



Antibacterial Activated Carbon Fibers

Prepared by a New Technology

Chen Chen, Hua Zhang, Xuechen Wang

Tianjin Municipal Key Lab of Fiber Modification and Functional Fiber, Tianjin Polytechnic University

Tianjin 300160, China

Tel: 86-22-24528453 E-mail: Hual210@126.com

Abstract

A new type of antibacterial and absorbent acrylonitrile (AN)-vinylidene chloride (VDC) copolymer fibers were used as base materials for preparing activated carbon fiber (ACF) absorbents by means of oxidation, carbonization, and activation in a continuous semi-open high temperature furnace. The PAN/VDC fibers were spun from the mixtures of AN-VDC copolymer-dimethylformamide solution and silver-impregnated activated carbon (Ag-AC) powders. The activated carbon fibers prepared by PAN/VDC fibers of various contents of Ag-AC were studied. Scanning electron microscopy was used to observe the surface morphology of the ACFs. The BET specific surface areas of the ACFs were determined from N_2 adsorption isotherms; and the absorbability was measured by methylene blue (MB) absorption. The results showed that the ACFs prepared by PAN/PVDC fibers containing Ag-AC have greater favorable adsorbing ability. The silver content was greater than 0.24wt% in the ACFs, which can provide antibacterial efficacy.

Keywords: Activated carbon fibers, Antibacterial, Adsorption, Silver-impregnated activated carbon

1. Introduction

There has been growing concern for public health and environmental safety over the last few decades. Various adsorbents have been applied to remove pollutants in water and air. Activated carbon fiber (ACF) with the highest specific surface area, proper mesopores and excellent adsorption capacity has been widely used in environmental treatment (Chen, Zeng and Lu, 1999. Chen and Zeng, 2002). The raw materials of the ACFs are polyacrylonitrile fibers, viscose, phenolic resin fibers or pitch fibers, etc (Tang, Zheng etc. 2007). They can be obtained by oxidation, carbonization and activation at a temperature of 700-1000°C in an atmosphere of steam or carbon dioxide (Donnet and Bansal, 1990). The highly adsorptive efficacy of ACF is mainly attributed to its porous structure, including the pore shape, the pore sizes and their distribution (Brasquet, C. and Le-Cloirec, 1997. Pelekani, C. and V.L., 1999). Supporting antibacterial agents, such as Ag, can not only keep the excellent adsorption capacity of the ACFs, but also endow these ACFs with antibacterial activity (Chen, Liu and Zeng, 2005). The application of ACF, however, is limited for economical reason. Increasing the recovery rate can be a solution to this obstacle.

Previous studies have shown that the metal additives can generate mesopores during activation, the metal often appear to coalesce during activation leading to a variation in pore sizes (Oya, Yoshida, Alcaniz-Monge, Linares-Solano, A. 1996. Yim, Kim, Gallego, N. and Edie, 2002. Tamai, Hisashi, Makiko, Shigeyuki and Yasuda, 1997. Lee, Basova, Edie, Dan, Laura, Steven, Seung-Kon, 2003). In this study, we introduced a new technique to produce ACFs, using PAN/PVDC fibers containing silver-impregnated activated carbon as raw material. The aim of this study was attempt to obtain ACFs that had more mesopores and higher recovery rate.

2. Experimental

2.1 Preparation of PAN-VDC /Ag-AC fibers

Predetermined mass of dried powders of silver impregnated activated carbon (Ag-AC; 1500 mesh) were mixed with PAN-VDC/dimethylformamide (DMF) solution containing 20wt% of polymers. The spinning solution was stirred for 3hrs at 70°C, filtered and then deaerated at 70°C for 4hrs. The spinning conditions for PAN-VDC/Ag-AC fibers are shown in Table 1.

2.2 Preparation of activated carbon fiber

The PAN-PVDC/Ag-AC fibers were physical activated with wet N_2 and chemical activated with $(NH_4)_3PO_4$ and $(NH_4)_2SO_4$ mixture respectively to prepare the activated carbon fibers. Before carbonization and activation, the samples were stabilized in muffle furnace at 250°C. The engineering process of carbonization and activation is shown in Figure 1. The samples F_0 - F_4

had been carbonized at 850°C in flowing N_2 for 30min and activated at 800°C in flowing wet N_2 for 40min. The sample was then cooled in flowing dry N_2 . The only difference between physical and chemical activation in this study was that the later fibers were first immersed in $(NH_4)_3PO_4$ and $(NH_4)_2SO_4$ mixture (4:6 wt/wt). The ACFs prepared by physical activation and chemical activation were labeled as AF_0 to AF_4 and P- AF_0 to P- AF_4 respectively.

2.3 Characterization of the fibers

UV spectrophotometer (7220, Beijing Rayleigh Analytical Instrument Corporation) was used to measure the absorbability of the fibers to methylene blue (MB)-water solution. 0.2g fibers were put in a 400ml flask; and 300ml of MB solution of various concentrations (10-50mg/l) were added. The pH of solution was in the range of 3.7-4.5.

The surface morphology of the fibers and the distribution of Ag-AC particles in the fibers were observed by a scanning electron microscope (SEM, Quanta 200).

The specific surface area (S_{BET}) was obtained from N_2 adsorption-desorption isotherms at 77K (CHEMBET-3000, Quantachrome, USA) on samples preheated at 200°C for 3h in N_2 .

3. Results and Discussion

3.1 Properties of the PAN-VDC /Ag-AC fibers

The PAN-VDC fibers containing 10wt%~25wt% Ag-AC were fabricated. There is no difference in the spinning condition of these samples. The spin ability of the fibers tended to decrease gradually with increasing the content of Ag-AC in the spinning solution.

The mechanical properties of these fibers are listed in Table 2. As the content of Ag-AC increased, the fiber tensile strength decreased correspondingly. It can be concluded that the compounding of the Ag-AC in spinning solution has significantly influence on the structure of the fibers.

3.2 Characteristic of the ACFs

In order to prevent melting and distortion, polyacrylonitrile fibers and pitch fibers generally need to be stabilized before carbonization (Jing, Fang, and Zhang, 2001). Effects of stabilizing to the fibers are listed in Table 3. During the process of stabilizing, fibers lost weight and shrank mainly in the first half hours. The existences of Ag-AC weaken the weight lost and the length shortened. Characteristics of the ACFs are shown in Table 4. The S_{BET} and the recovery rate rise with the increase of the Ag-AC content. The existence of ammonium salt has similar effect to the ACFs when it is compared with Ag-AC. PAN-PVDC fiber began to cyclization at 250°C, meanwhile, ammonium salt decomposed and released NH_3 which produced lots of mesospores in the fibers; and PO_4^{3-} reacted with fiber generated Carbon phosphate, which make C hard to release (CO_2 CO) (Zhao, Zang, Ma, Li, and Sheng, 2001). So the weight lost and the lengths shortened were weakened. As silver didn't lose in the entire ACF preparation, we can obtain the Ag content of ACF by dividing Ag content of precursor into ACF's recovery rate.

3.3 Morphology of the ACFs

The micrographs of the ACFs are shown in Figure 2. The side surface (a) of sample AF_0 is very smooth; and few holes can be found in the profile. By contrast, there are many strumae on the side surfaces of Samples AF_3 and P- AF_3 (see c, i).

When heated the precursor fibers, the fibers began to melt and shrink, the polymer chain was destroyed to form new framework regularly. However, the presence of Ag-AC destroyed this regularity. Both Ag-AC and $(NH_4)_3PO_4$ can produce more apertures on the ACFs (see f, d). When both of them were used on a sample, the effect will be more obvious (see j).

3.4 Adsorption Capacity of the ACFs

The adsorption capacities of the ACFs are presented in Figure 3. The ACF samples prepared by physical activation and chemical activation were labeled as AF and P-AF respectively. The absorbability of the ACFs tended to increase gradually with the increasing content of Ag-AC. The increase of absorbability, however, is not direct proportional to the content of Ag-AC. One of the reasons is that the Ag-AC, which has participated in absorption, mainly dispersed in the surface layer of the fiber. In addition, the Ag-AC dispersed in the core of the fibers had less influence on the absorption. The Ag-AC powders dispersed in the fibers produced a great deal of new micro-holes. 1g ACFs containing 20wt% Ag-AC absorb 48.26mg MB. By contrast, 1g ACFs without Ag-AC only absorbs 22.45mg MB. Therefore the fibers containing Ag-AC can provide greater adsorption capacity. Same as the S_{BET} results, samples P- AF_3 has the best absorbability of the methylene blue.

4. Conclusions

The ACFs based on PAN-PVDC/Ag-AC fibers were prepared. The presence of Ag-AC in precursor can greatly increase the ACFs' specific surface area, as well as its adsorbent capacity. $(NH_4)_3PO_4$ has introduced in the ACF preparation process and its presence also increased the specific surface areas of the ACFs. The best way to prepare ACF was using PAN-PVDC/Ag-AC fibers and $(NH_4)_3PO_4$ as precursor and activator respectively. The stabilizing should be last at least 1.5h at 250°C. The

S_{BET} can be as high as $350\text{m}^2/\text{g}$ and the silver content is 0.246wt%. The ACFs can provide antibacterial and adsorbent properties.

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Table 1. Spinning conditions of PAN-VDC/Ag-AC fibers

Spinneret Specification	0.1mm Φ ×1000
Spinning Speed	1.76m/min
Coagulation Bath I Composition	DMF:H ₂ O(mass ratio 60:40)
Temperature	23°C
Take up Roller Speed	1.80m/min, Draw ratio $\lambda_1=1.02$
Coagulation Bath II Composition	DMF:H ₂ O(mass ratio 15:85)
Temperature	35°C
Take up Roller Speed	3.9m/min, Draw ratio $\lambda_2=2.17$
Coagulation Bath III Composition	DMF:H ₂ O(mass ratio 0:100)
Temperature	75°C
Take up Roller Speed	7.8m/min, Draw ratio $\lambda_3=2.00$
Total Draw ratio($\lambda_1\lambda_2\lambda_3$)	4.43
Heat set	Relax
Temperature	120°C
Time	30min

Table 2. Properties of the PAN-VDC /Ag-AC Fibers

Sample No	Feed content of Ag-AC /wt%	Content of Ag /wt%	Titers/ dtex	Tensile strength /cN/dtex	Elongation /%
F ₀	0	0	6.4	2.3	38
F ₁	10	0.077	6.5	1.9	26
F ₂	15	0.115	6.8	1.7	30
F ₃	20	0.154	6.4	1.6	25
F ₄	25	0.192	6.5	1.4	20

Table 3. Recovery rate of the fibers after heated (%)

Time heated		AF ₀	P-AF ₀	AF ₁	P-AF ₁	AF ₃	P-AF ₃
0.5h	weight	73.65 *	93.25	76.62	98.57	77.17	98.86
	length	30.0 **	66.7	53.3	78.7	60.0	86.6
1.5h	weight	70.66	89.57	74.03	94.29	76.09	97.73
	length	28.7	61.3	51.3	76.7	56.7	84.0
2.5h	weight	70.66	88.96	74.03	94.29	76.09	97.73
	length	28.7	60.7	51.3	76.7	49.3	83.3

*weight recovery rate = (weight of fiber after 0.5h heated) / (weight of fiber before heated) × 100%;

**length recovery rate = (length of fiber after 0.5h heated) / (length of fiber before heated) × 100%.

Table 4. Characteristic of the ACFs

	AF ₀	AF ₃	P-AF ₀	P-AF ₃
S _{BET} (m ² /g)	86.51	151.8	190.2	385.2
Ag content (wt%)	0	28.6	0	24.6
Recovery rate (%)	38.76	50.38	46.15	62.51

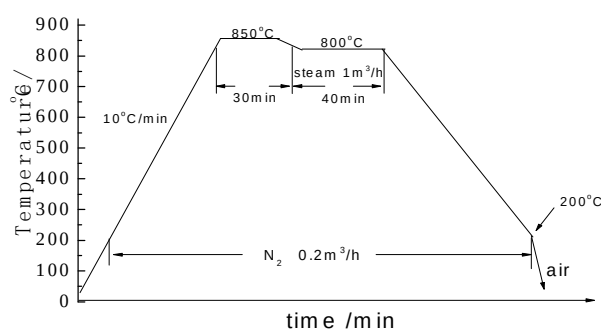
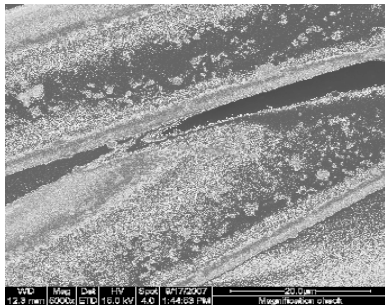
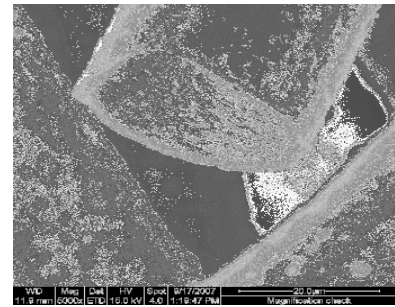


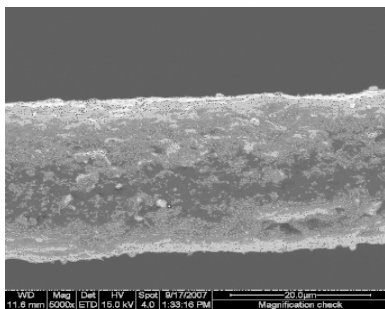
Figure 1. The engineering process of carbonization and activation



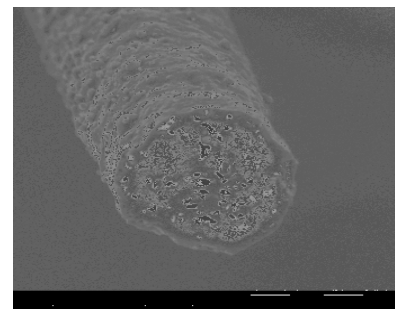
(a) Side surface of AF_0



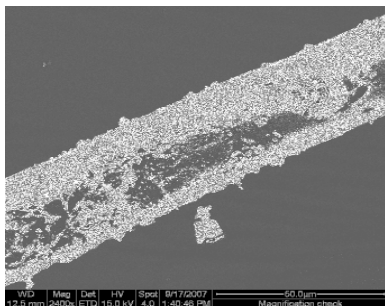
(b) Cross-section of AF_0



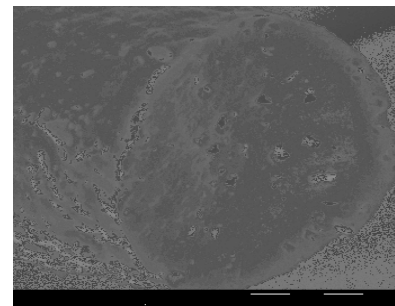
(c) Side surface of AF_3



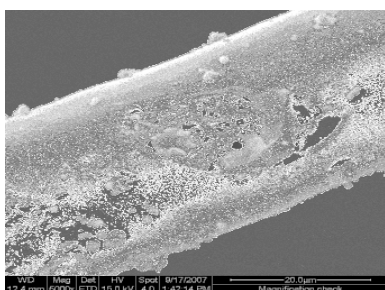
(d) Cross-section of AF_3



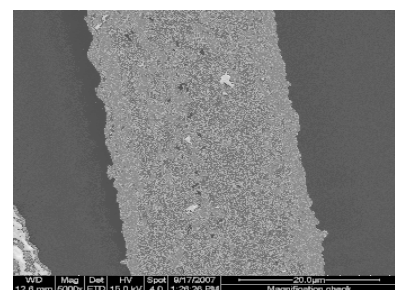
(e) Side surface of $P-AF_0$



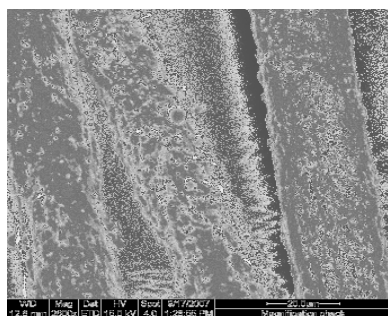
(f) Cross-section of $P-AF_0$



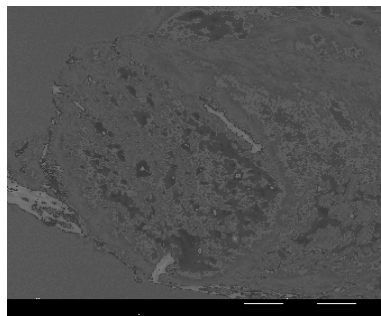
(g) Side surface of $P-AF_0$



(h) Side surface of $P-AF_3$



(i) Side surface of P- AF_3



(j) Cross-section of P- AF_3

Figure 2. SEM micrographs of the ACFs

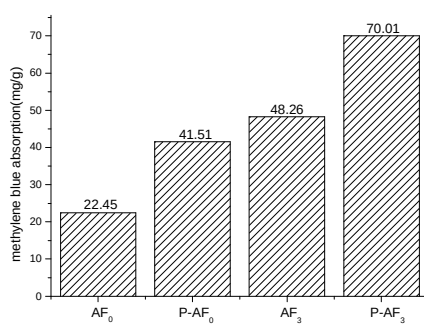


Figure 3. Maximum adsorption to MB