Use of activated carbon fibres (ACF) as selective molecular adsorbents presents many advantages over granulated activated carbons (GAC) on account of their greater adsorption rate and larger adsorption capacity. These properties increase the efficiency of adsorption bed and lead to simplified plant designs used for environmental pollution control. In this paper, various methods of activation for the production of ACF from PAN-based precursors have been discussed. Different adsorption techniques used for measuring the porosity (micropore <0.6 nm, mesopore >1.6 nm and macropore >200 nm), surface area and surface functional groups have been critically analysed. Specific applications of ACF in air and water purification, medicine and catalysis have been highlighted.

Keywords: Activated carbon fibres, Adsorption isotherm, Chemical activation, PAN precursor, Pollution control, Pore size distribution.

1 Introduction

Activated carbon fibres (ACF) are porous materials which selectively absorb various components from liquid or gaseous media through physical or chemical adsorption and have, therefore, found widespread applications in the purification of contaminated gases, adsorption of poisonous gases like NO and SO₂ from the environment, separation of gases, deodorizers for air conditioning of production facilities. ACFs have also found applications in water purification, recovery of some solvent vapours, and for making humidity sensors. In addition to their use in purification of air and water, activated carbon fibres have found extensive use in medicine: therapeutic approaches in fighting body intoxication, control of gastric juices, purification of biologically active substances due to their selective adsorption properties and in making antibacterial fibres. ACFs are also recognized as efficient catalysts or supports for catalytically active phase in heterogeneous catalysis. Despite higher costs, ACFs are preferred to granulated (finely divided active) carbons because of the following reasons:

- Higher bulk volume of the ACFs leads to higher adsorption rates.
- The sorption of ACFs is 12-15 times higher than that of the granulated activated carbons (GAC). ACFs have uniform micropores and adsorption in low pressure region is enhanced by strong micropore field.
- The mass transfer coefficient for activated carbon fibres is 10-100 times higher than that for granulated carbons.
- Small fibre diameter makes it possible to achieve homogeneous fibre activation which ensures homogeneity in the adsorption characteristics.

Depending on the nature of the raw materials and their carbonization and activation processes, the resulting ACF products show an increased amount of small pores and the total surface area, measured using BET (Brunauer, Emmett & Teller) method, in the range of 750-2500 m²/g. The differences in the average size distribution and in shape between ACF and GAC are shown in Figs 1 and 2.

The activated carbon fibres are produced from various precursors like PAN, cellulosics and phenolic resin. Mochida et al. have compared the porosity of activated carbon fibres produced from these precursors (Table 1). The ACFs produced from PAN precursors have unique adsorption capabilities and excellent strength.
This paper presents an overview on the recent developments relating to polyacrylonitrile (PAN) based activated carbon fibres. Relative performance of the ACFs produced from different precursors has also been given.

2 Production of Activated Carbon Fibres

Acrylonitrile (AN), methyl acrylate (MA) and itaconic acid (IA) based terpolymer fibres\(^4\) have generally been used as precursors for the production of activated carbon fibres. The production of activated carbon fibres from PAN precursors involves the following steps (Fig. 3):

- Thermo-oxidative stabilization
- Carbonization
- Activation

Production conditions and properties of some activated carbon fibres produced from PAN precursor are summarised in Table 2.

2.1 Thermo-oxidative Stabilization

Precursor fibres are stabilized with a continuous process\(^5\) in air or in an oxidising atmosphere\(^6\) in the temperature range of 180-400°C. During this process, the linear polymer chain is converted into infusible ladder polymer through nitrile oligomerization\(^6\)\(^-\)\(^4\)2.

![Diagram 2](image)

Table 1—Characterization of various commercial ACF samples

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Sample</th>
<th>Precursor source</th>
<th>Surface area, (\text{m}^2\text{g}^{-1})</th>
<th>Pore volume, (\text{cm}^3\text{g}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>OG-5A</td>
<td>Pitch base</td>
<td>480</td>
<td>0.25</td>
</tr>
<tr>
<td>2</td>
<td>OG-5A3/673/4</td>
<td>Pitch base</td>
<td>720</td>
<td>0.39</td>
</tr>
<tr>
<td>3</td>
<td>PAN-ACF</td>
<td>PAN base</td>
<td>740</td>
<td>0.36</td>
</tr>
<tr>
<td>4</td>
<td>PAN-ACF</td>
<td>PAN base</td>
<td>790</td>
<td>0.42</td>
</tr>
<tr>
<td>5</td>
<td>PR-ACF</td>
<td>Phenol resin</td>
<td>1520</td>
<td>0.81</td>
</tr>
<tr>
<td>6</td>
<td>PR-ACF</td>
<td>Phenol resin</td>
<td>1380</td>
<td>0.64</td>
</tr>
<tr>
<td>7</td>
<td>PAN-ACF</td>
<td>PAN base</td>
<td>1540</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>PAN-ACF</td>
<td>PAN base</td>
<td>800-2500</td>
<td></td>
</tr>
</tbody>
</table>

Source: Ref. 5 for samples 1-6, ref. 17 for sample 7, and ref. 48 for sample 8
Ko et al.\textsuperscript{31,32} carried out the continuous stabilization through the furnace for 2 h 25 min. The furnace was divided into four zones with different temperature zones of 190°C, 225°C, 275°C and 300°C respectively. The heating rate was kept less than 5°C/min.

The precursor fibres stabilized in air showed better strength and yield than in an inert atmosphere\textsuperscript{43-47}. Rate of disappearance of -CN groups was found to be more in air than in an inert atmosphere\textsuperscript{47}, which suggests that oxygen\textsuperscript{48} helps in oligomerization of the nitrile groups, leading to the formation of ladder polymer. Also, the stabilization in an oxidizing medium is preferred because it results in the formation of oxygen containing groups such as -OH, >C=O and -COOH in the backbone of

<table>
<thead>
<tr>
<th>Precursor composition (wt%)</th>
<th>Thermo-oxidative stabilization (S&lt;sub&gt;T&lt;/sub&gt;)</th>
<th>Carbonization/ activation</th>
<th>Properties</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAN (93 : 6 : 1)</td>
<td></td>
<td>Continuous carbonization and activation</td>
<td>Tensile strength (GPa)</td>
<td>Surface area (m&lt;sup&gt;2&lt;/sup&gt;g&lt;sup&gt;-1&lt;/sup&gt;)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Passed in a ceramic tube</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Temp.: 900°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Atmosphere: Nitrogen and CO&lt;sub&gt;2&lt;/sub&gt;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PAN (93 : 6 : 1)</td>
<td></td>
<td>(i) Carbonization</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Sample Temp:</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>A&lt;sub&gt;1&lt;/sub&gt; = 800</td>
<td>32</td>
<td>31</td>
</tr>
<tr>
<td></td>
<td></td>
<td>B&lt;sub&gt;1&lt;/sub&gt; = 900</td>
<td>1</td>
<td>538</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C&lt;sub&gt;1&lt;/sub&gt; = 1000</td>
<td>11</td>
<td>499</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Atmosphere: N&lt;sub&gt;2&lt;/sub&gt;</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(ii) Activation</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Temp.: 880°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Atmosphere: CO&lt;sub&gt;2&lt;/sub&gt;</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Time: 3-60 min</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PAN precursor filaments (diam. 0.1 μm)</td>
<td>Oxidation in ozone (0.3 vol% in air) at 150°C for 3 min.</td>
<td>Activation &amp; Carbonization</td>
<td>1540</td>
<td>48</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Atmosphere: CO&lt;sub&gt;2&lt;/sub&gt; + N&lt;sub&gt;2&lt;/sub&gt; (1:1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Temp.: 970°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Time: 100 min. Burn off: 64%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PAN</td>
<td></td>
<td>Activation</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Rate of passage of C-fibres through reactor: 750 g/h</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Atmosphere: steam (30-100 vol% steam)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Temp.: 980°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Sample: Time</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>A = 6 h</td>
<td>(A) 1072</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>B = 24 h</td>
<td>(B) 1036</td>
<td></td>
</tr>
</tbody>
</table>

Table 2—Production of activated carbon fibres from PAN precursor.
the ladder polymer. These groups subsequently help in fusion of the ladder polymer during carbonization. Stabilization of precursor fibres can also be carried out in ozone, hydrogen chloride gas, nitrous oxide or sulphur dioxide gas.

In a recent study by Lu et al., PAN precursor filaments of 0.1 μm diameter were taken and thermo-oxidative stabilization was carried out by exposure to ozone (0.3 vol% in air) at 150°C for 3 min. These fibres were subsequently carbonized and activated in a combined process (in CO₂ and N₂ mixture in 1:1 ratio) at 970°C for 100 min at 64% burn off. The resultant ACF had around 65Å pore size and specific area as high as 1540 m² g⁻¹.

Ko et al. studied the effect of shrinkage occurring during the stabilization process on the surface area, pore volume, density and tensile strength of the ACF produced subsequently. Stabilized fibres were prepared by controlling differential speed ratio (between the feed and pinch rollers) with shrinkage between 17% and 21%. Continuous carbonization and activation was done at 900°C in nitrogen and carbon dioxide atmosphere.

Tensile strength (0.62 GPa) of ACF with no shrinkage during stabilization was found to be higher than that of ACFs which had 17% shrinkage (0.43 GPa) (Table 2). The lower strength has been attributed to the disorientation of molecular chains in the stabilized fibres due to high shrinkage.

The two stabilized samples with 17% and 21% shrinkage produced misoriented ladder polymers and other defects which decrease the formation of carbon basal planes and promote the formation of closed pores during the activation stage. Iodine number, which is a measure of micropores (<2 nm), increased on increasing the shrinkage from 17% to 21%, indicating that very fine pore structures were formed in the activated carbon fibres from shrink stabilized fibres during activation and carbonization. Pore size distribution for all the activated carbon fibre was around 2.5-2.6 nm.

2.2 Carbonization Process

Stabilized precursor fibres are converted to carbon fibres in the process of carbonization. An inert atmosphere is necessary during the carbonization step to avoid oxidation at very high temperatures. For this purpose, nitrogen, argon or non-oxidizing media such as BB₅ have been recommended.

In the carbonization process, elimination of all other atoms but for carbon takes place in the form of byproducts and a graphite like structure is formed by heating the stabilized PAN fibres up to 1300°C under low tension in an inert atmosphere.

Generally, there are two zones for heating the fibres during the carbonization process. First zone requires a low heating rate (<5°C/min) up to about 600°C so as to reduce the mass transfer rate as the surface irregularities may be caused due to the faster mass transfer rate. The second zone requires higher heating temperatures, generally from 600°C to 1300°C, at a higher heating rate as the chance of damage due to the evolution of byproducts or exothermic reactions is reduced.

The effect of carbonization temperature on surface area and mechanical properties has been studied by Ko et al. It was observed that tensile modulus of carbon fibres increased significantly from 53 GPa to 70 GPa when temperature was increased from 700°C to 800°C, and from 70 GPa to 100 GPa when the carbonization temperature was further raised to 900°C. Around 500°C, the cross-linking reactions in the ladder polymer started taking place involving nitrogen release and formed carbon basal planes parallel to the fibre axis.

Above 700°C, carbon basal planes began to broaden and lengthen. Density increased very rapidly in relation to increase in the carbonization temperature below 900°C. However, above 900°C the density dropped. A similar phenomenon was observed by Gibson and Balasubramaniam et al. They proposed that the change in density was due to the conversion of open pores into closed pores during carbonization. As the consolidation and rearrangement of structure occurred around 900°C, the passages of open pores were blocked, thereby decreasing the density.

The effect of carbonization temperature on specific surface area was also critically analyzed by Ko et al. The specific surface area of carbon fibres was found to be 32 m²/g at carbonization temperature of 800°C. This decreased to 1 m²/g at 900°C but reached to a maximum of 161 m²/g at 1100°C (Fig. 4).
Fig. 4—Effect of carbonization temperature on the specific surface area of PAN-based carbon fibres [(1) Before activation, and (2) After activation in CO₂ atm.]

It is assumed that during the carbonization stage, gases such as HCN, N₂, etc. are evolved but as the formation of carbon basal planes takes place due to the crosslinking reaction and elimination of nitrogen, the passages of open pores on the fibre surfaces are covered, thereby enveloping the defects between the basal planes. Therefore, the surface area was only 1 m²/g at 900°C. Above 900°C, nitrogen gas continued to be evolved, so some smaller pores were formed in the fibres. This reaction led to further increase in surface area to 161 m²/g at 1100°C.

When the fibres were carbonized at 800°C, the diameter of the pores was greater than 4 nm which decreased to less than 4 nm at carbonization temperature of 1000°C and less than 3 nm at 1100°C.

2.3 Activation Process
The process of increasing the carbon porosity is known as carbon activation. The activation of carbon fibres can be carried out either by gas activation or chemical activation.

2.3.1 Gas Activation
The activating gases generally used are carbon dioxide, steam, oxygen or their combinations. The activation of carbonaceous materials with vapours or gases involves, along with physical processes like evaporation from the surface of activated material, removal of tarry products, loosening of the material and chemical processes. Generally, the chemical interaction of CO₂ and steam with carbon takes place as under:

\[ C + CO₂ → 2CO \]
\[ C + H₂O → CO + H₂ \]

or \[ C + 2H₂O → CO₂ + 2H₂ \]

Several researchers including Koenig et al. have studied the reaction of carbon fibres (Cₚ) with carbon dioxide and proposed the following complex formation as an intermediate which is a two site intermediate surface complex, e.g. lactone type species.

\[ CO₂ + 2Cₚ \]

The increase in surface area due to carbon dioxide activation has been explained. During carbonization, it is assumed that open porosity is converted to closed porosity. During the activation process, carbon dioxide etched the carbon basal planes of the carbon fibre and hence some structures could be etched and removed. This process led to the degradation of some structures consequently, resulting in the formation of new flaws and pores. The formation of new flaws and pores led to a remarkable increase in the surface area after activation. It has been found that the diameter of most of the pores after activation was less than 3.9 nm and the large sized pores of 10-30 nm disappeared. Hence, the remarkable increase in surface area after activation was due to the formation of small pores.

According to Ko et al., the surface area of carbon fibres produced after carbonization at 900°C was 1 m²/g and it increased to 538 m²/g when these same carbonized fibres were activated in CO₂ atmosphere at 880°C for 60 min (Table 2).

In case of steam activation, the formation of intermediate surface complex takes place similar to that in carbon dioxide-carbon interaction. This process is limited by the decomposition reaction of the intermediate surface complex. According to Sakawaki et al., activated carbon fibres could be produced at high speeds using steam activation by the following process:

Activated carbon fibres were prepared by countercurrently contacting carbon fibres in a reactor provided with an inlet and an outlet for the activating gas, a heating device and a stirring device under gas containing 30-100 vol % steam or gas containing 30-99.5 vol % steam and 0.5-15 vol % O₂ at 700-1200°C with temperature of gas fed to the reactor at 300-900°C.
The carbon fibres (PAN-based) were fed through a continuous reactor at the speed of 750 g/h and activated under steam at 980°C to give activated carbon fibres with specific areas 1072 and 1036 m²/g after a continuous operation for 6 and 24 h respectively.

As far as the use of activating agents is concerned, the steam is more frequently used than carbon dioxide or oxygen. There are certain limitations to the use of oxygen as an activating agent. During oxygen activation, some stable oxygen complexes may be formed in the pores on the surface of the activated material, which considerably reduce the accessible adsorption area in the micropores. Moreover, in the presence of oxygen the activation rates are high which cause surface burn off, resulting into macropore formation and poor strength of the activated carbon fibres.

Variations in activation conditions (the rate of gas flow, gas concentration and temperature during the process, textile forms, structural and chemical characteristics of activated materials, etc.) will influence the kinetics of the activation process and consequently the structure and physical properties of the final activated carbon fibres226.

A considerable increase in the activation temperature to over 830°C shifts the chemical reactions in the system (carbon - steam - gaseous product of activation). In case of CO₂ activation, the appropriate temperature is 880°C for PAN-based activated carbon fibres31,32. If CO₂ activation is carried out at 880°C on a sample carbonized at 900°C temperature, the surface area (SA) of the activated carbon fibres produced is 538 m²/g which is much greater than when carbonization is carried out at 800°C and subsequent activation at 880°C (SA=261 m²/g). This is mainly because of lower carbonization temperature i.e. 800°C than the activation temperature of 880°C. It is interesting to note that specific surface area remarkably increased from 1 m²/g before activation to 539 m²/g after activation (Table 2) when fibres were carbonized at 900°C.

The reason for this is that 900°C being above the activation temperature of 800°C, when activation is done, the degradation of structures and the pore formation takes place at a much faster rate than the formation of new carbon basal planes, and hence the pores formed are not covered by these planes, thereby remarkably increasing the pores and the active surface area (Fig. 4).

2.3.2 Chemical Activation

A pre-requisite to chemical activation is generally the presence of non-carbonized regions in the carbon fibre materials capable of being destroyed by activators with the formation of volatiles. This activation process is primarily directed at freeing the sealed micropores that are initially present in the polymer (from tar)58,59,63-65. Chemical activation is carried out in the presence of certain additives through gas activation or heat treatment. These additives are added either before stabilization or after stabilization or carbonization. They control the kinetics and mechanism of the activation reactions and influence the mechanical and adsorption characteristics of ACF13,7,26-33.

Surface modifications by chemicals can also be carried out after activation for generating the specific functional groups on the surface, but not throughout the volume.

Various additives used for the chemical activation are:

- Alkali Metals (Na, K, Li): These are generally introduced into the material to be activated in the form of carbonates, nitrates, chlorides or sulphates166. On heating, the hydrolysis of these salts takes place and only oxides and hydroxides remain in the carbon matrix. Catalytic activity of such alkaline metal salts increases with increase in the cation size. The general mechanism for reaction is that the cation forms a complex with the carbon matrix which reacts with the activating gases86.

In a recent study7, alkali metals Na and K were introduced into the PAN-based carbon fibres along with Ca and Mg prior to activation and a surface area of 800-2500 m²/g could be achieved by this process. Such ACFs have been used for the removal of chlorine from water.

- Alkaline Metal Oxides (M₂O): They can be used as additives133 and play the role of catalysing the carbon-activating gas interaction as under:

\[ \text{M}_2\text{O} + \text{C} \rightarrow 2\text{M} + \text{CO} \]
\[ 2\text{M} + \text{CO}_2 \rightarrow \text{M}_2\text{O} + \text{CO} \]

Here, the role of activating gas CO₂ is confined to regeneration of oxide from the reduced form. It has been proved that oxide formation on interaction of
CO₂ with a reduced metal occurs by the intermediate formation of carbonates.”

- Transition Metals: Introduction of nickel into carbon matrix considerably lowers the activation temperature. In contrast to alkali metal ions, which demonstrate no dependence of catalytic activity on the nature of the carbon, nickel shows this dependence. However, the catalytic effect of nickel ion depends on its counter ion and its activity follows the order as under:

  nitrate > acetate > oxalate > basic carbonate > oxide

The formation of metal-oxygen surface complexes due to the dissociation of water molecules accompanied by oxygen transfer to carbon is responsible for the catalytic action. Considerable effect on the interaction of activating gases with carbon has been observed due to the presence of iron compounds. For example, a sharp increase in the nitrous oxide sorption has been observed if iron is introduced in the structure of carbon fibres before activation.

Platinum group metals have also been considered as effective catalysts in the interaction of carbon and steam. Besides this, there is a remarkable lowering of the activation temperature in the presence of platinum compounds.

Impregnating the carbon fibres with transition metal halides makes it possible to increase their sorption capacity considerably with respect to gases and vapour of basic compounds—ammonia and amines. In case of CuCl₂, deposition of copper crystals takes place during pyrolysis. This causes carbon burn off in regions situated next to metal depositions, resulting in weakening of links between the filaments and thereby increasing the porosity considerably, although in this process the strength of ACF is reduced.

- Oxy acids of Phosphorus: Introduction of phosphorus into the initial PAN fibres or after stabilization (PANOX fibres) not only simplifies and intensifies the pyrolysis and the activation process but also makes it possible to obtain ACF with molecular sieve properties. If H₃PO₄ (2 vol% in methanol) is uniformly coated on the surface of PANOX fibres (PAN fibres oxidised at 200-300°C), then phosphorus which goes inside the fibre from the surface at higher temperatures prevents oxygen from reaching the interior, preventing higher weight loss at high temperature. Moreover, the phosphorus present in the interior catalyses the interaction of gas with carbon, thereby increasing the porosity.

2.3.3 Mechanism of Pore Formation

It is pertinent to observe that during the initial stage of carbonization (say around 600°C) a slight increase in the porous structure takes place. The adsorption capacity at this stage remains low which is due to the deposition of some tarry substances at the entrances of the sorbing pores which prevents adsorption at these sites. Further increase in the carbonization temperature does not remove the tar from the pores but enhances its carbonization which finally seals the pores against any external sorbate. All this nullifies the practical significance of such carbon materials as sorbents. To restore sorption properties of these materials, it is necessary to carry out the process of activation. During activation, the burn off process accompanied by the structural changes in the carbon fibres takes place. After activation, the pores formed on the surface or in the interior of ACF can be classified into following four groups depending on their size:

<table>
<thead>
<tr>
<th>Pore Type</th>
<th>Size Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Micropores</td>
<td>&lt; 0.6 - 0.7 nm</td>
</tr>
<tr>
<td>Super micropores</td>
<td>0.7 - 1.6 nm</td>
</tr>
<tr>
<td>Mesopores</td>
<td>1.6 - 200 nm</td>
</tr>
<tr>
<td>Macropores</td>
<td>&gt; 200 nm</td>
</tr>
</tbody>
</table>

During activation, the amorphous carbon regions are most prone to burn off. The sheath, showing micropore structure, is more dense while inner core exhibits large pores. Some researchers indicated the burn off of amorphous carbon which lies between the crystallites and the layers of turbostratic carbon results in the micropore formation. In ACFs, the micropores are represented by a system of slit like pores between the layers of polyaromatic crystallites. The microporous carbons contain ultramicropores, which are represented by narrow parallel spacing (0.35-0.6 nm) while super micropores are recognized as wider parallel spacings and non-parallel spacings (0.6-2.00 nm). Low temperature carbons display a small number of turbostratic spacing of 0.34 nm. The burn off from the walls separating micropores generates micropores of larger size (super micropores), their radius being approximately twice that of micropores formed.
3 Characterization of Activated Carbon Fibres

The physical and chemical structures of activated carbons have been studied by various techniques. One can analyze in detail the following aspects of activated carbon fibres:

- Surface area and porosity
- Active sites and functional groups

3.1 Surface Area and Porosity

Surface area and porosity can be measured by (i) direct techniques which involve adsorption isotherms, mercury porosimetry and surface energy data, and (ii) indirect methods through photoconductivity, electrical conductivity or X-ray diffraction.

3.1.1 Adsorption Isotherms

Activated carbon fibres and activated carbons (non-fibrous) have been analyzed for their porosity and surface area. Absorption by microporous carbons can be studied using absorptive molecules of selected sizes as molecular probes. In this way, micropore volume available to each molecular dimension can be determined. All these activated materials are first outgassed under high vacuum at 573K (ref. 83). Then the adsorption of the following gases is carried out at different temperatures for different samples: Argon at 77 K (ref. 82), Carbon-dioxide at 273 K (refs 82, 83, 86), Nitrogen at 77 K (refs 82, 83, 86, 88), n-Butane at 273 K (refs 82, 83, 86, 88). The characteristics of various adsorptives used in characterization of activated carbons are given in Table 3.

By using various adsorption isotherm equations, the quantitative analysis of the porosity (microporosity) and the apparent surface area of the activated carbon materials can be made.

- Small pores (0.6-0.7 nm) can be evaluated by the application of DR (Dubinin Radushkevich) equation to the adsorption isotherms of CO₂/273K.
- Medium micropores (0.7-1.0 nm) can be evaluated by the application of DR equation to the adsorption isotherms of argon/77K, nitrogen/77K and n-butane/273K.
- Large micropores (1.0-1.6 nm) can be measured either by n-nonane per adsorption or from plots of argon/77K, nitrogen/77K or n-butane/273K adsorption.

3.1.2 Mercury Porosimetry

In this process of evaluation of the total pore volume of an activated sample, it is assumed that mercury (Hg) does not penetrate the porous structure of carbons at atmospheric pressure but helium (He) does. The total pore volume \( V_p \) can be calculated from

\[
V_p = \frac{d_{He}}{d_{He}} - \frac{d_{He}}{d_{He}}
\]

Table 4 shows the densities and pore volumes of the carbons calculated from adsorption isotherms. By using various adsorption isotherm equations, the quantitative analysis of the porosity (microporosity) and the apparent surface area of the activated carbon materials can be made.

Table 3—Characteristics of adsorptives used for characterization of activated carbons

<table>
<thead>
<tr>
<th>Adsorptive</th>
<th>Adsorption temperature (K)</th>
<th>Minimum dimension (nm)</th>
<th>Cross-sectional area (nm²)</th>
<th>Liquid density (g/cm³)</th>
<th>Method of analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>77</td>
<td>0.20</td>
<td>0.1385</td>
<td>1.400</td>
<td>BET, DR, αs</td>
</tr>
<tr>
<td>CO₂</td>
<td>273</td>
<td>0.28</td>
<td>0.187</td>
<td>1.023</td>
<td>DR</td>
</tr>
<tr>
<td>N₂</td>
<td>77</td>
<td>0.30</td>
<td>0.162</td>
<td>0.808</td>
<td>BET, DR, αs</td>
</tr>
<tr>
<td>n-C₃H₆</td>
<td>273</td>
<td>0.49</td>
<td>0.415</td>
<td>0.600</td>
<td>BET, DR, αs</td>
</tr>
</tbody>
</table>

Table 4—Densities and calculated pore volumes of the carbons

<table>
<thead>
<tr>
<th>Carbon burn off (%)</th>
<th>( d_{He} ) (g/cm³)</th>
<th>( d_{He} ) (g/cm³)</th>
<th>( V_p ) (cm³/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.62</td>
<td>1.86</td>
<td>0.08</td>
</tr>
<tr>
<td>18</td>
<td>1.42</td>
<td>2.01</td>
<td>0.21</td>
</tr>
<tr>
<td>36</td>
<td>1.22</td>
<td>2.18</td>
<td>0.36</td>
</tr>
<tr>
<td>48</td>
<td>1.13</td>
<td>2.23</td>
<td>0.44</td>
</tr>
<tr>
<td>59</td>
<td>1.01</td>
<td>2.14</td>
<td>0.52</td>
</tr>
<tr>
<td>72</td>
<td>0.90</td>
<td>2.10</td>
<td>0.64</td>
</tr>
<tr>
<td>75</td>
<td>0.79</td>
<td>2.14</td>
<td>0.80</td>
</tr>
<tr>
<td>97</td>
<td>0.63</td>
<td>2.08</td>
<td>1.11</td>
</tr>
</tbody>
</table>

Adsorption isotherms can be obtained on two fully automated sorptomatic instruments (Carlo Erba). These isotherms give a graph of the amount of gas adsorbed per unit wt (mmol/g) vs relative pressure \( (P/P_o) \) at a particular temperature. All isotherm graphs cover the complete range of relative pressures \( (P/P_o) \) except CO₂ adsorption isotherms where the maximum relative pressure reached is only 0.035.
continuously with increasing burn off due to the creation of porosity in carbons. With respect to d_{in}, the anthracite has a relatively low density that increases as the burn off increases from anthracite G_{10} to G_{48}.

According to mercury porosimetry results, G_{10} has no transition pores and as the burn off increases, there is a development of mesoporosity especially for the highest degrees of burn off, i.e. for 97% burn off, d_{in} is only 0.63 g cm$^{-3}$.

3.1.3 Surface Area Measurement through Surface Energy Data

John$^{79}$ used surface energy method to determine the surface area of activated carbons using pure and binary mixture of gases and to prove that surface energy of a monolayer of binary mixture is equal to the sum of the products of the surface energy of each component multiplied by its mole fraction.

According to this study, when a gas is adsorbed at the surface, the excess free energy per unit area, $\gamma$ (surface energy) is given by:

$$\gamma = 2.303 \frac{RT \log (V_V/V_L)}{4SN}$$

where $V_V$ and $V_L$ are the molar volumes of absorbate in vapour and liquid states respectively; $S$, the area of a molecule of an adsorbate; and $N$, the Avogadro's number. Surface energy can be calculated from inverse gas chromatography also.

John and Aggarwal$^{94}$ showed that when $V_m$ of a pure gas is adsorbed to form a monolayer on 1 g of adsorbent, the specific surface area, $S_w$, could be given by:

$$S_w = \frac{2.303 RT \log (V_V/V_L)}{4\gamma V}$$

where $V$ is the molar volume of the gas at STP; and $R$, the gas constant (Table 5).

When a binary mixture is adsorbed, the specific surface area is given by:

$$S_w = \frac{2.303 RT \log (V_{m1}/V_{m2})}{4\gamma V}$$

where $V_{m12}$ is the volume (at STP) of the mixture adsorbed; $V$ is same for pure and mixture of gases; and $V_{m1}$, $V_{m2}$ and $\gamma_{m1}$, the molar volume of vapour mixture, molar volume of liquid mixture and surface energy of liquid mixture at temperature $T$ respectively.

3.1.4 Photoconductivity$^{95}$

This provides a method to measure surface area. As the surface area increases, the photoconductivity also increases. The increase in surface area due to more micropores creates more disorder, leading to an increase in the photocurrent. The measurement of the photocurrent of a single fibre was carried out to get an indication of its surface area. Laser beam irradiates the single ACF contained in a circular disc with two electrical contacts. About 10$^{14}$ photons are incident on the sample$^{95}$ to get the photoconductivity. To get an idea of photoconductivity, one should plot photoconductivity and temperature for fibres of various surface areas and then compare the photoconductivity values at a given temperature. It has been observed that photoconductivity increases with decrease in temperature due to decrease in the carrier recombination rate$^{95}$.

3.1.5 Electrical Conductivity$^{96,97}$

Temperature dependence of electrical conductivity ($\sigma$) of an ACF$^{96}$ has been described by 2D variable range hopping formula:

$$\sigma = \sigma_0 \exp \left[ \frac{-(T/T_0)^{3/2}}{2} \right]$$

When plots of conductivity vs temperature were drawn, there were different plots for the fibres having different surface areas. The functional form of conductivity did not change with specific surface area (SSA) but the magnitude of conductivity increased. This is because the greater the surface area, the greater will be the disorder and hence greater conductivity$^{97}$.

3.1.6 X-ray Diffraction

X-ray diffraction measurements on activated carbon fibres$^{96}$ show a broad diffraction line at the position of 002 line in graphite. This shows that ACF are graphite material (from the measured 002 line in graphite).

<p>| Table 5—Monolayer capacity and surface area by surface energy method$^{79}$ |
|-----------------|-----------------|-----------------|-----------------|</p>
<table>
<thead>
<tr>
<th>Adsorbate</th>
<th>Adsorbent</th>
<th>Monolayer capacity, cm$^3$ g$^{-1}$</th>
<th>Surface area m$^2$ g$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N_2$</td>
<td>Activatedarbon</td>
<td>32.4</td>
<td>165.1</td>
</tr>
<tr>
<td>$O_2$</td>
<td>Activatedarbon</td>
<td>45.2</td>
<td>159.6</td>
</tr>
<tr>
<td>$Ar$</td>
<td>Activatedarbon</td>
<td>41.4</td>
<td>153.2</td>
</tr>
</tbody>
</table>
d-spacing) with a high degree of disorder (from line width). From line width, one can get a good idea of Lc-e axis crystallite size corresponding to three graphene layers.

This is consistent with the results obtained from

\[
d = \frac{2}{(SSA)\rho}
\]

where \(d\) is the platelet thickness; \(\rho\), the density; and SSA, the specific surface area. This estimate is consistent with a simple model that relates the large surface area to the formation of pores around platelets of the stacked graphene layers in ACF. Thus, if \(d\) is equal to a monolayer \((d=3.4\AA)\), a crude estimate of SSA can be made using this formula.

3.2 Active Site and Functional Group Determination

Various methods have been adopted to measure the concentration and the distribution of functional groups present on the surface of activated carbon fibres.

Yoshida et al.58 used the electric double layer properties of ACF to determine the concentration of surface acidic functional groups \((C_p)\). A configuration of ACF/electrolyte solution/ACF was selected where a mixture of propylene carbonate with tetraethylammonium tetrafluoroborate was used as an electrolytic solution. ACF cloths were coated with a plasma sprayed aluminum layer60 and punched into small discs. Two ACF disks thus prepared were housed in a metal case with fibres. ACF cloths were dipped in 25ml of 0.2 N aqueous NaOH solution, shaken for 20 h at room temperature and their Na' ions that remained in the solution were titrated with 0.2 N aqueous HCl. The amount of Na' ions chemically adsorbed on the surface of ACF was reasonably assumed to be the concentration of acidic functional groups on the ACF surface.

4 Applications of Activated Carbon Fibres

Activated carbon fibres, due to their superb sorption qualities, have found widespread applications in various fields as discussed below:

4.1 Purification of Air and Other Gaseous Mixtures

Toxic gaseous wastes are released from the industries daily. One of the strict requirements of new industrial legislations is the low level of pollutants. Hence, there arises the need for air purification systems. In this context, activated carbon fibre filters are being used extensively.

Activated carbon fibres are used for removal of nitrogen oxide fumes. Activated carbon fibres demonstrate good sorption capacity, both at low temperatures (where the process of physical sorption is temperature dependent) and at elevated temperatures as shown below:

<table>
<thead>
<tr>
<th>Temp (K)</th>
<th>293 313 353 393</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sorption Capacity</td>
<td>151 127 68 39</td>
</tr>
</tbody>
</table>

Therefore, though the temperature of chimney smoke is usually well above that of ambient temperature, no smoke cooling is therefore required before purification.

In a recent study by Mochida et al.5, conversion of nitrous oxide into non-toxic nitrogen is carried out by passing it through stacked activated carbon fibres after mixing with ammonia. The stack of activated carbon fibres is pretreated with 12N sulphuric acid and annealed at 350°C for 4 h in nitrogen. The reduction of NOₓ at low concentrations is strongly inhibited by humidity, the H₂O adsorbed prevents adsorption.

Introduction of iron compounds into activated carbon fibres also increases the sorption capacity of the materials towards nitrogen oxides (NOₓ). In a study by Wang et al.6, ACF was treated with FeOOH and Fe₂O₃ which enhanced the absorptivity of ACF. In particular, the dispersion of Cu or Ti-doped FeOOH fine particles is efficient for improvement of NOₓ adsorptivity.

Activated carbon filters pretreated with iron, zinc and magnesium become effective adsorbents of ammonia. In comparison to granulated activated carbons, the ammonia adsorption capacity is almost twice in case of activated carbon fibres.
Activated carbon fibres can be used on an industrial scale to purify air from sulfurated methane. Sulfurated methane adsorption rate on ACF (due to its low density and diameter of around 6-7 μm) is 2-3 times higher than that on the granulated carbons. The mass-transfer coefficients are also 3-4 times higher compared to that for granulated carbon.1

Activated carbon fibre filter with a specific area of 500-2000 m²/g has been used to adsorb sulphur dioxide from nitrogen-based gas mixture containing SO₂, O₂ and water vapour.2

In another study by Yang et al.3, polyacrylonitrile-based hollow active carbon fibres were used for catalytic oxidation of SO₂ to sulphuric acid. ACF filters are also used for adsorption of carbon dioxide. Some activated fibres demonstrate a high adsorption capacity for CO₂ with degree of burn off over 50 wt%. Their sorption capacity is 18 times higher than that of granulated carbons, with satisfactory reproducibility of sorption effects even after carbon fibre regeneration. Therefore, it becomes possible to use these sorbents through many cycles to adsorb CO₂. To regenerate activated carbon fibres, it is necessary to heat them at 170°C for 15 min.4

It has been demonstrated that fabric from activated carbon fibres effectively adsorbs allyl methyl sulphide and benzene of 100 ppm concentration. Benzene vapour sorption rate on ACF is 2-3 times higher than that on granulated ones.5

The ability of carbon filter materials to adsorb various types of organic compounds makes it possible to use them as deodorizers for air conditioning of production plants.6-8 Activated carbon fibres have found widespread applications in the recovery of some solvent vapours. Recovery of such vapours is important in removing toxic substances from air, as a safety precaution in the production to keep the vapour concentration below that of the explosive hazard threshold limit.9

The use of carbon fibre adsorbents as filters in automobile air conditioners and in various respirators has been documented. They can also be used for the manufacture of protective clothing to prevent harm to the defence personnel from poisonous gases like Mustard gas and Nerve gas which are used during the chemical warfare. For professional activities concerned with workers exposed to polluted air (e.g., the work of excavator operating in the mining industry) use of ACF may be satisfactory.10

Moreover, ACF are used as stationary phase in the gas chromatography to separate individual components from a mixture of N₂, H₂, O₂, CO₂ and butane.

4.2 Purification of Water and Solutions
Activated carbon fibres have assumed great importance in the purification of industrially polluted water or house-hold water. Activated fibres score over granulated carbons as the granulated ones can be used only at a high concentration of organic pollutants. ACFs are most effective in removing toxic organic chlorine compounds. In a study by Shimazaki and Ono,17 ACFs having specific area of 800-2500 m²/g were used to remove chlorine from water. A super micropore volume with an effective pore diameter below 0.3 nm corresponds to an adsorption capacity towards low molecular weight compounds while the mesopore volume corresponds to a capacity towards high molecular weight compounds.

To purify deionized water, use of filters with 50% activated carbon fibres with a pore size of 3-4 μm and 15-38% burn off has been suggested.18 Upon fluorination, it becomes possible to apply these filters to separate water and organic solvents. Further impregnating the surface with silver makes it possible to sterilize drinking water and prolong its period of storage.

Activated carbon fibres may be successfully used instead of powdered carbon in the food industry, e.g., to correctly adjust the colour and organoleptic properties of wines. Decolourization of Japanese Sake (an alcoholic drink) was done by using PAN-based ACF by Shimazaki and Akao.19

4.3 Use of ACF in Chemical Reaction Catalysis
Activated carbon fibres are recognized as efficient catalysts or supports for the catalytically active phase in heterogeneous catalysis. The use of carbon materials as supports for the active phase is favoured because of their developed specific surface area, sufficient strength, heat and chemical stability and their resistance towards active metal phase.
The attractive features of carbon fibres useful in catalysis are their fibre form and specific surface structure. Moreover, the fibre form ensures low hydraulic resistance and due to small diameter of the fibres, the whole body of the material belongs to surface layers leading to higher flow rates.

Copper-carbon fibres produced by carbonization of copper 6-carboxyl cellulose salt demonstrate high catalytic activity towards dehydration of cyclohexanol and isopropanol. The efficiency of this catalyst is due to the presence of finely dispersed reduced copper in the structure of the elemental carbon which ensures large contact surface area with a comparatively low copper content in the sample.

4.4 Medical Applications

ACFs have adequate sorption capacity and selectivity and adsorb toxic compounds. Such fibres do not destroy blood cells and they do not liberate toxic substance or any other contacting liquid into the body. In addition, they are mechanically stable, easy to sterilize and stable under sterilization conditions. Hence, these fibres are more compatible with the human body than the granulated carbons. Thrombocyte count was two times low in ACF as compared to granulated carbons.

Endo- or exo-genic intoxication treatments are the encouraging examples of the uses of activated carbon fibre materials in the treatment of some liver ailments, pancreatitis and alcohol syndrome withdraw. Activated carbon fibres have potential in the elimination of cholesterol and lipoproteins. Activated carbon fibres with surface carboxyl groups introduced are more effective as specific sorbents towards some low and very low density lipoproteins that promote arteriosclerosis. Some carbon fibre immobilized enzymes like urease can be employed to remove urea in some renal cases.

Activated carbon fibres can be effectively used to improve upon the characteristics of stored blood. It has been demonstrated that blood filtration through fibre sorbents improves blood functional characteristics with the removal of certain metabolites and an admissible lowering of blood cell count.

Many sorbents have already found their applications in clinical use. For example, some synthetic ion exchange resins have been used to control the acidity of gastric juices, for selective bilirubin removal from blood, and for purification and concentration of biologically active substances.

ACF carrying Ag and iodine have been used as antibacterial materials.

4.5 Miscellaneous Uses

Some filters called K-filters were manufactured for panelling apartment walls to prevent water condensation. The material adsorbs not less than 30% of the moisture content at 80% RH. Such panels prevent mildew developments on walls in a humid climate and create more comfortable living conditions.

Fabrics and mats manufactured from activated carbon fibres having high adsorption capacity and sorption rates have been suggested for use in protecting sensitive elements of instruments operating in corrosive media. The technology has been developed for manufacturing carbon fibre based paper for packaging vegetables and fruits which prolongs their shelf life.

Use of ACF as a humidity sensor has been suggested for humidity sensing. Micropores of volume ≥0.5 cm³/g and diameter ≤20Å account for 85% of total pore volume of ACF used as a humidity sensor. Moisture content related to electrical resistance change of carbon fibres has been measured.

Activated carbon fibres have potential in the production of noble metals in view of the fact that they have high adsorption capacity, along with the possibility of increasing their selectivity toward noble metals through introduction of heteroatoms.

The properties of electrochemical metal coating depend, in many ways, on the impurities present in the electrolyte. The use of activated carbons makes it possible to considerably improve upon the quality of coating in a speedy and simple purification process.

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