Adsorbent Carbon Fabrics: New Generation Armour for Toxic Chemicals

K. Gurudatt, V.S. Tripathi & A.K. Sen


ABSTRACT

Activated carbon in the form of a regular fabric obtained using viscose rayon precursor is a new generation adsorbent material having superior sorptional properties and is finding varied defence applications. Carbonisation and activation mechanisms and properties and applications of adsorbent carbon fibres, made from viscose rayon precursor are reviewed in this paper.

1. INTRODUCTION

Any scheme of defence against chemical warfare (CW) agents invariably has activated carbon at its centre. Personal protection devices, viz., antigas canisters, suits, gloves and socks, collective shelters, air supply system and nuclear biological & chemical (NBC) water treatment plants, etc. incorporate activated carbon in granular or powder form. The technology of protection against CW agents has rightly been termed as 'black art' by Hall and Sing due to large scale use of carbon in different forms. It is therefore not surprising that research on development of activated carbon having superior adsorption potential has gone on unabated since the first application of carbon in canisters in the first World War. Activated carbons derived from coconut shell, wood and coal are well-known and so are the advantages and disadvantages associated with them. Activated carbon derived by carbonisation and activation of viscose rayon fabric (Figs 1 and 2) is the latest addition to the above list. The full potential of this adsorbent carbon fabric has not yet been realised, but this form of carbon has begun to replace traditional carbon in devices-like facelet masks. In this review, an attempt has been made to
summarise the information on processes and mechanisms of carbonisation and activation of viscose rayon precursor and uses of adsorbent carbon fabrics.

Among the new applications of activated carbon fabrics, protective clothing sector is a prominent one. A majority of the protective clothings even today is made by coating activated carbon on to a textile substrate. This invariably results in a stiff, heavy, thick fabric with significant loss of air permeability, resulting in physiological discomfort to the wearer. The new textile made from the activated carbon is light, flexible and highly permeable, providing maximum comfort to the wearer. Many polymeric materials in textile forms have been used for this purpose. These include viscose, acetate, phenol formaldehyde, phenolic textiles and Saran. Addition of activated carbon into polymer dopes before spinning has also been studied. Sheath core composite fibres with ceramic core and activated carbon sheath have also been produced.

The main advantages of activated carbon in textile form over other forms are: (i) favourable combination of filtration and sorption properties, (ii) higher kinetic parameters of sorption resulting in faster sorption rates, (iii) low-layer resistance resulting in faster mass transfer, (iv) high homogeneity of activation due to small fibre diameter, and (v) ease of introducing specific adsorption.

Invariably, these activated carbon fabrics have been used as inner or middle layer of a multilayer fabric for protective clothing. Reinforcements help improve strength and abrasion resistance.

2. CHARACTERISTICS OF ACTIVATED CARBONS

2.1 Sorptional Properties

The adsorption capacity of activated carbon is characterised in terms of surface area and pore size distribution. Different mechanisms of sorption are applicable to different pore types. The mechanisms have been summarised by Ernolenko, et al. Layer-wise adsorption and capillary condensation occur in mesopores (width 2-100 nm) and macropores (width>100 nm). An altogether different mechanism is applicable in case of ultramicropores (width 0.3-0.7 nm) and supermicropores (width 0.7-2 nm). Volume filling of these pores is driven by a high adsorption potential due to the field of dispersion forces. Marsh, et al. recommended the use of equivalent surface area to characterise active carbon, as in their opinion, the true surface area of a solid does not exist.

The evaluation of porosity and surface area of adsorbants are done by determining and interpreting adsorption isotherms. The adsorption data are interpreted using theoretical equations, such as those of Langmuir, BET, Dubinin-Radushkevich and Dubinin-Astakhov. Scattered references are available for not so well-known isotherm analysis theories. Small angle X-ray scattering, pre-adsorption of nonane and desorption kinetics have also been used for characterising active carbons.

2.2 Structure of Activated Carbon Fibres

The most accepted structural model of a carbon fibre, is the turbostratic arrangement of basal planes of sp² hybridized planar hexagonal lattice, shown in Fig. 3(d). The turbostratic structure is different from the graphitic structure shown in Fig. 3(b). The hexagonal aromatic planes of carbon in them are placed at random orientation to each other. This results in somewhat inferior tensile properties of these fibres. The structure of activated carbon fibres, where superior sorptional properties take precedence over tensile properties is essentially turbostratic. The basal planes are formed through polymerisation of the four carbon residue resulting from the pyrolysis reactions.
Pores are developed during carbonisation itself, but the tarry substances evolved are redeposited on these pores, lowering the adsorption capacities. The carbonized fibre is activated to open up these pores. Three approaches have been adopted to carry out activation. These are: (i) chemical activation: thermal treatment of partially carbonised fibre after incorporating chemicals in them, (ii) vapour/gas activation: high temperature oxidation with suitable gases, and (iii) mixed activation: gas activation of the pre-treated fibre.

In commercial techniques for activated carbon fibre production, the third approach is adopted.

3.2 Carbonisation

3.2.1 Process of Carbonisation

The process of carbonisation has been divided into four steps.23

(i) Removal of physically bound water (90-150 °C),

(ii) Dehydration (150-240 °C) resulting in the formation of fragments with carbonyl groups and C=C bonds,

(iii) Thermal bond dissociation (240-400 °C) that may yield levoglucosan or dehydrocellulose, and

(iv) Aromatisation (> 400 °C).

In Stage (i) of carbonisation, evaporation of water molecules occurs, which are bound to secondary hydroxyl groups, as well as those attached to other water molecules.37 The water molecules bound to the primary hydroxyl groups are held strongly and evolve only at 230-245 °C.39,40 Complete removal of water is necessary, because excessive formation of volatiles would be favoured in its presence, resulting in higher decomposition and mass loss rate.41 Cellulose pyrolysis in Stages I and II has been investigated extensively using dynamic TGA, gas chromatography-mass spectra (GC-MS), in vacuum, differential thermal analysis and
Figure 4. Mechanism for conversion of cellulose to carbon (Ref. 51).
GURUDATT, et al: ADSORBENT CARBON FABRICS

Dehydration of cellulose is shown to proceed both intramolecular and intermolecular. The latter produces functional groups capable of participating in condensation reactions, while the former enhances cross linking and brings about rigidity in the carbon fibre.

Cellulose pyrolysis in Stage (iii) involves the competitive reactions of depolymerisation and dehydration. Further dehydration of the partially dehydrated elementary chains would result in dehydrocellulose. On the other hand, cleavage of glycosidic bonds during depolymerisation results in levoglucosan. Levoglucosan undergoes partial evaporation and the remaining take part in the formation of an aromatic structure. The depolymerisation process not only reduces carbon yield, but also results in structural defects, which reduce strength of the fibres. Further thermal degradation of dehydrocellulose and other carbonaceous intermediates results in the formation of four carbon residues (Fig. 4).

Cellulose pyrolysis above 400 °C in stage (iv) results in transformation of the four carbon residues to a turbostratic structure. The strength begins to increase due to the formation of condensed aromatic networks. Appearance of new peaks in wide angle X-ray diffraction pattern at \(2\theta = 12^\circ\) and \(22^\circ\) confirms turbostratic structure formation.

Two alternative schemes for polymerisation of the assumed four carbon residues, as proposed by Bacon, et al, are shown in Fig. 5.
3.2.2 Factors Influencing the Carbonisation of Cellulose

Carbonisation of cellulose depends on nature of the raw material, the process conditions, and material, process modifications. The structure of the starting material as well as its degree of order and orientation influence char yield, strength retention, rate of reaction, etc. during carbonisation.

Among the process conditions in carbonisation, time, temperature and heating rate of carbonisation are very important. Brunner, et al. studied the effect of heating rate on char yield, micropore volume and surface area (Fig. 6). Heating rate above the optimum favours depolymerisation over dehydration and introduces inhomogeneity in the fibres. Application of optimum tension during carbonisation is essential. This aligns the molecules along the fibre axis, resulting in better tensile properties. Stretching below the optimum level results in lower strength and modulus. If it exceeds the optimum value, defects appear in the final fibre. Heating rate at the carbonisation stage influences the development of molecular sieve properties in the fibres. Higher yields and strength properties at higher heating rates have been obtained using active carbonisation media or by using special additives.

3.3 Activation

The property of specific adsorption by carbon materials was discovered by Lovits in 1785. The properties of activated carbon fibres depend on the method of activation, conditions of activation like temperature, time and heating rate and structure of carbonised fibre.

The activation process depends either on diffusion of the activator or chemical interaction of the activator, depending on the method of activation used. When the activation is done by chemical interaction, it proceeds predominantly in crystalline regions, resulting in micro- and meso-pores. On the other hand if diffusion is the determining factor, it would proceed in the amorphous region, resulting in macropore formation.

3.3.1 Effect of Additives on Activation

Commercially, activation is done by incorporating chemical agents into the fibres, which differ widely in their mode of action and
One of the major requirements of activated carbon fibres is high strength. Elastic fibres with tensile strengths of 40 MPa (otherwise only 10 MPa for pure carbon fibre) have been produced with the introduction of phosphorus and nitrogen in the structure of precursor. Maggs, et al have shown the effects of various metal chlorides on the strength of activated carbon fibres (Table 1). Incorporation of specific additives can also induce special sorptional properties, such as selective adsorption and molecular sieve effects, in the fibres. Studies have also been carried out to ascertain the effects of additives at very high temperatures.

Table 1. Properties of carbon materials produced by pyrolysis of hydrated cellulose pretreated with 0.5 mol/l solutions of chlorides (HTT 850°C)

| Cation introduced | Yield by mass (%) | Yield by length (%) | Breaking strength (g cm⁻¹) | Flexural rigidity (mg.cm)
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<tr>
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<tbody>
<tr>
<td>None</td>
<td>15.0</td>
<td>66.6</td>
<td>740</td>
<td>550</td>
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<tr>
<td>Na</td>
<td>21.8</td>
<td>74.5</td>
<td>480</td>
<td>2150</td>
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<tr>
<td>K</td>
<td>23.6</td>
<td>69.6</td>
<td>240</td>
<td>4620</td>
</tr>
<tr>
<td>Cd</td>
<td>27.0</td>
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<td>27.6</td>
<td>70.7</td>
<td>1380</td>
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<tr>
<td>Cu</td>
<td>28.0</td>
<td>73.4</td>
<td>2960</td>
<td>215</td>
</tr>
<tr>
<td>NH₄</td>
<td>28.4</td>
<td>72.8</td>
<td>2640</td>
<td>345</td>
</tr>
<tr>
<td>Zn</td>
<td>32.3</td>
<td>78.6</td>
<td>520</td>
<td>3170</td>
</tr>
<tr>
<td>Co</td>
<td>33.7</td>
<td>78.7</td>
<td>470</td>
<td>160</td>
</tr>
<tr>
<td>Ca</td>
<td>35.6</td>
<td>78.2</td>
<td>220</td>
<td>8800</td>
</tr>
</tbody>
</table>

The optimum physical characteristics are obtained at certain specific concentration levels of the additive (Ref.6).

4. APPLICATIONS OF ACTIVATED CARBON FIBRES

Applications of the activated carbon fibres are very much different from those of carbon and graphite fibres. Some of the interesting applications are:

4.1 Protective Clothing

The fibre forms of activated carbon are destined to replace the coated textiles in this sector. Charcoal cloth in laminates with high performance...
fabrics are already in use in NBC items like canisters, hoods, tents, gloves and casualty bags. However, some deficiencies like poor abrasion resistance have to be overcome.

4.2 Separation of Gas Mixtures

Incorporation of additives like Al, Zn and La leads to the development of pores < 5 Å in activated carbon fibres. These fibres, known as carbon molecular sieves, are part of an ever-expanding field of molecular sieves. These materials with highly selective sorptional properties could be used for separating gas mixtures using pressure swing adsorption.

4.3 Chemical Catalysis

Properties like specific surface area, homogeneous sorptional capacity, combined with good thermal and chemical stability make activated carbon fibres effective as catalysts or gives catalytic support in catalysis.

4.4 Medical Applications

Activated carbons are used for adsorbing toxic compounds from blood because of their high rate of sorption and better compatibility with blood. Activated carbon fibres have been used in the treatment of some liver ailments, pancreatitis, alcohol withdrawal syndrome, elimination of cholesterol, lipo proteins, etc.

4.5 Gas & Water Purification

Active carbon fibres are used as filters to adsorb toxic gases like N₂O, NH₃, allyl methyl sulphide, etc. They have also been used as deodorisers for air conditioning, for purification and deodorisation of water. Activated carbon fabrics impregnated with organic and inorganic compounds can be used for adsorption of many contaminants (Table 2).

5. CONCLUSION

It may be inferred that adsorbent carbon fibre has many advantages over activated carbon obtained from natural resources. However, its high cost and fragile nature stand in the way of its large scale acceptance. In specialised applications where a rigid control over surface properties is required, the carbon obtained using well characterised polymeric precursor is the material of choice.

ACKNOWLEDGEMENT

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REFERENCES


Table 2. Impregnants for Incorporation into Activated Carbon Fibres for Adsorption of Specific Toxics Contaminants

<table>
<thead>
<tr>
<th>Contaminant</th>
<th>Impregnant</th>
<th>Mechanism of action</th>
</tr>
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<tbody>
<tr>
<td>Organic vapours</td>
<td>Nil</td>
<td>Physical adsorption</td>
</tr>
<tr>
<td>Chlorine</td>
<td>Sodamide/amines</td>
<td>Adsorption and chemical reaction</td>
</tr>
<tr>
<td>Arsine</td>
<td>Silver nitrate</td>
<td>Adsorption and chemical reaction</td>
</tr>
<tr>
<td>Phosphine</td>
<td>Copper salts</td>
<td>Adsorption and chemical reaction</td>
</tr>
<tr>
<td>Radioactive iodine</td>
<td>Pot. hydroxide</td>
<td>Ion exchange</td>
</tr>
<tr>
<td>Hydrogen cyanide</td>
<td>Copper salts</td>
<td>Adsorption and chemical reaction</td>
</tr>
<tr>
<td>Cynogen chloride</td>
<td>Copper and chromium</td>
<td>Catalytic decomposition</td>
</tr>
<tr>
<td>Phosgene</td>
<td>Copper salts</td>
<td>Adsorption and chemical reaction</td>
</tr>
</tbody>
</table>


GURUDATT, et al : ADSORBENT CARBON FABRICS


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