Preparation and Characterization of Activated Carbon Fibre/Filament (ACF) from Indigenous Cellulosic Precursors

T. H. USMANI
Industrial Chemical Research Centre
PCSIR Laboratories Complex, Karachi-75280, Pakistan

(Received 24th September, 2001, revised 4th April, 2002)

Summary Activated carbon fibre / filament (ACF) has been prepared from different cellulosic precursors by chemical activation method, using zinc chloride and phosphoric acid as activating agents. It has been found that adsorptivity capacity of zinc chloride activated ACF products was better than phosphoric acid activated ones. It has also been inferred that all ACF products have microporous structure having absence of meso and macropores. An ACF product of reasonable activity and having good strength characteristics may be prepared by zinc chloride activation of bleached cotton cloth.

Introduction

There is a long history in the use of adsorbent properties of activated carbon as a purification and separation media. Until the mid of 1980, much of the R&D work done worldwide in the field of activated carbons, was in that of powdered and granular activated carbons [1]. These authors have also done work on the development of technology for the preparation and characterization of powdered (PAC)and granular (GAC) activated carbons from different cellulosic and mineral based raw materials by the methods of chemical and physical activation [2-4]. During the last fifteen to twenty years, trend has diverted, and a new form fibrous activated carbon or active carbon filament (ACF) has been developed and industrialized. In addition to their outstanding physico- mechanical properties and high chemical resistance, the adsorption properties of active carbon fibre materials make then superior to PAC and GAC in a number of specific applications in industry, medicine and protection fields [5]. Most of the work reported in scientific literature in this particular area is covered by patents. Hirai produced ACF from acrylic fibres by their air oxidation and physical activation [6,7]. Further, activated carbon cloth was produced by Norman from viscose cloth by pretreatment with a Lewis acid and subsequent activation with carbon dioxide [8]. Ishizaki *et al.*, produced short fibrous activated carbon from regenerated cellulose fibres [9].

ACF are nowadays prepared mostly from organic precursors. These have unique characteristics and offer high adsorption performances as compared to PAC and GAC. At present, different grades / qualities of ACF products are successfully being used in solvent recovery, different gas phase adsorption requirements and also used in producing protective clothes, most commonly used in chemicals warfare. At a later stage, the use of A C F was also extended to different liquid/water purification systems and also in manufacture of electric double layer capacitor [10-12].

The present studies have been aimed to exploit certain indigenous cellulosic precursors like bleached cotton cloth, bleached and unbleached drill cloth, jute fabric (gunny bag), cotton roll etc., for their potentiality of preparing filament / fibrous activated carbon. The mode of activation adopted in these investigations is that of chemical activation. The activity of different finished products obtained was evaluated both in liquid as well as gas phase systems, and were also examined for their strength characteristics.

Results and Discussion

Different indigenous cellulosic precursors, like bleached cotton cloth, cotton roll, jute fabric, bleached and unbleached (Khaki) drill clothes were being explored as possible precursors, for the preparation of fibrous/filament activated carbon by the process of chemical activation. Zinc chloride and phosphoric acid, which are the most common activating agents used for cellulosic raw materials, were being used in their chemical activation.

Table 1 shows various physical and chemical properties of ACF samples, prepared from different indigenous raw materials, by their chemical activation with zinc chloride and phosphoric acid.

Table-1:Effect of Chemical Activation with Different Activating Agents on Various Physical and Chemical Characteristics of Activated Carbon Filament Samples Prepared from Indigenous Cellulosic Precursors

PRECURSOR	*ACTIVATING AGENT	SAMPLE CODE	YIELD (%)	ASH CONTENT % Blank	Sample	BULK DENSITY (gm/c c)
Bleached Cotton Cloth	Z C	F_1	33.0	06	1.1	0.5072
Bleached Cotton Cloth	P A	F_2	31.6		6.9	0.6465
Jute Gunny Bag Cloth	Z C	F_3	38.5	3.78	4.3	0.4290
Jute Gunny Bag Cloth	P A	F_4	35.5		14.0	0.6301
Cotton Roll	Z C	F_5	51.8	1.46	2.2	0.3203
Cotton Roll	P A	F_6	37.2		3.7	0.5014
Khaki Drill Cloth	Z C	F_7	50.2	1.80	7.5	0.5458
Khaki Drill Cloth	P A	F_8	34.7		4.7	0.4955
Bleached Drill Cloth	Z C	F_9	44.6	0.48	3.3	0.4987
Bleached Drill Cloth	P A	F_{10}	37.7		1.6	0.5162

* ZC = Zinc Chloride, PA = Phosphoric Acid

Table-2: Effect of Chemical Activation with Different Activating Agents on Various Adsorptive Properties of Activated Carbon Filament Samples Prepared from Indigenous Cellulosic Precursors

PRECURSOR	*ACTIVATING AGENT	SAMPLE CODE	IODINE NO. (mg/g)	METHYLENE BLUE NO. (mg/g)	CCl_4 ADSORPTION (%)	CCl_4 RETENTIVITY (%)
Bleached Cotton Cloth	Z C	F_1	868	60	58.7	45.0
Bleached Cotton Cloth	P A	F_2	354	8	5.0	NIL
Jute Gunny Bag Cloth	Z C	F_3	800	60	40.1	22.0
Jute Gunny Bag Cloth	P A	F_4	153	2	3.7	NIL
Cotton Roll	Z C	F_5	1245	74	84.6	64.8
Cotton Roll	P A	F_6	633	40	42.8	40.7
Khaki Drill Cloth	Z C	F_7	122	2	2.4	NIL
Khaki Drill Cloth	P A	F_8	500	12	3.1	NIL
Bleached Drill Cloth	Z C	F_9	289	4	9.2	3.5
Bleached Drill Cloth	P A	F_{10}	470	28	3.2	NIL

* ZC = Zinc Chloride, PA = Phosphoric Acid

A review of this table shows that, zinc chloride activated samples in all the cases, had a higher yield, lower bulk density and ash content, as compared to phosphoric acid activated ones. Highest yield of 51.8%, with a lower bulk of 0.3203 gm/c.c, were obtained in ACF sample 'F_5'-- zinc chloride activated sample of cotton roll. However, lowest ash content was obtained in ACF sample prepared by zinc chloride activation of bleached cotton cloth 'F_1'. Moreover ash contents of the untreated precursor samples show the same pattern as that of their respective ACF samples. Table 2 presents different adsorptive characteristics of ACF samples, prepared from different indigenous precursors against various adsorbates, in liquid as well as vapour phase.

It may be seen here, that highest activity in respect of their iodine No., methylene blue No. and carbon tetrachloride adsorption/retention was obtained in ACF sample 'F_5', prepared by zinc chloride activation of cotton roll, while sample 'F_1', prepared from bleached cotton cloth, with the same mode of activation, was found to be second in order. In case of phosphoric acid activation, although sample 'F_6', prepared from cotton roll had reasonable activity, but not in any way comparable to zinc chloride activated samples in both the phases. It may also be seen in Table-2, that all ACF samples except 'F_1' and 'F_5', had quite low methylene blue Nos. It corresponds with the observations of several earlier workers, that ACF has a monodistibuted microporous structure, without meso and macropores [13,14].

Table – 3 presents the quantitative intake of different inorganic chemicals, used as activating agents, by different specimens after the process of chemical impregnation.

A review of Table-3 clearly shows that this intake is comparatively more in zinc chloride activated samples (F_1, F_3, F_5, F_7 & F_9), as compared to phosphoric acid activated ones. Further it is also observed from a comparative study of Table – 2 and 3, that this intake of impregnating chemicals is rather directly proportional to the resultant microporous adsorptive activity being established in different finished products obtained. This pattern is followed by both the activating agents pursued in this study and is quite evident in Figs. 1 & 2. It is therefore inferred, that quantitative amount of the activating

Table-3: Data on Intake of Activating Chemical by Samples Before Chemical Activation

PRECURSOR	ACTIVATING AGENT	SAMPLE CODE	INTAKE OF ACTIVATING AGENT (g/g)
Bleached Cotton Cloth	Z C	F_1	0.35
Bleached Cotton Cloth	P A	F_2	0.11
Jute Gunny Bag Cloth	Z C	F_3	0.32
Jute Gunny Bag Cloth	P A	F_4	0.04
Cotton Roll	Z C	F_5	2.48
Cotton Roll	P A	F_6	0.18
Khaki Drill Cloth	Z C	F_7	0.14
Khaki Drill Cloth	P A	F_8	0.16
Bleached Drill Cloth	Z C	F_9	0.19
Bleached Drill Cloth	P A	F_{10}	0.12

* ZC = Zinc Chloride, PA = Phosphoric Acid

Table-4: Effect of Chemical Activation with Different Activating Agents on Strength Characteristics of Activated Carbon Filament Samples Prepared from Various Indigenous Cellulosic Precursors

PRECURSOR	ACTIVATING AGENT	SAMPLE CODE	TENSILE STRENGTH (kg / cm²)		ELONGATION (%)	
			Blank	Sample	Blank	Sample
Bleached Cotton Cloth	Z C	F_1	26.4	22.8	19.0	18.6
Bleached Cotton Cloth	P A	F_2		14.2		11.0
Jute Gunny Bag Cloth	Z C	F_3	16.7	17.5	15.7	12.2
Jute Gunny Bag Cloth	P A	F_4		16.2		10.0
Cotton Roll	Z C	F_5	9.6	7.8	5.3	4.1
Cotton Roll	P A	F_6		7.1		3.2
Khaki Drill Cloth	Z C	F_7	23.5	18.2	16.8	14.1
Khaki Drill Cloth	P A	F_8		20.7		16.0
Bleached Drill Cloth	Z C	F_9	22.8	19.1	17.2	16.7
Bleached Drill Cloth	P A	F_{10}		17.8		15.3

* ZC = Zinc Chloride, PA = Phosphoric Acid

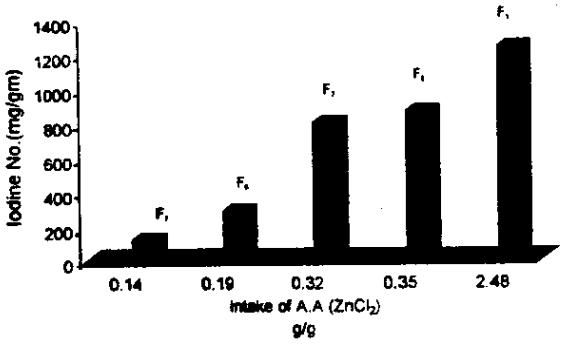

Fig. 1: Effect of intake of A.A.($ZnCl_2$) on microporous activity

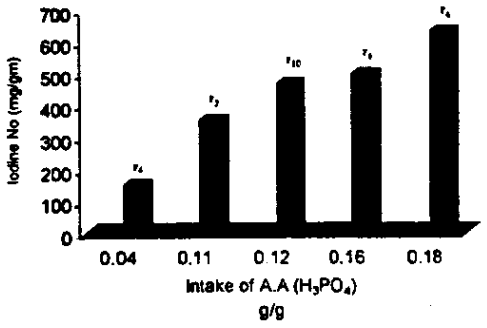

Fig. 2: Effect of intake of A.A.(H_3PO_4) on microporous activity

chemicals play a significant role during the processes of carbonization and chemicals activation, carried out simultaneously. Table-4 depicts different strength properties, in respect of tensile strength and % elongation, of various untreated precursor samples and their respective ACF samples, 'F_1' – 'F_{10}', prepared by chemical activation with different activating agents of various indigenous cellulosic precursors.

It shows that, highest tensile strength and % elongation was obtained in ACF sample 'F_1', of bleached cotton cloth. A review of Tables 1 to 4 also signifies that, although highest activity as well as yield was obtained in sample 'F_5', but it miserably failed in respect of its strength properties. Moreover, ACF samples prepared from drill cloth ('F_7' and 'F_8') had quite good strength properties, but these have failed in respect of creation of sufficient micropore structure, as is evident by their lower iodine No. and carbon tetrachloride adsorption capacity.

Henceforth, AFC sample 'F_1', prepared by zinc chloride activation of cotton cloth, was found to be appropriate, in respect of its excellent strength properties as well as reasonable activity, in liquid and vapour phase systems.

Experimental

Sample Preparation

The samples of bleached cotton cloth, jute fabric, cotton roll, bleached and unbleached (Khaki) drill cloth were procured. A 16 mesh stainless steel sieve cloth was taken and shaped in the form of a roll.

The above mentioned cellulosic raw materials were cut in triplicate, as per size of mettalic roll and dried in an oven at 105 – 110°C to constant weight.

Product Preparation

Different specimens of cellulosic raw materials prepared, were coiled on a 16 mesh stainless steel roll and weighed. These specimens (without roll) were then soaked in solutions of different activating chemicals like 35% aqueous zinc chloride and 30% syrupy phosphoric acid, for a period of 30 minutes in separate set of experiments. The chemically soaked specimens were then hung on a wire, dried in an air oven and weighed. The percent intake of impregnating chemical by each specimen was thus calculated. These chemically impregnated samples were then again coiled on stainless steel roll and re-weighed. The roll containing the respective chemically treated cellulosic specimen was carbonized in a S.S.Vessel at 550 – 600°C for 90 minutes in an inert atmosphere of nitrogen. The temperature of carbonization was monitored by a Ni-Cr thermocouple and the vessel was thereafter allowed to cool in an inert atmosphere. The roll having carbonized filament was then taken out of the vessel and weighed. The carbonized samples were then boiled/refluxed in distilled water, filtered, dried and weighed. ACF samples prepared by each set of experiment were kept in airtight bottles for their evaluation.

Product Characterization

The percent yield obtained in each set of experiment was calculated. Ash content and bulk density of each ACF sample were determined by Standard methods [15]. Activity or ultimate adsorptive capacity of the samples was determined, in liquid as well as vapour phase, against adsorbates of iodine, methylene blue and carbon tetra chloride, and were also evaluated for their percent retentivity of CCl_4 [16-18]. The tensile strength and % elongation of different ACF samples were measured by an Instron machine.

Conclusions

Activated carbon filament/fibre (ACF) of good adsorptive capacity and strength characteristics may be prepared by chemical activation of bleached cotton cloth. Further all ACF products have microporous structure.

References

1. T.H. Usmani, M. T. Motan and A.H.K. Yousufzai, *J. Chem. Soc. Pak*, **22** (1), 73 (2000)
2. T. H. Usmani, T.W. Ahmed and A. H. K. Yousufzai, *Bioresource Technology*, **48**(1), 31 (1994).
3. T. H. Usmani, T. W. Ahmed, S. Z. Ahmed and A. H. K. Yousufzai, *Carbon*, **34**(1), 77 (1996).
4. T. H. Usmani, T. W. Ahmed, M. Adil and M. Mumtaz, Pak Patent 136319, 03 Dec (1999).
5. M. Petkovska and M. Mitrovic, *Chem. Biochem. Eng*, **3** (4), 153 (1989).
6. H. Hirai, *Japan Kokai Tokyo Koho* **76**, 132,193, 28 Feb (1975).
7. H. Hirai, *Japan Kokai Tokyo Koho* **76**,137,694, 27 Nov (1976).
8. M. B. Norman, *S. African* **76**, 07, 108, 22 Sept (1977).
9. N. Ishizaki, K. Sugie, H. Shimizu, *Japan Kokai Tokyo Koho*, **79**, 160, 588, 8 June (1978).
10. Toho Belson Co Ltd., *Japan Kokai Tokyo Koho*, **59**, 76, 924, 5 Oct (1982).
11. A. Nishino, A. Yashida, Y. Takeuchi and K. Tanahashi, *Japan Kokai Tokyo Koho*, **61**, 10, 229., 26 June (1984).
12. A. Nishino, A. Yashida, Y. Takeuchi and F. Tanahashi, *Japan Kokai Tokyo Koho*, **61**,10,228, 26 June (1984).
13. R. L. Pigford, B. Baker and D.E. Blum, *Ind. Eng. Chem., Fundam.*, **8**, 848 (1969).
14. D. M. Ruthven, "Principles of Adsorption and Adsorption Process" John Wiley, N. Y. (1984).
15. F. J. Welcher, "Standard Methods of Chemical Analysis" pp. 1131, 1151, D. Van Nostrand Co. Inc., N. J. (1963).
16. F.D. Snell and C. L. Hilton, "Encyclopedia of Industrial Chemical Analysis", Vol. 1, p. 557, Vol. 8, p. 148, John Wiley, N. Y. (1969).
17. A. J. Dandy, Newzealand J. Sci, 20, 291 (1977).
18. M. Bonnevie-Svendsen, "Sorption and Filtration Methods for Gas and Water Purification", p. 275 (1975).