matched against experimental isotherms. This section is not an attempt to review exhaustively all the theories and models available for isotherm interpretation; rather, the most common are presented and commented upon.

The term “surface area” does not describe a carbon unequivocally. Carbons with similar effective surface areas (ESA) can be very different from each other structurally. Further, values obtained using one adsorbate at a certain temperature can differ when other adsorbates at other temperatures are used. When quoting surface areas it is important to qualify them by including the technique, adsorbate and temperature used, and to state that these are effective surface areas which describe how an adsorbent is responding to a particular adsorbate.

2.7.1.3 Langmuir equation

Surface areas can be obtained from *Type I* (Figure 2.7) isotherms by the Langmuir equation^(15,16)

$$\frac{P}{V} = \frac{P}{V_m} + \frac{1}{bV_m} \quad (2.1)$$

where:

V = equilibrium amount (mmol g⁻¹) of gas adsorbed per unit mass of adsorbent at relative pressure p/p^0 ;

V_m = amount of gas required for monolayer coverage of adsorbent (mmol g⁻¹);

b = constant, dependent on temperature but independent of surface coverage and describing in some way the energetics of the surface.

Surface areas are obtained using the relationship

$$S = V_m L \sigma \quad (2.2)$$

where

S = surface area ($\text{m}^2 \text{g}^{-1}$);

L = Avogadro's number ($\text{molecules mol}^{-1}$);

σ = projected area of adsorbate molecule ($\text{m}^2 \text{molecule}^{-1}$), as in **Figure 2.8**.

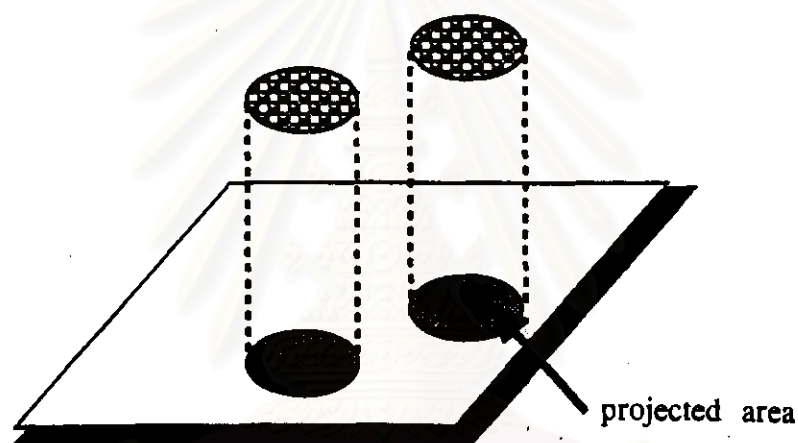


Figure 2.8 Projection of “area” of an admolecule to the “surface” of adsorbent (modelled)

The langmuir equation is based on the following assumptions:

- only monolayer adsorption can occur;
- adsorption is localized with no adsorbate-adsorbate interactions;
- the heat of adsorption is independent of surface coverage, i.e. the adsorbent has a homogeneous surface.

It is certain that these assumptions are invalid for any carbon. However, the equation is applicable to many isotherms and is therefore useful.

2.7.1.4 BET equation

The Brunauer, Emmett and Teller (BET) equation⁽¹⁷⁾ was devised to improve the Langmuir model to account for multilayer adsorption⁽¹⁵⁾. *Type II* isotherms (Figure 2.7) describe unrestricted multilayer formation, whereas *Type IV* isotherms describe restricted multilayer formation.

The equation (for unrestricted multilayer formation) is as below. Equations describing restricted adsorption were discussed by Gregg and Sing⁽¹⁵⁾.

$$\frac{P}{V(P^0-P)} = \frac{1}{V_m c} + \frac{c-1}{V_m c} \cdot \frac{P}{P^0} \quad (2.3)$$

where:

P^0 = saturation vapour pressure;

c = $\exp[(\Delta H_A - \Delta H_L) / RT]$;

ΔH_A = heat of adsorption;

ΔH_L = heat of liquefaction.

The BET equation is widely used to interpret isotherms obtained using nitrogen at 77 K. Because the BET equation has such wide applications, researchers tend to use it indiscriminately; hence, as indicated above carbon have been reported with surface areas as high as 5000 m²g⁻¹. These values are misleading as the calculated surface area for an extended graphite layer counting both sides is ~1800 m²g⁻¹. However, the use of the term “effective surface area” can be applied and the values obtained indicate adsorption capacity and therefore provide useful information. The basic problem is that the modelling used for the BET equation dose not describe the process of adsorption in such porous carbon.

2.7.2 Bulk density ⁽¹⁰⁾

The bulk density is defined as the mass per unit volume of the activated carbon sample in air including both the pore system and the void between the particles. The bulk density of activated carbon, depending on the shapes, sizes and densities of the individual particles is indispensable for determining the size of unit packages.

2.7.3 Adsorption test ⁽¹⁰⁾

The adsorption properties of activated carbon is generally estimated by determining the isotherms of adsorption from the liquid phase. The determination of the adsorption of one test substance from an aqueous solution is often insufficient for characterizing the adsorption properties of a carbon. Thus the properties of activated carbon is estimated by comparing the results of measurements for different adsorbates, e.g. by comparing the adsorptions of fairly large molecules of methylene blue or iodine.

- *Iodine adsorption.* The study of the process of iodine adsorption and also the determination of the iodine number is a simple and quick test for estimating the specific surface area of activated carbon. The iodine number is defined as the number of milligrams of iodine adsorbed by 1 g of activated carbon from an aqueous solution when the iodine concentration of the residual filtrate is 0.02 N. If the final values obtained are different from 0.02 N but lie in the range of 0.007-0.03 N, appropriate corrections are necessary. In this method it is assumed that iodine at the equilibrium concentration of 0.02 N is adsorbed on the carbon in the form of a monolayer, and this is the reason why there is a relationship between the iodine number of activated carbon and its specific surface area which may be determined, for example, by the BET method. The specific surface areas of activated carbon with highly developed microporous structures as determined by the iodine number method are too low.

This is because iodine is adsorbed chiefly on the surface of pores much larger than 1 nm, while in activated carbon with large specific surface areas the proportion of very fine pores inaccessible to iodine molecules is significant.

- *Methylene blue adsorption.* The methylene blue value gives an indication of the adsorption capacity of an activated carbon for molecules having similar dimensions to methylene blue, it also gives an indication of the specific surface area of the carbon which results from the existence of mesopores of dimensions greater than 1.5 nm.

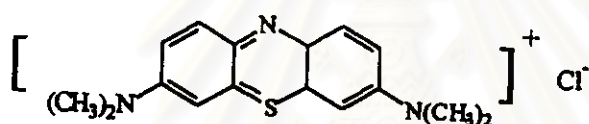


Figure 2.9 The chemical structure of methylene blue⁽¹⁰⁾.

2.7.4 Physico-chemical test ⁽¹⁰⁾

- *Volatile matter content.* The international standard used for determination of volatile matter in hard coal and coke is also applicable to activated carbon. A sample of powdered (<0.1 mm) activated carbon is heated at 950 ± 25 °C for 7 min \pm 10 s. Volatile matter content is determined by establishing the loss in mass resulting from heating an activated carbon sample under rigidly controlled conditions.

- *Moisture content.* A simple method of determining the water content is drying activated carbon in a dryer. The sample of powdered (1-2 g) or granular (5-10 g) carbon is dried at 150 °C to constant weight (usually about 3 hr). The weight loss is expressed as a percentage of the weight of the original sample.

- *Ash content.* The ash content in various types of activated carbon varies over a wide range, depending primarily on the type of raw material. The relative ash content also increases with increase in the degree of burning of the coal during activation. Ash consists mainly of oxides and, in smaller amounts, of sulfates, carbonates, and other compounds of iron, aluminium, calcium, sodium, potassium, magnesium and many other metals. Depending upon the type of raw material, it may comprise different and often fairly large quantities of silicon. The commonly used method of removing ash is to leach activated carbon with acids. Due to the complex composition of ash, mixture of acids, e.g. hydrochloric or hydrofluoric acid, are often used if ash contains substantial quantities of silicon.

The ash content of activated carbon can be determined by ignition of the crucible in an electric muffle furnace. Ignition is conducted at 650 ± 25 °C for 3 to 16 hr, depending on the type of activated carbon and dimensions of its particles, to constant mass. The weight of the ashed carbon is expressed as a percentage of the weight of the original carbon sample.

2.8 Literature reviews

Gergova, Petrov and Minkova (1993)⁽¹⁸⁾ produced activated carbon from apricot stones, grape seeds and cherry stones by a new one-step steam / pyrolysis activation which combined the process of carbonization and activation with water vapor. The experiments had been carried out at temperatures of 600, 650 and 700°C and soak time 1, 2 and 3 hr. The adsorption and porosity characteristics of the activated carbon produced from different agricultural by-products are shown in Table 2.2

Table 2.2 Adsorption and porosity characteristics of the activated carbons produced from different agricultural by-products⁽¹⁸⁾.

Raw material	Yield (wt%)	S _{B.E.T.} (m ² /g)	IA (mg/g)	MB (mg/g)	V _{total} (cm ³ /g)	V _{micro} (cm ³ /g)	V _{meso} (cm ³ /g)	V _{macro} (cm ³ /g)
Apricot stones	18.16	1175	894	285	0.91	0.76	0.14	0.01
Grape seeds	26.23	487	607	192	0.62	0.16	0.22	0.24
Cherry stones	11.17	836	907	185	0.77	0.20	0.09	0.48

Activated carbon obtained from apricot stones had the best properties. It was characterized to have a large specific surface area and micropores volume and high iodine and methylene blue adsorption activity. The activated carbon was produced from cherry stones and grape seeds, had predominating meso- and macropore structures.

Budinova *et al.* (1994)⁽¹⁹⁾ studied the adsorption of Pb²⁺, Cu²⁺, Zn²⁺, and Cd²⁺ from aqueous solution at 293 K by activated carbon obtained from different raw materials. The activated carbon was prepared by a simple single-stage method "pyrolysis in the presence of water vapor" (PPWV) of apricot stones, coconut shells

and lignite coal. The results presented that all activated carbon (PPWV) had an ability to adsorb metal ions from aqueous solution with the capacity increasing in the order $Cd^{2+} < Zn^{2+} < Cu^{2+} < Pb^{2+}$. The adsorption of metallic ions was negligible at low pH values and increased considerably in the pH range of 3-4.

Boonchai Thakunmahachai (1994)⁽²⁰⁾ produced activated carbon from palmyra palm shells by physical or chemical method. The physical activation in the fluidized bed and the chemical activation in the fixed bed were studied. In order to get the charcoal which could be ground easily, the palmyra palm shells were carbonized at temperature of 200°C for 2 hr. The sample of charcoal was mixed with the solution of 60% (wt) zinc chloride at the ratio of 3 : 2 in the porcelain crucible for 72 hr. The optimum condition for the charcoal particle size of 1.68 - 2.38 mm was at 500°C activation temperature for 1 hr. The properties of the activated carbon was 1600-1700 m²/g surface area, 1100-1200 mg/g iodine adsorption, 350-400 mg/g methylene blue adsorption, 2-5% ash and 40-45 % yield. The palmyra palm shells were physically activated with the mixed gas of flue gas which had been obtained from diesel oil and superheated steam in fluidized bed. The optimum condition for charcoal particle size of 1.19-1.68 mm was at activation temperature of 900°C for 5 min and gas velocity of 6.44 m/sec. The properties of activated carbon were 1800-1900 m²/g surface area, 1000-1300 mg/g iodine adsorption, 250-350 mg/g methylene blue adsorption, 10-15 % ash and 30-45 % yield.

Arriagada, Gercia and Reyes (1994)⁽²¹⁾ studied the partial gascification of *Eucalyptus globulus* charcoal, using carbon dioxide and steam as activating agents. The influences of some production variables such as temperature and reaction time on textural were given. *Eucalyptus globulus* chips (5-10 cm in diameter, 30-40 cm in length) were carbonized in a metallic kiln. The carbonization time was 2-3 hr and the yield of charcoal was 23 %. The charcoal, sieved between 10 and 20 mesh was activated in a vertical fixed bed reactor. The reaction temperature was between 800-

900°C for 10-360 min with flow of the activating agent 200 cm³/min (STP) of carbon dioxide or 140 cm³/min (STP) of steam (100%). The results showed that both activating agents produced microporous activated carbon with a large increase in meso- and macroporosity when steam and high burn-off were used. Table 2.3 summarizes the textural characteristics of the activated carbon.

Table 2.3 Textural characteristics of the activated carbon ⁽²¹⁾

Activating agent	Time(min)	Surface area (m ² /g)	IA(mg/g)	MB (mg/g)
CO ₂	10	380	286	16
	60	549	474	84
	120	678	640	125
	180	847	725	220
	270	994	929	318
	360	1089	936	345
Steam	10	466	471	14
	60	622	690	113
	120	778	819	221
	270	1193	968	311

Gergova, Klimkiewicz and Brown (1995) ⁽²²⁾ carried out the production of activated carbon from anthracite using one-step steam pyrolysis-activation. 50 g anthracite were heated in a tube furnace for pyrolysis-activation at a rate of 20 K/min at atmospheric pressure. The samples, with particle size < 1 mm, were heated in the presence of steam at 850°C for 3-6 hr and at 900°C for 3 and 4 hr at atmospheric pressure. Two samples were treated initially in air at 300 and 350°C for 3 and 2 hr, followed by steam activation at 850°C for 4 hr. The activated carbon produced by steam activation at 850°C for 6 hr had the highest

surface area and a well-developed porous structure. Substantial activation of anthracite surfaces and formation of extensive porosity occurred under the same conditions but with steam at 270 Pa instead of atmospheric pressure. Air treatment at 300°C for 3 hr before steam activation at 850°C for 4 hr also led to production of activated carbon with well-developed porosity. The porosity characteristics of activated carbon from anthracite are shown in Table 2.4

Table 2.4 Porosity characteristics of activated carbon from anthracite ⁽²²⁾

Air flow		Steam flow		Yield (wt%)	Surface area (m ² /g)				Pore volume (cm ³ /g)	
T (°C)	t (hr)	T (°C)	t (hr)		S _{B.E.T}	L(h)*	D-R*	IA	Total	Micro
300	3	850	4	37.2	720	1420	1310	620	0.56	0.34
350	2	850	4	36.0	670	1340	1230	650	0.53	0.32
-	-	850	3	45.8	530	1130	950	470	0.42	0.25
-	-	850	4	31.2	610	1280	1130	580	0.48	0.29
-	-	850	5	28.4	630	1310	1150	610	0.50	0.30
-	-	850	6	25.3	720	1460	1360	540	0.57	0.35
-	-	900	3	23.6	620	1280	1180	620	0.49	0.30
-	-	900	4	13.5	510	1120	1050	450	0.40	0.24

* Langmuir(high relative pressure)

* Dubinin-Radushkevich

Hussein *et al.* (1995) ⁽²³⁾ prepared the activated carbon by ZnCl₂/CO₂ activation of the chips of oil palm trunk. Ten grams of the air-dried chips of oil palm trunk were mixed with 100 cm³ of 1-30% (w/w) ZnCl₂ and activated at 500°C under an inert flow of nitrogen gas for 3 hr. After this time, CO₂ was passed through the reactor for an hour. Activated carbon prepared by impregnation of 0-10% of ZnCl₂ had a microporous structure. Introduction of 15% (or more) ZnCl₂, however, had modified the pores of the resulting activated carbon to include a mesoporous structure.

An optimum micropore volume occurred at 5% ZnCl_2 . Thus, it was believed that at high concentrations of ZnCl_2 , a relatively large portion of ZnCl_2 could modify some of the original micropores to mesopores. This experimental method could be used for production of activated carbon with a fairly high surface area more than $2000 \text{ m}^2/\text{g}$ from the chips of oil palm trunk.

Tancredi *et al.* (1996)⁽²⁴⁾ prepared activated carbon from eucalyptus wood chars. The results of CO_2 , $\text{CO}_2 - \text{O}_2$ and steam activation were compared. The sawdust of eucalyptus 0.5-1.6 mm was first carbonized in a continuous N_2 flow (100 mL/min at s.t.p.) in a horizontal tube furnace consisting of a 75 mm diameter quartz tube heated electrically. The carbonization temperature was maintained $400-800^\circ\text{C}$ for 2 hr. The chars obtained from this carbonization step were sieved and the 0.5-0.8 mm size fraction was activated in the same furnace using CO_2 , steam and $\text{CO}_2 - \text{O}_2$ mixtures as activating agents. Activated carbon was obtained, by CO_2 activation of the 800°C chars with surface area of 780 up to $1190 \text{ m}^2/\text{g}$ and 810 up to $1190 \text{ m}^2/\text{g}$, for steam activation at 800°C . The carbonization step gave rise to a narrow micropore structure and highly developed macroporosity which increased slightly upon CO_2 activation and significantly upon steam activation. This last process led also to a widening of micropore size distribution and developed the mesoporosity more than CO_2 activation did. Steam activation appears to have a particularly relevant effect on macroporosity development. As steam had a higher reactivity than CO_2 , diffusional limitations could be more significant and would favour gasification in large pores, giving rise to meso- and macroporosity development. This was also consistent with the increase in meso- and macropore volumes with increasing of steam activation temperature. The presence of O_2 accompanying CO_2 in the activating gas small increased the micro- and macroporosity of the carbons, compared with pure CO_2 activation.

Philip and Girgis (1996)⁽²⁵⁾ the apricot stone shells were impregnated with varying H_3PO_4 acid concentrations 20-50 wt%, followed by carbonization at 300-

500°C for 3 hr in a closed-end quartz tube reactor. A series of wide range micropores of activated carbon were obtained, with surface area of 640 up to 1600 m²/g, pore volumes of 0.34 up to 1.32 cm³/g and mean pore radii of 7.8-20.2 angstrom.

Patra Panyawatanakit (1997)⁽²⁶⁾ produced activated carbon from palm oil shells. The processes of carbonization and activation with superheated steam were studied. Some of the characteristics of palm-oil shells were found to be : moisture of 11.87 %, ash of 2.20 %, volatile matter of 69.87 %, fixed carbon of 16.06 %, total surface area of 12.20 m²/g, mesopore area of 12.20 m²/g and micropore area of 0.00 m²/g. The palm-oil shells were carbonized at 400°C for 1 hr. The characteristics of the palm-oil shell charcoal were yield of 31.50 %, ash of 6.24 %, volatile matter of 27.76 %, fixed carbon of 64.48 %. Next, the charcoal was activated with superheated steam. The optimum condition for activation was 0.850-0.355 mm of charcoal size at 900°C for 1 hr. The resulting characteristics were yield of 19.31 %, bulk density of 0.53 g/cm³, iodine number of 779.0 mg/g, methylene blue number of 136.96 mg/g, total surface area of 670.1 m²/g, mesopore area of 67.24 m²/g, micropore area of 602.8 m²/g and average pore area of 10.11 angstrom.

Sai *et al.* (1997)⁽²⁷⁾ produced activated carbon from coconut shell chars using steam or carbon dioxide as the reacting gas in a 100 mm diameter and 1250 mm length fluidized bed reactor. Experimental data showed that an increase in reaction time, fluidizing velocity, particle size, and temperature resulted in better activation. However, at lower reaction time, a decrease in iodine numbers was observed, which was due to coalescence or widening of already formed pores. Static bed heights greater than the diameter of the column gave lower iodine numbers due to poor gas-solid contact, because of slugging. Steam as the activating gas enhanced the activation compound to a mixture of steam and CO₂ or pure CO₂. From the experimental data, it was observed that maximum iodine number could be obtained for the following process

condition: fluidization velocity of 24.7 cm/s; particle size of 1.55 mm; static bed height of 100 mm; temperature of 850°C; fluidizing medium, steam and raw material, coconut shell char.

Terachai Suravattanasakul (1998)⁽²⁸⁾ produced activated carbon from palm-oil shells by one step pyrolysis and steam activation in a fixed bed reactor with the diameter of 100 mm. The studied variables were temperature, time, palm-oil shell size and flow rate of air. The optimum condition for activation was 1.18-2.36 mm of palm-oil shells at 750°C for 2 hr with air flow rate of 0.72 nl/min, using steam as an activating agent. The characteristics of the resulted activated carbon with the yield of 19.66 % were bulk density of 0.5160 g/cm³, 6.03 % ash, iodine number of 620.16 mg/g, methylene blue number of 176.75 mg/g and 559.48 m²/g B.E.T. surface area. In addition, it had been found that when including another step of pyrolysis time with air before steam activation led to higher porosity development than one step pyrolysis and steam activation. From these experimental data, it was observed that the maximum surface area and adsorption capacity could be obtained from using 200 g of 1.18-2.36 mm of palm-oil shells at 750°C for 3 hr by adding pyrolysis with air for 30 min (0.72 nl/min) before steam activation. The resulting characteristics of the final product with the yield of 12.18% were bulk density of 0.5048 g/cm³, 7.54 % ash, iodine number of 766.99 mg/g, methylene blue number of 189.20 mg/g and 669.75 m²/g B.E.T. surface area.

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