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Porous carbons

SATISH M MANOCHA

Department of Materials Science, Sardar Patel University, Vallabh Vidyanagar
388 120, India

Abstract. Carbon in dense as well as porous solid form is used in a variety of applications. Activated porous carbons are made through pyrolysis and activation of carbonaceous natural as well as synthetic precursors. Pyrolysed woods replicate the structure of original wood but as such possess very low surface areas and poor adsorption capacities. On activation, these exhibit increased adsorption volumes of $0{\cdot}5$–$0{\cdot}8\,\mathrm{cm}^3/\mathrm{gm}$ and surface areas of 700–$1800\,\mathrm{m}^2/\mathrm{gm}$ depending on activation conditions, whether physical or chemical. Former carbons possess mixed pore size distribution while chemically activated carbons predominantly possess micropores. Thus, these carbons can be used for adsorption of wide distributions of molecules from gas to liquid. The molecular adsorption within the pores is due to single layer or multilayer molecule deposition at the pore walls and hence results in different types of adsorption isotherm. On the other hand, activated carbon fibres with controlled microporous structure and surface area in the range of $2500\,\mathrm{m}^2/\mathrm{gm}$ can be developed by controlled pyrolysis and physical activation of amorphous carbon fibres. Active carbon fibres with unmatchable pore structure and surface characteristics are present and futuristic porous materials for a number of applications from pollution control to energy storage.

Keywords. Porous carbons; activated carbon fibres; surface area; microporosity; double layer capacitor.

1. Introduction

In recent times, carbon has been one of the magnificent elements which have revolutionised materials science. Carbon provides materials with excellent properties for a large spectrum of industrial applications (Pierson 1993; Burchell 1999). From carbon we obtain the strongest fibres (carbon fibres), one of the best solid lubricants (graphite), one of the best electrically conducting materials (graphite electrodes), the best structural material for high temperature tribological application (carbon–carbon composites), one of the best porous gas adsorbers (activated carbon), an essentially non-crystalline impermeable material (vitreous carbon), the hardest material (diamond), and now the most fascinating material, the fullerenes. All these forms are made by meticulously choosing the raw materials and processing conditions.

Porous carbons can be grouped into two categories: (i) Carbon foams with desired architecture of pores for structural and thermal applications; recently, these have been used as templates for making ceramics, (ii) activated carbons consisting of porous carbons with added active surface chemical groups. Porous carbons, especially activated porous carbons, constitute one of the most important types of industrial carbons and have been in use for thousands of years. Their use in water purification can be dated back to 2000 BC when ancient Egyptians used charcoal to purify water for medicinal purposes. It was during World War I that major developments in the use of porous carbons began and there was no going back afterwards. Newer and more modern technologies have since then developed both for the manufacturing and application of this versatile material (Bansal 1988). Activated carbon fibres with very high surface area (around 2000 m^2/gm) have been the latest addition in the family of porous carbons (Suzuki 1994). These fibrous materials have widened the application potential to gas storage and energy areas.

The term activated carbon defines a group of materials with highly developed internal surface area and porosity, and hence a large capacity for adsorbing chemicals from gases and liquids. Activated carbons are extremely versatile adsorbents of industrial significance and are used in a wide range of applications which are concerned principally with removal of undesired species by adsorption from liquids or gases, in order to effect purification or the recovery of chemical constituents. They also find use as catalysts or catalyst supports (Patrick 1995; Jin *et al* 1996; Mochida *et al* 1997). The strong market position held by the activated carbon adsorbents relates to their unique properties and low cost compared with that of possible competitive inorganic adsorbents like zeolites. Moreover, in porous carbons a broad distribution in pore size and shape is usually obtained in sharp contrast to almost constant pore size in zeolites. This makes activated carbons more versatile adsorbing materials.

Porous adsorbing carbons are associated with new processes for development of these materials, mechanisms, material characterization and newer application. More than 30% of the carbon research worldover revolves around activated carbons; newer precursors, methods of activation and applications.

2. Processing of activated carbon

Activated carbons are manufactured by the pyrolysis of carbonaceous materials of vegetable origin, such as wood, coal, peat, fruit stones, and shells or synthetic polymers such as viscose rayon, polyacrylonitrile (PAN) or phenolics followed by activation of the chars obtained from them. The pyrolysis of any carbonaceous material in absence of air involves decomposition of organic molecules, evolution of tarry and gaseous products, and finally in a solid porous carbon mass. The porous carbons so obtained contain predominantly macropores and practically inactive materials with specific surface area of the order of several square metres per gram (Bansal 1988). An adsorbent with a highly developed porosity and a correspondingly large surface area is obtained only by activating the carbonised material either by physical or chemical activation. The processing of activated carbon basically involves selection of raw material, carbonisation and activation.

2.1 *Raw materials*

For the selection of an appropriate raw material for preparation of porous carbon, several factors are taken into consideration. Industrially, inexpensive material with high carbon and low inorganic (i.e. low ash) content is preferred as raw material for the production of activated carbon. High density of the precursor and sufficient volatile content are of considerable importance. Evolution of volatiles during pyrolysis results in porous char, essential for making activated carbons, while high density contributes to enhanced structural strength of the carbon, essential to withstand excessive particle crumble during use.

Table 1. Characteristics of various conventional raw materials used for making activated carbon.

Raw materials	Carbon (%)	Volatile (%)	Density (Kg/M^3)	Ash (%)	Texture of activated carbon	Application of activated carbon
Softwood	40–45	55–60	0·4–0·5	0·3–1·1	Soft, large pore volume	Aq. phase adsorption
Hardwood	40–42	55–60	0·55–0·8	0·3–1·2	Soft, large pore volume	Aq. phase adsorption
Lignin	35–40	58–60	0·3–0·4	–	Soft, large pore volume	Aq. phase adsorption
Nut shells	40–45	55–60	1·4	0·5–·6	Hard, large multi pore volume	Vapour phase adsorption
Lignite	55–70	25–40	1·0–1·35	5–6	Hard small pore volume	Waste water treatment
Soft coal	65–80	25–30	1·25–1·50	2·12	Medium hard, medium micropore volume	Liquid & vapour phase adsorption
Petroleum coke	70–85	15–20	1·35	0·5–0·7	Medium hard, medium micropore volume	Gas–vapour adsorption
Semi hard coal	70–75	1–15	1·45	5–15	Hard large pore volume	Gas–vapour adsorption
Hard coal	85–95	5–10	1·5–2·0	2·15	Hard large volume	Gas–vapour adsorption

Raw materials used for preparation of activated carbons vary with their application. Conventional raw materials in order of their importance as porous carbon production capacity, characteristics and market are: wood, coal, lignite, coconut shell, peat and others. A comparison of these is given in table 1.

Amongst woods, pine is by far the precursor for the largest production of activated carbon and forms about 50% of precursor, while all other woods contribute about 40%. Regional biowastes and woods have also been investigated and have been found to be promising precursors for porous carbons.

In the last two decades, extensive studies have been made on the selection and pyrolysis behaviour of new synthetic precursors to develop active carbons with very high adsorption capacities and controlled pore size distributions for specific energy applications. These precursors are polymer-based fibrous materials. The examples are viscose rayon, polyacrylonitrile, saran, phenolic, PFA etc. (Patrick 1995; Jin *et al* 1996; Mays 1999; Inagaki 2000).

2.2 *Carbonisation*

During carbonisation, most of the non-carbon elements, hydrogen and oxygen are first removed in gaseous form by pyrolytic decomposition of the starting materials, and the free atoms of elementary carbon are grouped into organised crystallographic formations known as elementary graphite crystallites. The mutual arrangement of the crystallite is irregular, so that free interstices exist between them. Thus carbonisation involves thermal decomposition of carbonaceous material, eliminating non-carbon species producing a fixed carbon mass and rudimentary pore structure (Derbyshier *et al* 1995). The process is usually carried out at temperature below 800°C in a continuous stream of an inert atmosphere. The important parameters that determine the quality and the yield of the carbonised product are: (i) rate of heating, (ii) final temperature and (iii) soaking time. The carbonisation process involves various important stages that markedly determine the properties of the final product to be obtained. The basic microstructure of the char with microporosity is formed around 500°C. Some of these pores are blocked by the tarry products evolved during pyrolysis and could be available only when further heat treatment to about 800°C is given. Further heat treatment to temperature of 1000°C and above normally lead to hardening of the carbon structure due to partial alignment of graphitic planes and decrease in porosity which deaccelerate activation.

2.3 *Activation*

Basically, carbons are described as graphitic or non-graphitic depending upon degree of crystallographic ordering. Graphitic carbons possess three-dimensional symmetry while non-graphitic carbons do not (Inagaki 2000). As discussed above, during carbonisation the free interstices present in the carbon become filled or at least partially blocked by disorganised “amorphous” carbon apparently as a result of deposition of tarry substances. The resulting carbonised product has only a very small adsorption capacity. Presumably, at least for carbonisation at lower temperature, part of the tar remains in the pores between the crystallites and on their surfaces. Such carbonised materials can be then at least partially activated by removing tarry products by heating in steam or under inert gas or by extraction with a suitable solvent or by chemical reaction.

Thus activation is carried out to enlarge the diameters of the pores which are created during the carbonisation process and to create some new porosity thus resulting in the formation of a well-developed and readily accessible pore structure with very large internal surface area. Activation is carried out by two ways as in the following sections.

2.3a *Chemical activation:* Chemical activation is carried out with wood as the starting material. In the beginning, wood is impregnated with a concentrated solution of activating agents. It results in degradation of cellulosic material. Chemical-impregnated material is then pyrolysed between 400 and 600°C in the absence of air. Pyrolysed product is cooled and washed to remove activating agent, which is recycled. On calcination, impregnated and chemically dehydrated raw material results in charring and aromatization, and creation of porous structure. Various type of activating agents are used. Some of them are: phosphoric acid, zinc chloride, H_2SO_4, K_2S, KSNS, alkali metal hydroxide, and carbonate and chlorides of Ca^{+2}, Mg^{+2} and Fe^{+3} (Bansal 1988; Derbyshier 1995). All activating agents are dehydrating agents which influence the pyrolytic decomposition and inhibit the formation of tar. They also decrease the formation of acetic acid, methanol etc. and enhance the yield of carbon.

2.3b *Physical activation:* It is a process by which the carbonised product develops porous structure of molecular dimensions and extended surface area on heat treatment in the temperature range of 800–1000°C in presence of suitable oxidising gases such as steam, CO_2, air (ACS 1996). Gasification of the carbonised material with steam and carbon dioxide occurs by the following endothermic reactions:

$$
\begin{aligned}
C + H_2O &\rightarrow CO + H_2 \text{ (29 kcal)},\\
C + CO_2 &\rightarrow 2CO \text{ (39 kcal)},\\
CO + H_2O &\rightarrow CO_2 + H_2 \text{ (10 kcal)}.
\end{aligned}
$$

The H_2O molecule is smaller than the CO_2 molecule and diffuses faster into the pores of the carbon. Consequently reaction with steam is faster than that with CO_2.

Activation with CO_2 promotes external oxidation and development of larger pores as compared to activation with steam. The relative amounts of external and internal oxidation depends on how well-developed the pores are in the carbonised material. Activation of chars without development of significant pore structure only results in decrease in carbon granule size.

Activation is associated with carbon loss and hence with decrease in weight of host carbon. Weight loss increases linearly with activation temperature and time. Activation at lower temperature predominate in the development of mesopores and macropores. Formation efficiency of pores which have no adsorption ability, i.e. macropores, increase at higher activation temperature, while mean pore diameter decreases with increasing activation temperature.

In case of activation with oxygen, both the reactions

$$C + O_2 \rightarrow CO_2 + 92{\cdot}4\ \text{kcal},$$

and

$$2C + O2 \rightarrow 2CO + 53{\cdot}96\ \text{kcal},$$

take place. Since both reactions are exothermic, there is excessive burning and the reaction is difficult to control.

Moreover, since there is always some local overheating, the product obtained is not uniform. As the reaction is very aggressive, burning is not restricted and also occurs on the surface of the grains, causing excessive weight loss.

2.4 *Mechanism of activation*

The structure of the pores and pore size distribution are largely dictated by the nature of the raw materials and the history of their carbonisation (Manocha 2002). Carbon atoms differ from each other in their reactivity depending on their spatial arrangement. Activation eliminates the disorganised carbon, exposing the aromatic sheets to the action of activation agents and leads to development of a microporous structure. Since activation is associated with weight loss of the host carbon, the extent of burn-off of the carbon material is taken as a measure of the degree of activation (Manocha *et al* 2002). At a particular temperature, weight loss increases linearly with activation time. Normally, in the first phase, the deorganised carbon is burnt preferentially when the burn-off is about 10%. This results in the opening of blocked pores. Subsequently, the carbon of the aromatic ring system starts burning, producing active sites and wider pores.

In the latter phase, excessive activation reaction results in knocking down of the walls by the activated agents and a weight loss of more than 70%. This results in an increase in transitional pores and macropores. The volume of the micropores decreases and there is no significant increase in adsorption capacity or internal surface area.

At higher burn-off, the difference in porosity created by different activating agents become more pronounced. In a typical example, activation of a hard wood with water vapour results in progressive development and widening of all size pores until, at a burn-off of 70%, the activated product contains a well-developed porous system with wide pore size distribution. Activation with 50–70% burn-off causes an increase in the total adsorption volume from 0·6 to $0{\cdot}83\,\text{cm}^3/\text{gm}$ (Rodriguez 1995). But as it is associated mainly with widening of pores, the surface area remains almost the same. Activation with carbon dioxide mainly develops microporosity over the entire range of burn-off. The micropores account for about 73% of the total adsorption pore volume, for over 90% of total surface area. The micropores contribute only 33% towards total pore volume and 63% towards surface area in the case of steam-activated carbon. Thus carbon produced by CO_2 activation has lower total pore volume (0·49 cm^3/gm) than those of corresponding samples obtained by activation of steam. However the effective surface area in both cases is almost the same. This is mainly due to the contribution of micropores to the surface area.

Moreover, the carbon atoms which are localised at the edges and the periphery of the aromatic sheets or those located at defect position and dislocations or discontinuities are associated with unpaired electron or have residual valancies; these are rich in potential energy. Consequently, these carbon atoms are more reactive and have a tendency to form surface oxygen complexes during oxidative activation (Patrick 1995). These surface chemical groups promote adsorption and are beneficial in certain applications. Alternatively, these surface oxygen complexes break down and peel off the oxidised carbon from the surfaces as gaseous oxides leaving behind new unsaturated carbon atoms for further reaction with an activating agent.

Thus, activation mechanism can be visualised as an interaction between the activating agent and the carbon atoms which form the structure of intermediate carbonised product resulting in useful large internal surface area with interconnected pores of desired dimension and surface chemical groups.

2.5 *Activated carbons from synthetic precursors*

Carbonisation of synthetic precursors such as phenolic, polyfurfuryl alcohol, polyacrylonitrile, saran etc. result in glass-like carbons with closed porosity. Activation of these chars, therefore, requires very stringent conditions of temperature, time and environment. However, if carbonisation is carried out to 800–1000°C in presence of CO_2, ultimate char exhibits very high surface area and open accessible pores (Inagaki & Sunahara 1998). In this case, normal pyrolysis takes place up to 700°C heat treatment. Above 700°C, CO_2 starts activation reaction before the pores close down. Thus pyrolysis and activation can be performed on synthetic precursors using CO_2 environment.

3. Structure of porous carbons

The pores in activated carbons are scattered over a wide range of size and shape. The pores are classified by their sizes usually into three groups: (i) macropores having average diameter more than 50 nm, (ii) mesopores with diameter 2–50 nm, and (iii) micropores having average diameter less than 2 nm. These are further divided into supermicropores (0·7–2·0 nm) and ultramicropores of diameter less than 0·7 nm. The pore structure in wood derived carbons is a memory of the texture of the precursor wood and hence differ based on the type of wood/plant (see figure 1). Basically these consist of slit-like voids and macropores. In some woods like pine, these are of similar shape and size and are equally distributed, whereas in bagasse, *Babool*, castor oil wood etc., pores are of very different shapes and sizes and are organised in circular fashion. These macropores are in turn connected to mesopores and micropores. This is shown in figure 2. Figure 2 also includes the structure of activated carbon fibres which, in contrast to wood-based activated carbon, predominantly consists of micropores directly exposed to the surface of the fibres.

Different techniques have been used to determine pore size distribution in porous carbons. These are mercury porosimetry and gas adsorption isotherms and recently, the scanning tunneling microscopy (Patrick 1995; Inagaki 2000).

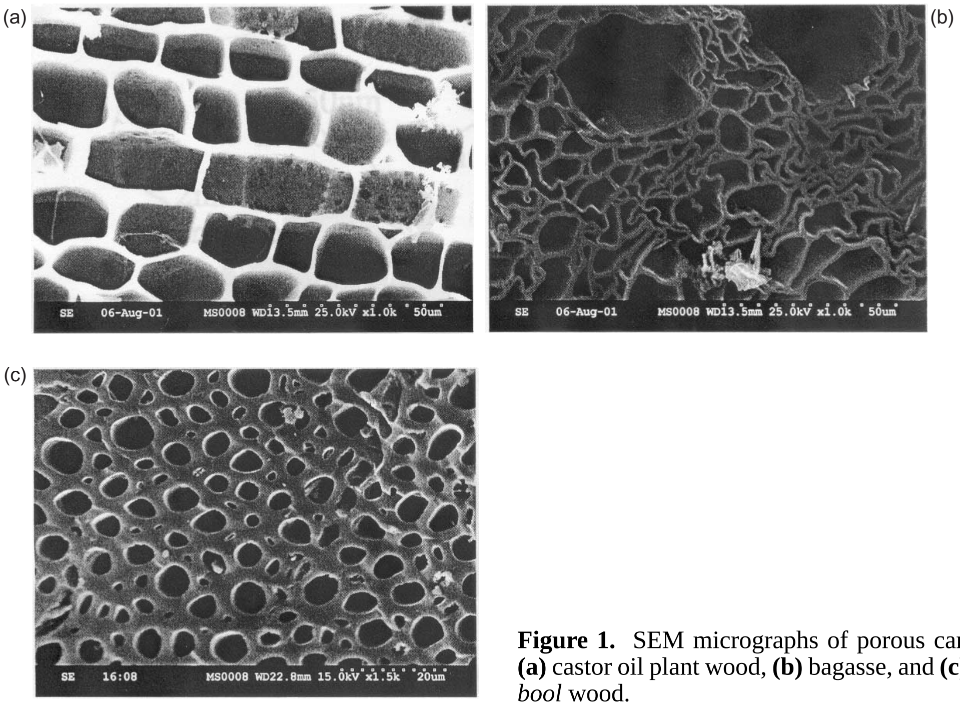

Figure 1. SEM micrographs of porous carbons: **(a)** castor oil plant wood, **(b)** bagasse, and **(c)** *babbool* wood.

4. Adsorption by activated carbons

Adsorption is formation of a gaseous or liquid layer by molecules in a fluid phase on the surface of a solid by molecular attraction of the van der Waals type. Atoms at the surface of solids like active carbons have imbalanced forces as compared to those within the solids and, consequently, foreign molecules in a bid to satisfy this imbalance get attracted to the surface. These molecules (adsorbates) form a monolayer on the surface of the solid (adsorbent). Figure 3 depicts the adsorption process showing transfer of adsorbate molecules through the bulk gas phase to the surface of the solid and diffusion onto the internal surfaces of the pores in the solid adsorbent. Therefore the adsorption capacity of activated carbon depends on the type of pores and the total surface area available for adsorption.

Activated carbons are characterised by their strong adsorption capacity, which can be as high as 0·6–0·8 $\mathrm{cm}^3/\mathrm{gm}$ which occur mostly in cavities of molecular dimensions called micro-

Figure 2. Pore structure of activated carbon: **(a)** granular and **(b)** fibrous.

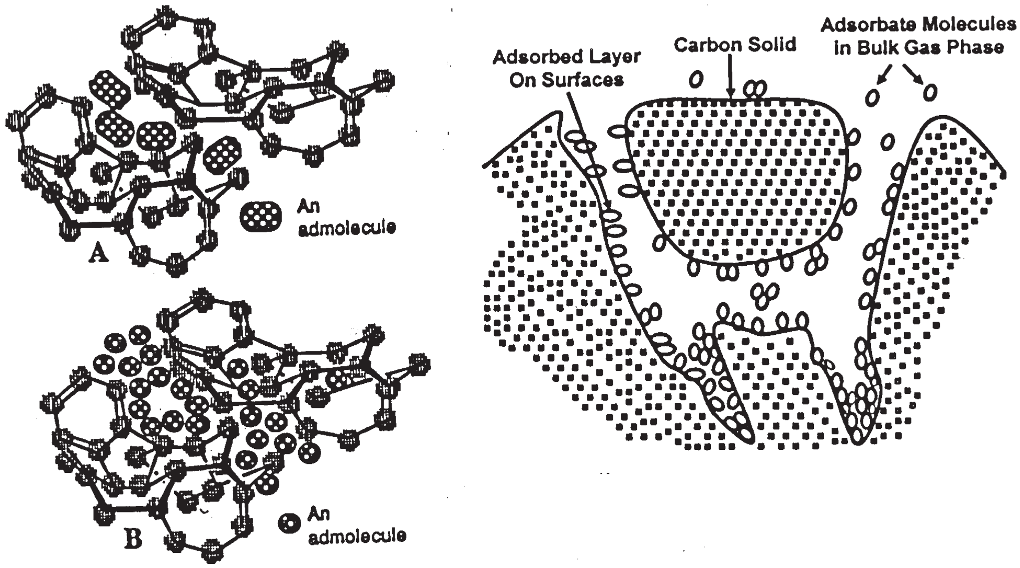

Figure 3. Adsorption processes in activated carbons: Transfer of adsorbate molecules to adsorbent.

pores. Adsorption is a dynamic process in which some adsorbate molecules are transferred from the fluid phase on to the solid surface while some are released again to the fluid state. These processes are functions of partial pressures. When the rates of two processes become equal, an adsorption equilibrium or so-called adsorption isotherm is obtained. This expresses the amount of adsorbate adsorbed as a function of gas phase concentration measured by equilibrium partial pressure p/po at constant temperature. Adsorption isotherms are used to estimate surface area, pore volume in various porosity regime, assessments of the surface chemistry of the adsorbent and fundamental information on the efficiency of industrial carbon employed in separation/purification techniques.

Six general types of isotherms have been observed and the shapes of these characteristic isotherms are shown in figure 4 (Sing *et al* 1985). Type I isotherms are typical of microporus solids where only monolayer adsorption occurs. In these, micropore filling occurs significantly at relatively low partial pressure $< 0{\cdot}1p/po$, the adsorption process being complete at $\approx 0{\cdot}5p/po$. Example include the adsorption of N_2(g) on microporous carbon at 77K and ammonia on charcoal at 273K. Type II isotherms describe physical adsorption of gases by nonporous solids. Monolayer coverage is succeeded by multilayer adsorption at higher p/po values. Type III isotherms are obtained from carbons with mixed micro-and mesoprosity wherein the amount of material adsorbed increases without limit and its natural adsorption approaches unity. Type IV and type V isotherms are convex towards the relative pressure axis. These isotherms are characteristic of weak gas-solid interaction. Type IV isotherms describe a multilayer adsorption process where complete filling of the smallest capillaries has occurred. Type IV isotherms originate from both non-porous and mesoporous solids and type V isotherms from microporous or mesoporous solids. An example is the adsorption of water vapor on graphitised carbon black. The type VI isotherm, in which the sharpness of the steps depends on the system and the temperature, represents stepwise multilayers adsorptions on a uniform nonporous surface. The step-height now represents the monolayer capacity for each adsorbed layer and, in the simplest case, remains nearly

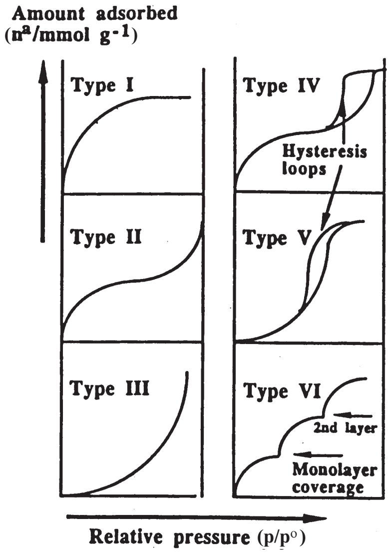

Figure 4. Classification of adsorption isotherms.

constant for two or three adsorbed layers. Amongst the examples of type VI isotherms are those obtained with argon or krypton on graphitised carbon black at liquid nitrogen temperature.

Information concerning effective surface areas, pore size distribution, micropore volume etc., is incorporated within the isotherms. However, a knowledge of adsorption mechanism in different sizes of porosity is necessary to explain the isotherms shape. Adsorption process in micro porosity is more difficult to describe accurately. The adsorption process occurring within mesopores are more easily understood. Macro porosity behaves in the same way as an open surface to adsorption, and accounts for $< 1\%$ of the adsorption process within microporus carbons.

5. Classification of activated carbon

Activated carbons are complex products which are difficult to classify on the basis of their behaviour, surface characteristics and preparation methods. However, some broad classification is made for general purpose based on their physical characteristics.

5.1 *Powdered activated carbon*

Traditionally, active carbons are made in particular form as powders or fine granules less than 100mm in size with an average diameter between 15 and 25 μm. Thus they present a large internal surface with a small diffusion distance.

5.2 *Granulated activated carbon*

Granulated activated carbon have a relatively larger size of particles compared to powdered activated and consequently, present a smaller external surface. Diffusion of the adsorbate is thus an important factor. These carbons are therefore preferred for all adsorption of gases and vapours as their rate of diffusion are faster. Granulated carbons are used for water treatment, deodorisation and separation of components of flow system.

5.3 *Spherical activated carbon*

These are made of small spherical balls wherein pitch is melted in the presence of naphthalene or tetorlin and converted into spheres. These spheres are contacted with solution naphtha, which extracts naphthalene and creates a porous structure. These porous spheres are then heated at temperatures between 100 and 400°C in the presence of an oxidising gas containing about 30% of oxygen by weight. The oxidised spheres are then heated between 150 and 700°C in the presence of ammonia to introduce nitrogen into spheres which are then activated in steam or CO_2. The spheres have high mechanical strength and excellent SO_2 and NO_2 adsorption capacity.

5.4 *Impregnated carbon*

Porous carbons containing several types of inorganic impregnant such as iodine, silver, cation such as Al, Mn, Zn, Fe, Li, Ca have also been prepared for specific application in air pollution control especially in museums and galleries. Silver loaded activated carbon is used as an adsorbent for purifications of domestic water (Oya 1997; Wang *et al* 2001; Manocha *et al* 2002). Drinking water can be obtained from natural water by treating the natural water with a mixture of activated carbon and flocculating agent $Al(OH)_3$. Impregnated carbons are also used for the adsorption of H_2S and mercaptans.

5.5 *Polymers coated carbon*

This is a process by which a porous carbon can be coated with a biocompatible polymer to give a smooth and permeable coat without blocking the pores. The resulting carbon is useful for homoperfusion.

6. Various applications of activated carbon

Activated carbons are unique and versatile because of their extended surface area, microporous structure, high adsorption capacity and high degree of surface reactivity. Their impor tant applications relate to their use in the removal of odour, colour, taste and other undesirable organic impurities from potable water in the treatment of domestic and industrial waste water, solvent recovery, air purification in inhabited species such as restaurants, food processing and chemical industry, for removal of colour from various types of sugar syrup, in air pollution control, in purification of many chemicals, pharmaceutical and food products and in a variety of gas phase applications. Along with other inorganics these are used as a catalyst and catalyst support. Their use in medicines to combat certain types of bacterial is well-known. These are used effectively for isolation and separation purposes. In separation of amino acids from their solutions in acetic acid, activated carbon can be used for separating aromatic acids. In order to effect chromatographic separation and to make the elution of absorbed substances easier, activated carbon is often modified, for example by treatment with nitric acid, making the surface more hydrophilic.

7. Advanced active carbons

In addition to general purpose active carbons, advanced active carbons with specific control on pore structure have been developed over the past few decades for specific applications. Research and development efforts are continuing for more and more efficient applications of these materials. Some of these products and their applications are discussed below.

7.1 *Carbon molecular sieves*

Carbon molecular sieves (CMS) are a special class of active carbons having small pore sizes with a sharp distribution in a range of micropores, as compared with other activated carbons (see figure 5) (Inagaki 2000). They are used for adsorbing and eliminating gas and liquid phase adsorbate of very low concentration like ethylene gas adsorption to keep fruits and vegetables fresh, filtering of hazardous gases in power plants etc. However, the most important application of these CMSs is in gas-separation systems (swing adsorption method). The pore size in CMSs is comparable to the size of adsorbate molecules, such as nitrogen, hydrogen. In addition, the temperature of adsorption governs the rate of adsorption of a gas because of the activated diffusion of adsorption molecules in micropores; the higher the temperature the faster the adsorption. By controlling (swinging) these parameters, the temperature and pressure (i.e. concentration) of adsorbate gas, gas separation can be performed more effectively. CMSs have been used in separation of nitrogen and oxygen. This swing adsorption method for gas separation has the advantages of low energy cost, room temperature operation, compact equipment, etc.

7.2 *Activated carbon fibres*

Amongst latest addition to porous carbons are the activated carbon fibres. Activated carbon fibres with higher and most effective pore structure have developed a new field of applications (Suzuki 1994). The technology of activated carbon fibres is the combination of the technology for carbon fibre manufacturing and their activation. Since high mechanical properties are not the requirements in this case, it is not intended to use special precursors for making carbon fibres, rather precursors resulting amorphous carbon structure are preferred. Moreover, such carbon structures are suitable for activation. Therefore activated carbon fibre process consist of development of amorphous carbon fibres at around 1000°C from rayon, pitch, PAN and phenolic etc. followed by activation by steam at 800–1000°C. A very high specific surface area up to 2500 m^2/g and a high micropore volume up to 1·6 ml/g can be obtained in general purpose pitch-based carbon fibres (Suzuki 1994; Schmidt *et al* 1995; Mays 1999). Another advantage of activated carbon fibres is the ability to prepare the products in different shapes such as woven clothes and non-woven mats etc. These increase the ease of handling these materials and packing efficiency for specialised applications such as candles for small water purification systems, as deodorant in refrigerators, batteries etc.

Activated carbon fibres have a number of advantages over granular activated carbons. The principal merit to prepare carbon in fibrous morphology is its pore structure and a large

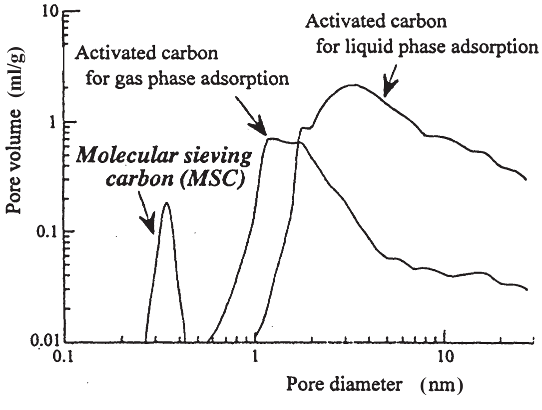

Figure 5. Pore size distribution of molecular sieve carbons (MSC) and activated carbons for gas and liquid adsorbates.

physical surface area. Their pore structure is schematically shown in figure 2. Activated carbon fibres mostly contain easily accessible micropores exposed to their surfaces. In granular activated carbons, the adsorbate gas molecules always have to reach micropores by passing through macropores and mesorpores, whereas in activated carbon fibres, most micropores are exposed directly to the surface of the fibres and hence to the adsorbate gas. Therefore, the adsorption rate as well as the amount of adsorption of gases into activated carbon fibres are much higher than those into granular activated carbons. Figure 6 shows comparison of the adsorption and desorption behaviours of toluene on these two type of carbons. Desorption of gas can be accelerated by raising the temperature on activated carbon fibres.

Active carbon fibres with high surface area have advantage over traditional materials for effective elimination of SO_2 and NO_x from flue gases from combustion of coal and gasoline fuels (Daley *et al* 1997; Mochida *et al* 1997). Active carbon fibres are the best adsorbers for removing volatile organic compounds from air. These compounds are toxic, low boiling point aromatics such as toluene, xylenes etc. and are produced in various industrial processing units of mass consumption. In application such as environmental protection, a rayon-based ACF cloth impregnated with organo-metallic compound such as copper (II) nitrate has been shown to be a useful adsorbent for hydrogen cyanide gas. Impregnated ACFs as adsorbents for toxic gases are vital for military applications. Active carbon fibres are used as alternative water purification media to granulated active carbon especially for both low molecular weight as well as high molecular contaminants such as phenolics, humic substances and pesticides etc. ACFs offer high adsorption capacities and rates and are more easily regenerated. The bacterial breeding problem is taken care of by impregnating these with minute particles of different metals, such as Ag, Cu and Mn. There are many other emerging applications of ACFs which include their use in medicines as enteroadsorbents, in vapour sensors etc.

7.3 *Porous carbons for car canisters*

Automobiles are a major source of global warming gases. There is strong demand to reduce and control the composition of exhaust gas from automobiles. In order to treat the exhaust gases, different catalysts have been used and are being studied extensively. Car canisters with activated carbon have recently been developed to adsorb gasoline vapour in the tank of a car during parking or running. The adsorbed gasoline is desorbed during running by introducing air and transferred to the engine. This helps in saving gasoline and to avoid contamination of the air (Johnson & Setsuda 1999).

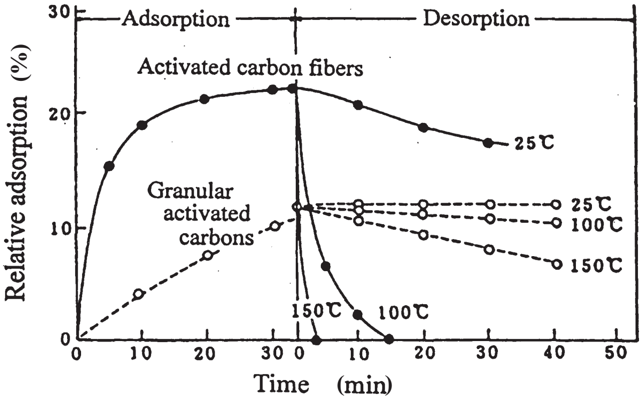

Figure 6. Adsorption/desorption of toluene onto different types of activated carbons.

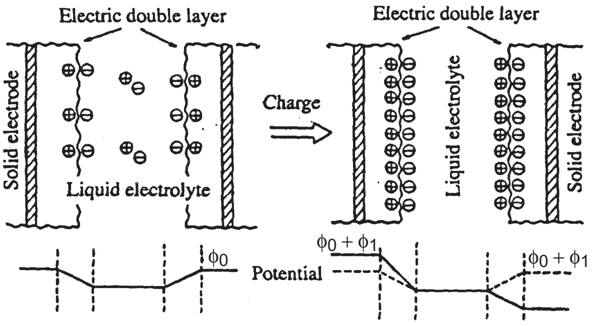

Figure 7. Fundamental scheme of an electric double layer capacitor.

7.4 *Active carbon fibres for energy applications*

One of the potential gas phase application of active carbon fibres are in the adsorbed natural gas (ANG) containers. ANG in active carbon is a useful alternative to compressed natural gas (CNG). As much lower pressure (about 4 MPa) are required to achieve effective liquifaction in small carbon pores as compared to about 25 MPa pressure required for CNG.

Another application of ACF is in electric double-layer capacitors (Tanahashi *et al* 1990; Ishikawa *et al* 1994). The electric double-layer capacitor is regarded as an attractive rechargeable power device because of its high rate charge/discharge ability and high energy density compared with common rechargeable batteries.

The fundamental concept of this capacitor is illustrated in figure 7. At the interface between two different phases, in the present case between a solid electrode and a liquid electrolyte, a very thin layer is formed in which two charges, positive and negative, are aligned. By using porous carbon materials with a very high surface area in both positive and negative electrodes, a large amount of electrical charge is found to be stored. The total amount of electric charges aligned in double layers on both electrodes increases by the application of potential difference which in turn depends on the area of this interface, i.e. the surface area of solid electrodes. The large specific surface areas of activated carbon fibres coupled with their electrical conductance are highly beneficial in electric double-layer capacitors. Particularly by using activated carbon fibre cloth prepared from phenol resin and organic electrolytes such as propylenecarbonate with tetraethylammonium perchlorate, small capacitors with a coin-shape have been developed, with a high capacitance, high working voltage and high reliability (Tanahashi *et al* 1990).

8. Concluding remarks

Carbon in dense form utilises its outstanding mechanical, thermal and electrical characteristics in a host of applications from common lead pencil to advanced management systems for spacecrafts. At the same time its affinity for oxygen at high temperature can be beneficially utilised in making porous carbons.

Porous carbons are prepared through controlled pyrolysis of carbonaceous materials, naturally occurring woods or synthetic polymeric materials. Though these are used as insulating materials, templates for ceramics etc., but the maximum applications is as active carbon produced by chemical activation or physical activation. Chemical activation results in active carbons with mixed pore structure i.e. micro, meso, macropores; physical activation leads to formation of predominantly micropores with dia < 2 nm and pore volume 0·6–0·8 cm^3/gm.

These active carbons are prepared in many physical forms and are used as such or after impregnation with metal salts in a large number of applications depending upon imagination. Active carbon fibres are increasingly getting attention because of ease of fabrication, controlled pore structure, higher adsorption capacity, faster adsorption/desorption rates. Active carbon fibres have been tried successfully in number of advanced technologies such as adsorbents, catalyst support, ANG, gas and liquid phase environmental control, water purification and energy storage. There is still wide scope for development of active carbon fibres in various forms with tailored porous structures for desired specific applications. Active carbons in different forms have a great role in modern life can help in providing energy sufficient, trouble free, living in clean environment.

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