Adsorption Properties of Polyacrylonitrile-Based Activated Carbon Hollow Fiber

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ABSTRACT: In this work, polyacrylonitrile (PAN) hollow fibers are pretreated with ammonium dibasic phosphate and then further oxidized in air, carbonized in nitrogen, and activated with carbon dioxide. The adsorption properties of the resultant activated carbon hollow fibers (ACHF) prepared in different conditions were studied. The results show that the adsorption properties of ACHF change regularly with preparing conditions of ACHF. The different adsorption ratios to three adsorbates reflect the number of micropores and mesopores in PAN-based ACHF. Pretreatment with phosphate can increase the number of mesopores. Proper oxidation temperature and time can increase the number of micropores and mesopores. When carbonization temperature is more than 900°C and carbonization time ranges from 50 to 90 min, the number of micropores and mesopores, especially mesopores, greatly increases. Compared with other treatments, activation treatment greatly increases the number of micropores and mesopores, and the dominant pore sizes of mesopores in PAN-based ACHF are from 2 to 10 nm. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 93: 602–607, 2004

Key words: adsorption properties; activated carbon hollow fibers; polyacrylonitrile

INTRODUCTION

Activated carbons are excellent adsorbents and thus are widely used for purification processes such as decolorization, deodorization, dechlorination, detoxification, filtration, removal or modification of salts, separation, and concentration. Activated carbon is usually characterized by micropore volume and pore size depending on the structure of the carbon precursor and its activation process.[1,2] Recently, the PAN-based activated carbon hollow fibers (ACHF) have brought on many investigators' interest,[3–8] since PAN-based ACHF shows the largest adsorption capacity among the carbon surfaces.

There have been numerous applications of hollow fiber technology to separation and purification in both industry and medicine, including the preparation of drinkable, high quality water for the electronics and pharmaceutical industries, treatment of secondary effluent from sewage processing plants, gas separation for industrial application, hemodialyzers, and the controlled release of drugs to mention only a few applications.[9] However, attempts to commercialize hollow fibers or other membrane systems for such separations have been unsuccessful, largely because of relatively low permeation rates and poor environmental resistance.

Yang and Yu[3–6] studied the structure and properties, pore-size distribution, surface area, and mechanical properties of PAN ACHF. Linkov et al.[10] reported that hollow fibers have been used for gas separation and show high fluxes and good selectivities. Schindler and Maier[11] obtained a patent for making hollow carbon fiber membrane, in which the PAN hollow fiber was pretreated with hydrazine and followed by oxidation and carbonization and was suitable for separating particles.

In this research, the PAN hollow fibers were dipped in ammonium dibasic phosphate aqueous solution, oxidized in air, carbonized in nitrogen, and activated with carbon dioxide. We discuss the adsorption properties of the resultant PAN-based ACHF to creatinine, VB_{12}, and bilirubin. According to their molecule sizes, creatine < bilirubin < VB_{12}, the molecule sizes of creatine and bilirubin are less than 2 nm and are primarily adsorbed by micropores (<2 nm). However, the molecule size of VB_{12} is larger than 2 nm and is primarily adsorbed by mesopores (2 ~ 50 nm). There are various types of pores in the ACHF. Macropores have small specific surface area and are thus insignificant to adsorption. However, these pores control the access of adsorbate and also serve as the space for deposition. Mesopores provide channels for the adsorbate to the micropores from the macropores and simultaneously adsorb matter of mesomolecules. As re-
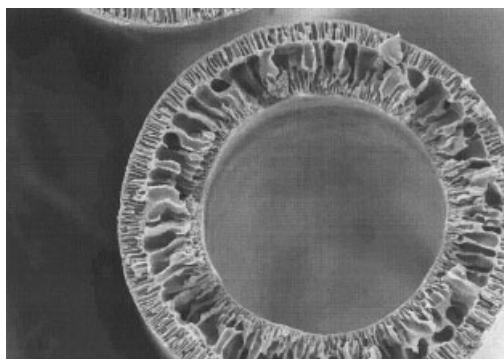
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Figure 1 Cross section of virgin PAN hollow fiber (×200).

ported in the literature, mesopore can function as capillary condensation, thus it is indispensable for the adsorption of liquid and gas. Micropores determine the adsorption capacity of the ACHF and primarily adsorb the matter of micromolecules.

EXPERIMENTAL

PAN (a copolymer of acrylonitrile, methyl methacrylate, and itaconic acid) hollow fiber spun by dry-wet spinning setup was used as the precursor. The resultant hollow fiber had an inside diameter of 400 μm and an outside diameter of 500 μm. Figure 1 shows the porous structure of the PAN hollow fiber.

Virgin PAN hollow fibers were first dipped in ammonium dibasic phosphate aqueous solution. Afterward, the pretreated fiber was oxidized in the air, carbonized in nitrogen, and activated with carbon dioxide. The pretreating condition (including the concentration of ammonium dibasic phosphate aqueous solution and dipping time), oxidization condition, carbonization condition, and activation condition are changed.

A scanning electron microscope (SEM; JEOL Model JSM-5600LV) was used to examine a cross section of hollow fibers.

Adsorption study of creatinine, VB_{12}, and bilirubin was carried out by a static process. A known quantity of the ACHF was immersed in a known volume of aqueous solution at 37°C for 24 h. The amount of creatinine, VB_{12}, and bilirubin adsorbed was determined by the concentration difference before and after immersion in the solution. The creatinine, VB_{12}, and bilirubin concentrations of the solution were determined with a UV/VIS spectrophotometer (Shanghai Techcomp Corp. 7500) at wavelengths of 510, 361, and 438 nm, respectively. Absorbency of creatinine, VB_{12}, and bilirubin in the aqueous solutions reflects the difference of solution concentration. The adsorption ratio was calculated as follows:

adsorption ratio (wt %)

$$= \frac{\begin{array}{c}\text{absorbency before adsorption} \\ - \text{ absorbency after adsorption}\end{array}}{\text{absorbency of before adsorption}} \times 100\%$$

Samples of PAN–ACHF were characterized by measuring specific BET surface area and pore size distribution using an autoadsorption apparatus (Micrometrics Tristar 3000). The surface area was calculated using the multipoint BET method. Pore volume and pore size distribution were determined from the nitrogen adsorption isotherms using the Barrett, Joyner, and Halenda (BJH) method.[12]

RESULTS AND DISCUSSION

Effect of pretreating condition on adsorption properties

The incorporation of phosphorous to the fiber is effected in the form of a phosphorous compound. Oguwa et al.[13] reported that, by adding the phosphorus compound, the activation yield at the activation treatment of the fibers can be increased as well as the strength, abrasion, resistance, and adsorptive property of ACF. By adding phosphorous, the reaction of phosphorous and carbon produces diversified by-products that continuously flee from the surface of fibers and pores are formed. Figure 2 shows that adsorption ratios of PAN-based ACHF to three adsorbates change with ammonium dibasic phosphate concentration, respectively. The adsorption ratio of ACHF not pretreated with ammonium dibasic phosphate is 100% to
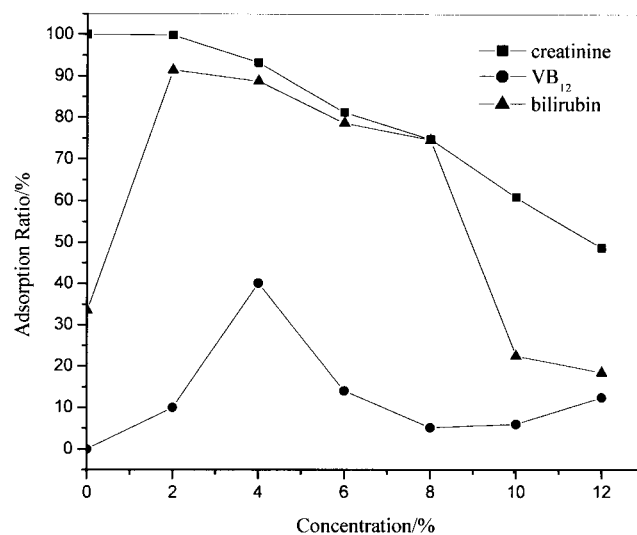

Figure 2 Adsorption ratios of PAN-based ACHF pretreated with ammonium dibasic phosphate of different concentrations (samples are pretreated for 30 min, oxidized at 230°C for 5 h, carbonized at 900°C for 30 min, and activated at 800°C for 40 min).
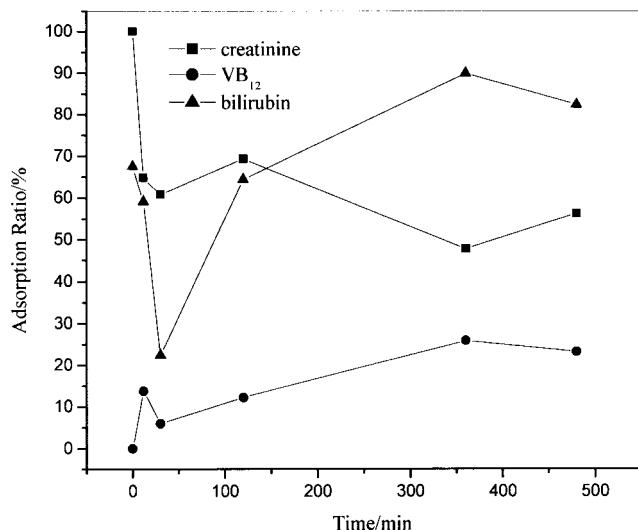
Figure 3 Adsorption ratios of PAN-based ACHF pretreated with ammonium dibasic phosphate for different times (samples are pretreated with 4% (wt %) concentration, oxidized at 230°C for 5 h, carbonized at 900°C for 30 min, and activated at 800°C for 40 min).
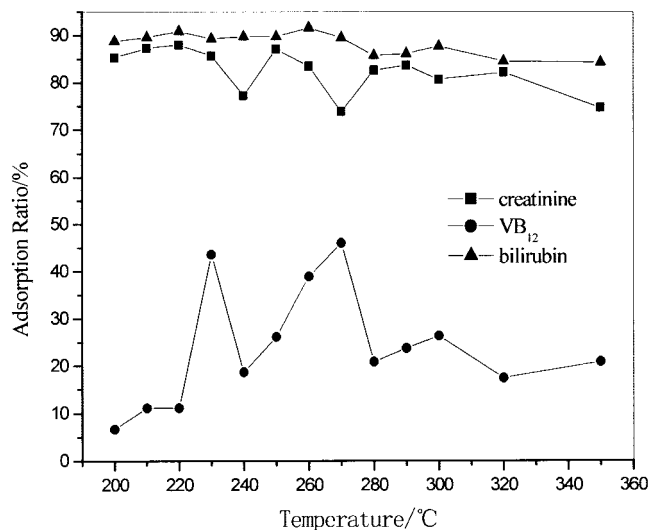

Figure 4 Adsorption ratios of PAN-based ACHF oxidized at different temperatures (samples are pretreated with 4% (wt %) concentration, oxidized for 5 h, carbonized at 900°C for 30 min, and activated at 800°C for 40 min).

creatinine, 35% to bilirubin, and nearly zero to VB_{12}. It is suggested that the ACHF not pretreated with ammonium dibasic phosphate is primarily formed by micropores. The adsorption ratios of ACHF to creatinine and bilirubin decrease with pretreating concentration. However, the adsorption ratio of ACHF to VB_{12} reaches the maximum value at 4%. It is assumed that the number of micropores decreases and the number of mesopores in ACHF increases with pretreating concentration and simultaneously the specific surface area increases with it. When pretreating concentration surpasses 4%, the number of micropores continuously decreases and the number of mesopores in ACHF increases; the diameter of mesopores enlarges; the specific surface area in unit volume of ACHF is reduced.

In general, the content of phosphorous increases with dipping time of PAN hollow fibers in the ammonium dibasic phosphate aqueous solution. Figure 3 shows that adsorption ratios of PAN-based ACHF to three adsorbates change with dipping time of PAN hollow fibers in the ammonium dibasic phosphate aqueous solution, respectively. The adsorption ratios of ACHF to creatinine and bilirubin decrease sharply with dipping time within 30 min. The adsorption ratio of ACHF to creatinine then slowly decreases and tends to stabilization and that to bilirubin, gradually increases and tends to stabilization. It is suggested that the number of micropores in ACHF decreases with dipping time. To VB_{12}, the adsorption ratio slightly increases from 0 to 30 min and then decreases, and finally gradually increases. But as a whole, the adsorption of VB_{12} is low. This suggests that a few mesopores are formed with dipping time.

Effect of oxidation condition on adsorption properties

Figures 4 and 5 show variation of adsorption ratios with oxidization temperature and oxidization time. It can be seen that the adsorption ratios to creatinine and bilirubin throughout the oxidization treatment are high, increasing from 70 to 100%. In Figure 4, the adsorption ratio to VB_{12} is high at 230 and 270°C. In Figure 5, the adsorption ratio to VB_{12} is high with short time treatment of oxidation (time increasing from 0.5 to 3.0 h) and a significant drop in value is
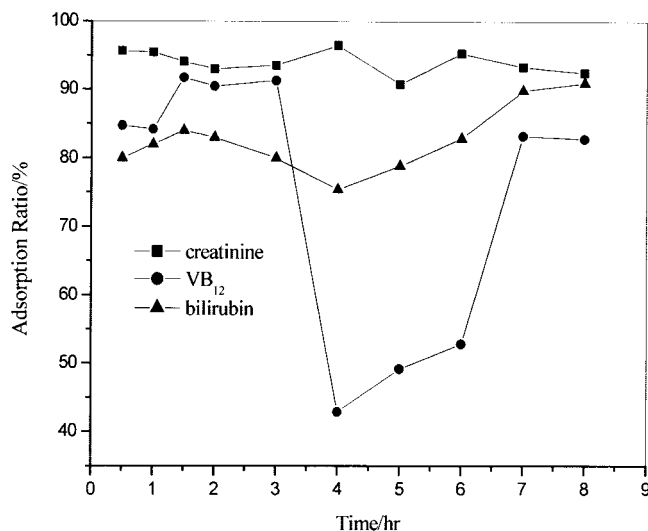

Figure 5 Adsorption ratios of PAN-based ACHF oxidized for different times (samples are pretreated with 4% (wt %) concentration, oxidized at 230°C, carbonized at 900°C for 30 min, and activated at 800°C for 40 min).
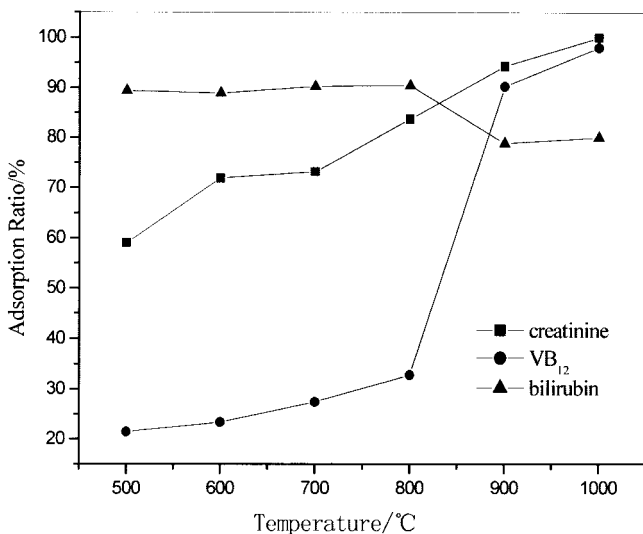
Figure 6 Adsorption ratios of PAN-based ACHF carbonized at different temperatures (samples are pretreated with 4% (wt %) concentration, oxidized at 230°C for 5 hr, and activated at 800°C for 40 min).

observed in 4 h, and then the rate of increase becomes gradual.

When PAN hollow fibers were thermally oxidized in air, chemical reactions such as dehydrogenation, oxidation, degradation, and crosslinking also took place. During the oxidation stage, the molecular structure of the polymer changed from linear to cyclic and scission of the molecular chains on the surface of the fiber occured. These regions of chain scission are more likely to be attacked and to develop into pores during the activation stage. It is suggested from Figures 4 and 5 that more micropores are formed at different oxidation temperatures and for different oxidation times, and the number of micropores changes little. However, more mesopores are formed in short oxidation times.

Effect of carbonization condition on adsorption properties

Figures 6 and 7 show variation of adsorption ratios with carbonization temperature and carbonization time. It can be seen that the adsorption ratios to creatinine and bilirubin throughout the carbonization treatment are high. In Figure 6, the adsorption ratio to VB_{12} increases slowly during the initial range of carbonization treatment (temperature increasing from 500 to 800°C). After that, the adsorption ratio to VB_{12} demonstrates a rapid increase over the remaining temperature region. In Figure 7, the adsorption ratio to VB_{12} increases from 0 to 50 min and then remains constant. After that, a small drop in the adsorption ratio to VB_{12} is observed.

It has been proposed that, during the early stages of carbonization, the stabilized fibers undergo further cyclization in the uncyclized portions, forming ladder structures, crosslinking, and some chain-scission reactions, while evolving some small molecules like water, hydrogen, and other volatiles. Meanwhile, as these reactions and structure rearrangements occur within the fiber, consolidation and densification are expected. It is suggested from Figures 6 and 7 that many micropores are formed at different oxidation temperatures and for different oxidation times, and the number of micropores changes little. However, more mesopores are formed when the carbonization temperature rises over 900°C and when the carbonization time ranges from 50 to 90 min.

Effect of activation condition on adsorption properties

Figures 8 and 9 show variation of adsorption ratios with activation temperature and activation time. It can be seen that the adsorption ratios to creatinine and bilirubin throughout the carbonization treatment are much higher. In Figure 8, it is found that the adsorption ratio to VB_{12} is high and registers a general tendency to increase over the activation. In Figure 9, the adsorption ratio to VB_{12} is high and increases rapidly with time, then becomes relatively constant from 60 to 100 min. It is suggested from Figures 6 and 7 that more micropores are formed at different activation temperatures and times. The higher activation temperature is, the greater the number of mesopores formed. The longer activation time (range from 20 to 60 min) is, the greater the number of mesopores formed. It can be
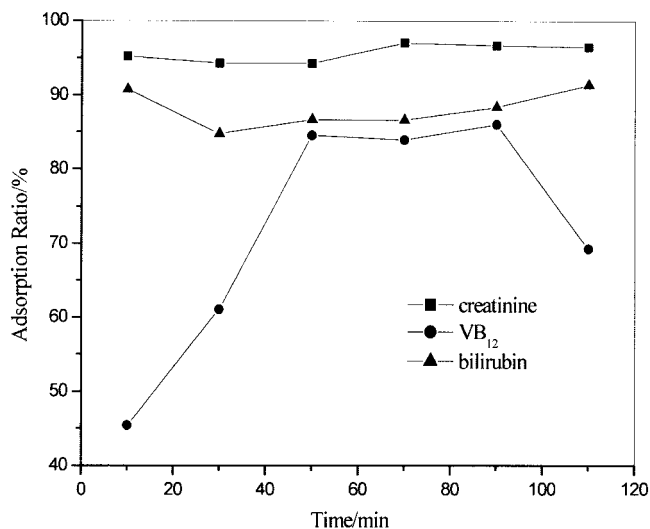

Figure 7 Adsorption ratios of PAN-based ACHF carbonized for different times (samples are pretreated with 4% (wt %) concentration, oxidized at 230°C, carbonized at 900°C, and activated at 800°C for 40 min).
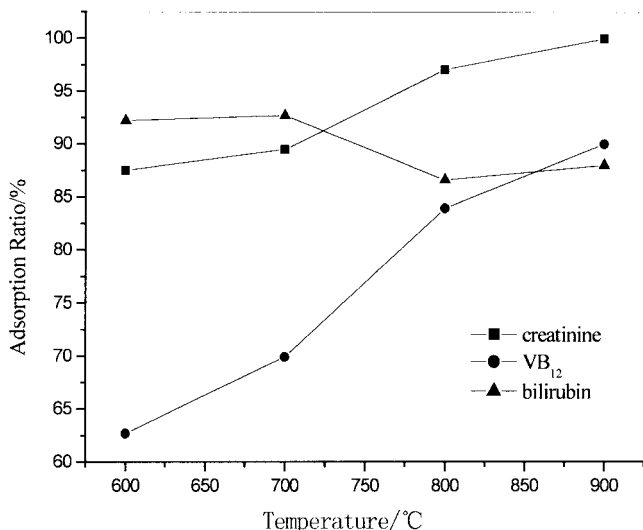
Figure 8 Adsorption ratios of PAN-based ACHF activated at different temperatures (samples are pretreated with 4% (wt %) concentration for 30 min, oxidized at 230°C for 5 hr, carbonized at 900°C for 30 min, and activated at 800°C for 40 min).

concluded that the effect of activation on pores forming, especially on mesopores forming, is remarkable.

By activating in CO_2 at high temperature, micropores suitable for adsorption purpose would appear on the surface and the inside of the carbon fiber.[14] With temperature increasing and time extending, the diffusion of CO_2 into the defects of the molecular structure, vigorous reaction caused the tunneling of the skin layer and the pores, and larger pores including mesopores were thus formed. So both increasing activation temperature and extending activation time
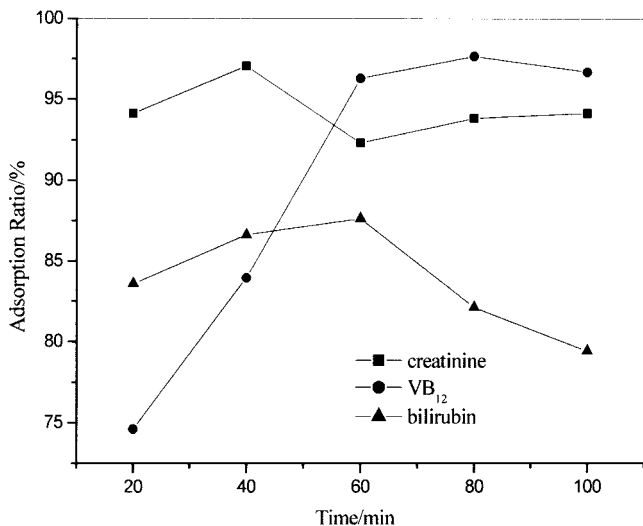

Figure 9 Adsorption ratios of PAN-based ACHF activated for different times (samples are pretreated with 4% (wt %) concentration for 30 min, oxidized at 230°C for 5 hr, carbonized at 900°C for 30 min, and activated at 800°C).
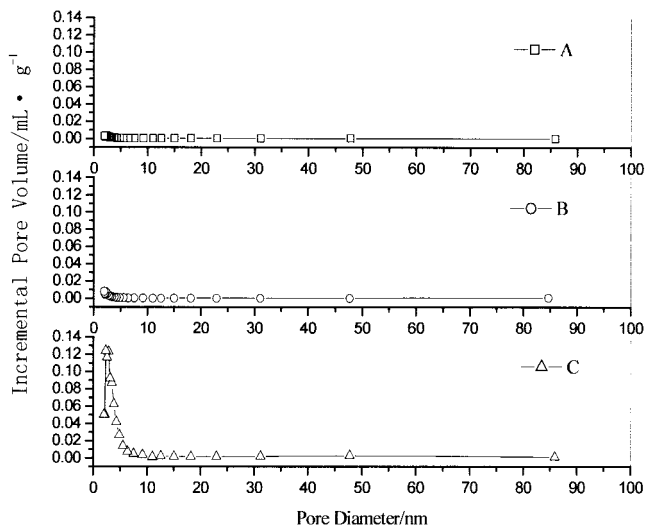

Figure 10 Incremental volume of PAN-based ACHF developed at different activation temperatures (samples A, B, and C are activated at 700, 800, and 900°C, respectively, for 40 min).

remarkably increase the number of micropores and mesopores.

Pore size distribution and surface area of PAN-based ACHF

Figure 10 shows the pore size distribution of the PAN-based ACHF made of fiber activated at 700, 800, and 900°C for 40 min, respectively. Due to the limits of apparatus, pore diameters of less than 2 nm could not be tested. However, the distribution of mesopores (2 ~ 50 nm) and macropores (>50 nm) can be observed in Figure 10. As shown in Figure 10, when activation temperatures are 700 and 800°C, the value of incremental pore volume with various pore diameter is low. As shown in Table I, the surface areas of mesopores in PAN-based ACHF activated at 700 and 800°C are much lower than that activated at 900°C. It indicates that the pores in PAN-based ACHF activated at 700 and 800°C were mainly formed by micropores and there is a small quantity of mesopores. However, the

TABLE I
Surface Area of PAN-Based ACHF Developed at Different Activation Temperatures for 40 min[a]

Activation temperature (°C)	700	800	900
BET surface area (m^2/g^{-1})	269	557	1,422
Surface area of mesopores (m^2/g^{-1})	34	75	1,234

[a] Samples are pretreated with 4% (wt %) concentration for 30 min, oxidized at 230°C for 5 h, carbonized at 900°C for 30 min, and activated at different temperatures for 40 min.

surface area of mesopores in PAN-based ACHF activated at 900°C reaches 1,234 $m^2 g^{-1}$ (as shown in Table I), and the dominant pore sizes of mesopores are 2 to 10 nm (as shown in Fig. 10).

Figure 11 shows the pore size distribution of the PAN-based ACHF made of fiber activated at 800°C for 20, 40, and 60 min, respectively. As shown in Figure 11, the maximal value of incremental pore volume with activation time increasing increases and the surface area of mesopores in PAN-based ACHF increases from 44 to 174 $m^2 g^{-1}$ at the same time (as shown in Table II). It is suggested that the number of mesopores in PAN-based ACHF increases with activation time, and the dominant pore sizes of mesopores are 2 to 5 nm (as shown in Fig. 11).

CONCLUSION

When PAN-based hollow fibers are pretreated with phosphate, the adsorption ratios to creatinine and bilirubin decrease, but the adsorption ratio to VB_{12} increases. By adding phosphorous, the reaction of phos-

TABLE II
Surface Area of PAN-Based ACHF Developed at 800°C for Different Activation Times[a]

Activation time (min)	20	60	80
BET surface area (m^2/g^{-1})	446	717	766
Surface area of mesopores (m^2/g^{-1})	44	113	174

[a] Samples are pretreated with 4% (wt %) concentration for 30 min, oxidized at 230°C for 5 h, carbonized at 900°C for 30 min, and activated at 800°C for different times.

phorous and carbon produces diversified by-products that continuously flee from the surface of fibers and more mesopores are formed. Proper oxidation temperature and time can increase the number of micropores and mesopores. When carbonization temperature is more than 900°C and carbonization time ranges from 50 to 90 min, the number of micropores and mesopores, especially mesopores, greatly increases. Compared with other treatments, activation treatment greatly increases the number of micropores and mesopores, and the dominant pore sizes of mesopores in PAN-based ACHF are 2 to 10 nm.

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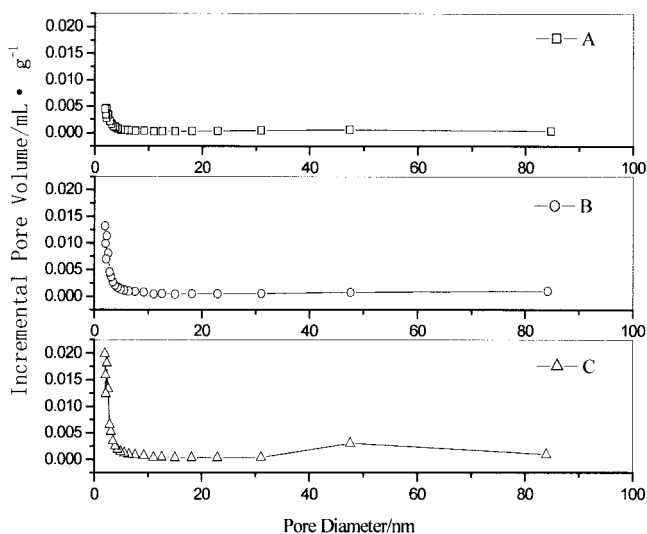
Figure 11 Incremental volume of PAN-based ACHF developed for different activation times (samples A, B, and C are activated at 800°C for 20, 60, and 80 min, respectively).