

# Structure and Properties of PAN-Based Activated Carbon Hollow Fibers: Effect of Ammonium Dibasic Phosphate Pretreatment

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**ABSTRACT:** Polyacrylonitrile (PAN) hollow fibers were pretreated with ammonium dibasic phosphate aqueous solution, then further oxidized in air, carbonized in nitrogen, and activated with carbon dioxide. The effects of pretreatment concentration of ammonium dibasic phosphate aqueous solution on the microstructure, specific surface, pore size distribution, and adsorption properties of PAN-based activated carbon hollow fibers (PAN-ACHF) were studied in this work. After the activation process, the Brunauer-Emmett-Teller (BET) surface area of the PAN-ACHF and surface area of mesopores in the PAN-ACHF increases and reaches  $513 \text{ m}^2\text{g}^{-1}$  and  $66 \text{ m}^2\text{g}^{-1}$  respectively when the concentration of ammonium

dibasic phosphate aqueous solution is 4% (wt %). The adsorptions to creatinine are much high, reach more than 90% over all the concentration of ammonium dibasic phosphate aqueous solution. The adsorptions to  $\text{VB}_{12}$  of PAN-ACHF reach 86% when the concentration of ammonium dibasic phosphate aqueous solution is 4% (wt %). The dominant pore sizes of mesopores in PAN-ACHF range from 2 to 5 nm. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 2023–2028, 2010

**Key words:** polyacrylonitrile; ammonium dibasic phosphate; pretreatment concentration; surface area; adsorption

## INTRODUCTION

Activated carbon fibers (ACF) are a comparatively modern form of porous carbon material with a number of significant advantages over the more traditional powder or granular forms. These include high surface area and adsorption capacity, as well as very high rates of adsorption from the gas or liquid phase.<sup>1</sup> These materials are generally produced by pyrolyzing in an inert atmosphere with elevated temperature using polymeric materials, such as viscose rayon, phenolic polymers, polyacrylonitrile, and other fiber-forming materials.<sup>2</sup> Recently, the PAN-based activated carbon hollow fibers (PAN-ACHF) brought on many investigators' interests,<sup>3–8</sup> as PAN-ACHF shows the largest adsorption capacity among the carbon surfaces. In a previous study,<sup>9–14</sup> we

reported effects of oxidation, carbonization, activation on the properties, and structure of PAN-ACHF.

The properties and structure of PAN-ACHF strongly depend on the activation process and activation methods. Phosphate salts and ammonium salts are often used as chemical activating agents.<sup>15</sup> In our previous research,<sup>16</sup> the structure and properties of PAN-ACHF pretreated with five different compounds containing phosphorus, such as ammonium dibasic phosphate, ammonium dihydrogen phosphate, triammonium phosphate, phosphoric acid, and metaphosphoric acid, were discussed. It indicates that ammonium dibasic phosphate is the best pretreating agent among five different compounds containing phosphorus.

In this research, the PAN hollow fibers were pretreated with ammonium dibasic phosphate aqueous solution, oxidized in air, carbonized in nitrogen, and activated with carbon dioxide. Ammonium dibasic phosphate as a pretreatment agent was used to prepare PAN-based activated carbon hollow fiber (PAN-ACHF). This study examined the effects of ammonium dibasic phosphate pretreatment concentration for 30 min on the adsorption and structural

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properties, such as specific surface area, pore size distribution, and morphology of PAN-ACHF. We discussed the adsorption properties of the resultant PAN-ACHF to creatinine and VB<sub>12</sub>, which molecular weights are 113 and 1355.4, respectively. VB<sub>12</sub> is a kind of vitamin. It is the purpose of this article to discuss, what pretreatment condition provides high surface area and high adsorption ratio for the PAN-ACHF prepared from PAN hollow fibers.

## MATERIALS AND METHODS

PAN (a copolymer of acrylonitrile, methyl methacrylate, 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.

Original PAN hollow fibers were first dipped in ammonium dibasic phosphate aqueous solution of different concentration for 30 min. Then the pretreated fibers were dried. Afterwards, the pretreated fibers were oxidized in the air at 270°C for 2 h, carbonized in nitrogen at 900°C for 30 min, activated

with carbon dioxide at 800°C for 40 min to obtain PAN-based activated carbon hollow fiber (PAN-ACHF). The concentration of ammonium dibasic phosphate aqueous solution varied from 0 to 10%.

A scanning electron microscope (SEM) (JEOL Model JSM-5600LV) was used to examine the cross section and external surface of fibers.

Adsorption study to creatinine and VB<sub>12</sub> was carried out by a static process. The concentrations of creatinine and VB<sub>12</sub> aqueous solutions are 20 mg/L. 100 mg PAN-ACHF was immersed in 20 mL creatinine and VB<sub>12</sub> aqueous solutions, respectively at 37°C for 24 h. The amount of creatinine and VB<sub>12</sub> adsorbed was determined by the concentration difference before and after immersion in the solution. The creatinine and VB<sub>12</sub> concentrations of the solution were determined with a UV/VIS spectrophotometer (Shanghai Techcomp, 7500) at the wavelength of 510 nm and 361 nm, respectively. Absorbency of creatinine and VB<sub>12</sub> in the aqueous solutions reflects the difference of solution concentration. Then the adsorption ratio was calculated as follows:

$$\text{adsorption ratio (wt\%)} = \frac{\text{absorbency before adsorption} - \text{absorbency after adsorption}}{\text{absorbency before adsorption}} \times 100\%$$

Samples of PAN-ACHF were characterized by measuring specific BET surface area, surface area of mesopores, and pore size distribution using an auto-adsorption apparatus (Micromeritics Tristar 3000). The surface area was calculated using the multi point BET method. Pore volume and pore size distribution were determined from the nitrogen adsorption isotherms using the Barrett, Joyner, and Halenda (BJH) method.<sup>17</sup>

## RESULTS AND DISCUSSION

### Dipping ratio of PAN hollow fiber

Chemical activation with hydroxide,<sup>18</sup> zinc chloride,<sup>19</sup> phosphoric acid,<sup>20</sup> and other activating agents is an effective method to prepare PAN-based activated carbon fiber or activated carbons with high surface area. In this study, ammonium dibasic phosphate was used as activating agent to activate PAN-based hollow fiber.

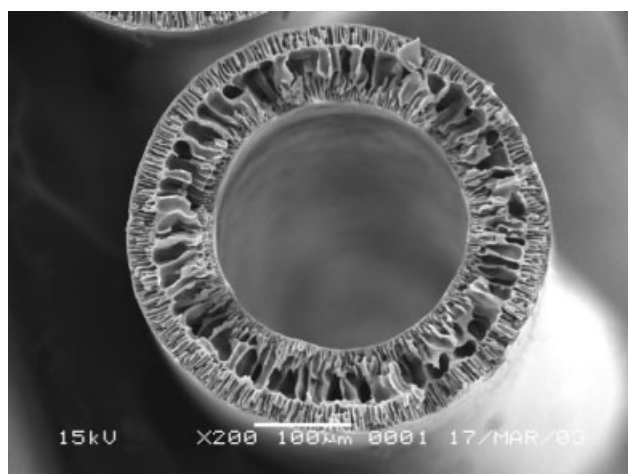
Figure 2 shows the variation in dipping ratio of PAN hollow fiber with the concentration of ammonium dibasic phosphate aqueous solution. The dipping ratio was determined from a change in weight of PAN hollow fibers before and after dipping. As shown in Figure 2, dipping ratio of PAN hollow

fiber sharply increases with the concentration of ammonium dibasic phosphate aqueous solution increasing. It is suggested that the amount of ammonium dibasic phosphate in PAN hollow fiber increases with the concentration of ammonium dibasic phosphate aqueous solution increasing.

### Surface area and adsorption properties of PAN-ACHF

When PAN fibers are subjected to heat treatment, they undergo obvious changes in the length. The shrinkage is considered to consist of two categories: physical shrinkage and chemical shrinkage, or initial shrinkage and secondary shrinkage.<sup>21,22</sup> The physical shrinkage below 180°C corresponds to entropic shrinkage and is due to oriented amorphous polymeric chains reverting to their random-coil configuration. The chemical shrinkage is mainly due to the cyclization and crosslinking reaction.<sup>23</sup>

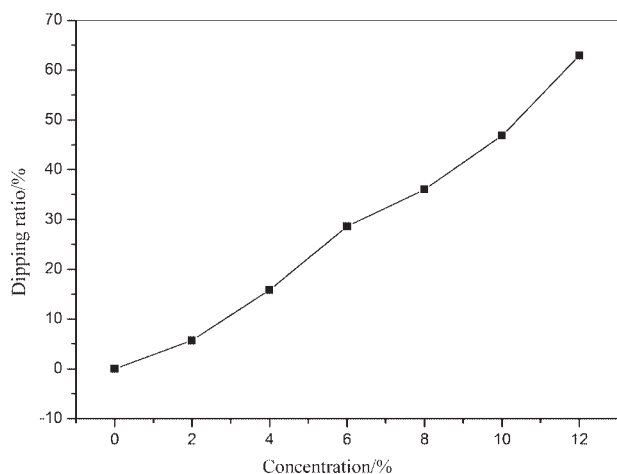
Figure 3 shows the variation in burn-off and shrinkage ratio of PAN-ACHF with concentration of ammonium dibasic phosphate aqueous solution. The weight loss and shrinkage ratio were determined from a change in weight and length before and after activation. As shown in Figure 3, the weight loss of the fibers decreases slowly with concentration of



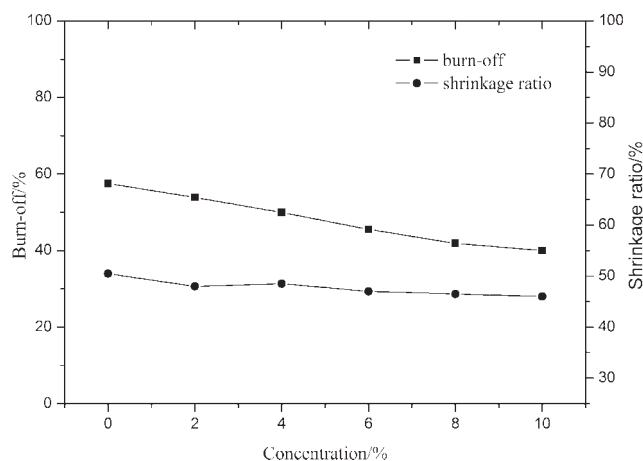
**Figure 1** The cross section of original PAN hollow fiber ( $\times 200$ ).

ammonium dibasic phosphate aqueous solution increasing. The shrinkage ratio changes little over all concentration of ammonium dibasic phosphate aqueous solution. It is suggested that the physical and chemical shrinkage of PAN hollow fibers by increasing concentration of ammonium dibasic phosphate aqueous solution is similar.

Figure 4 shows the variation in BET surface area of PAN-ACHF and surface area of mesopores in PAN-ACHF with concentration of ammonium dibasic phosphate aqueous solution. As shown in Figure 4, BET surface area of PAN-ACHF and surface area of mesopores in PAN-ACHF gradually increase when the concentration of ammonium dibasic phosphate aqueous solution is less than 4% (wt %), and reach the maximum ( $513 \text{ m}^2\text{g}^{-1}$  and  $66 \text{ m}^2\text{g}^{-1}$ , respectively) when the concentration of ammonium dibasic phosphate aqueous solution is 4% (wt %), and sharply decrease when the concentration of am-

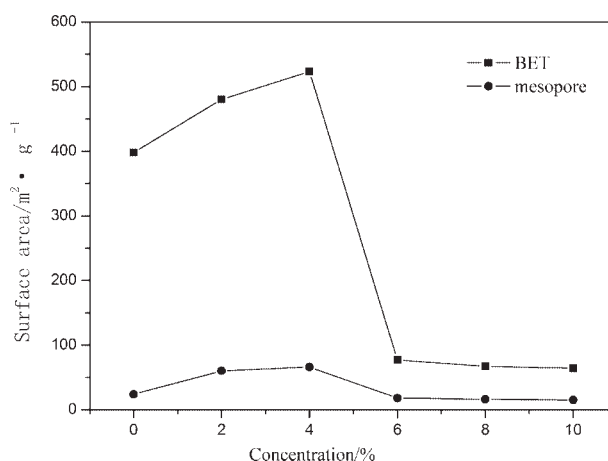


**Figure 2** Dipping ratio of PAN hollow fiber versus concentration of ammonium dibasic phosphate aqueous solution.

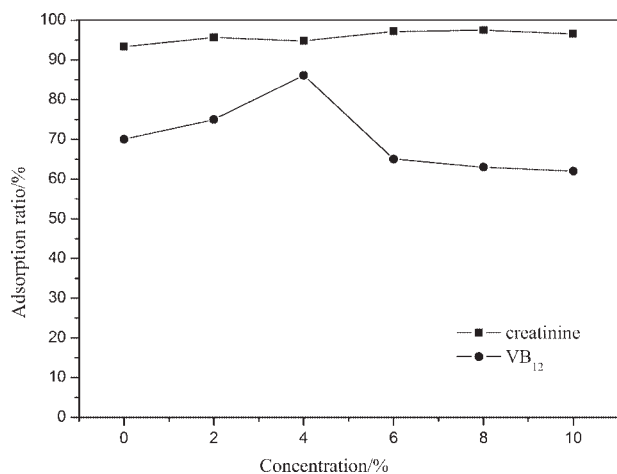


**Figure 3** Burn-off and shrinkage ratio of PAN-ACHF versus concentration of ammonium dibasic phosphate aqueous solution.

monium dibasic phosphate aqueous solution is 6% (wt %), then gradually decrease with the concentration of ammonium dibasic phosphate aqueous solution increasing. It is suggested that the number of micropores and mesopores is most in PAN-ACHF pretreated with the ammonium dibasic phosphate aqueous solution of 4% concentration, and the pores in PAN-ACHF are mainly composed of micropores. The ammonium dibasic phosphate coated on the surface of PAN hollow fibers is able to diffuse or migrate into the interior of hollow fiber through misaligned sheath layers and microstructural flaws and cracks in the hollow fibers with increasing temperature. Hollow structure of PAN fibers improves the diffusion of ammonium dibasic phosphate in the fibers. Micropores and mesopores produce on the surface and in the interior of PAN-ACHF when ammonium dibasic phosphate decomposes at lower temperature as decomposing temperature of ammonium dibasic phosphate is lower. In the later



**Figure 4** Surface area of PAN-ACHF versus concentration of ammonium dibasic phosphate aqueous solution.



**Figure 5** Adsorption ratio of PAN-ACHF versus concentration of ammonium dibasic phosphate aqueous solution.

reaction, activation gas, carbon dioxide in this experiment, can easily diffuse to the interior of PAN-ACHF because of the existence of micropores and mesopores in PAN-ACHF at the beginning of activation process. Thus, a mass of micropores and mesopores produce in the interior of PAN-ACHF and the surface area of PAN-ACHF is higher. Therefore, the amount of pores including micropores and mesopores formed in PAN-ACHF increases and the surface area of PAN-ACHF increases when the concentration of ammonium dibasic phosphate aqueous solution increases from 0–4% (wt %). But, a mass of micropores and mesopores turned into macropores when the concentration of ammonium dibasic phosphate aqueous solution is higher than 4% (wt %) and there are excessive ammonium dibasic phosphate in PAN hollow fibers. Because macropores have small specific surface area, the surface area of PAN-ACHF decreases when the concentration of ammonium dibasic phosphate aqueous solution exceeds 4% (wt %). So, higher surface area of PAN-ACHF can be obtained when PAN hollow fibers are pretreated in ammonium dibasic phosphate aqueous solution with suitable concentration for some times.

There are various types of pores in the ACHF. According to IUPAC definitions of pore size,<sup>24</sup> Micropore, width less than 2 nm; mesopore, width from 2 to 50 nm; macropore, width greater than 50 nm. 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 reported in the literature, mesopore can function a capillary condensation, thus it is indispensable for the adsorption of liquid and gas. Micropores determine the adsorption capacity of the

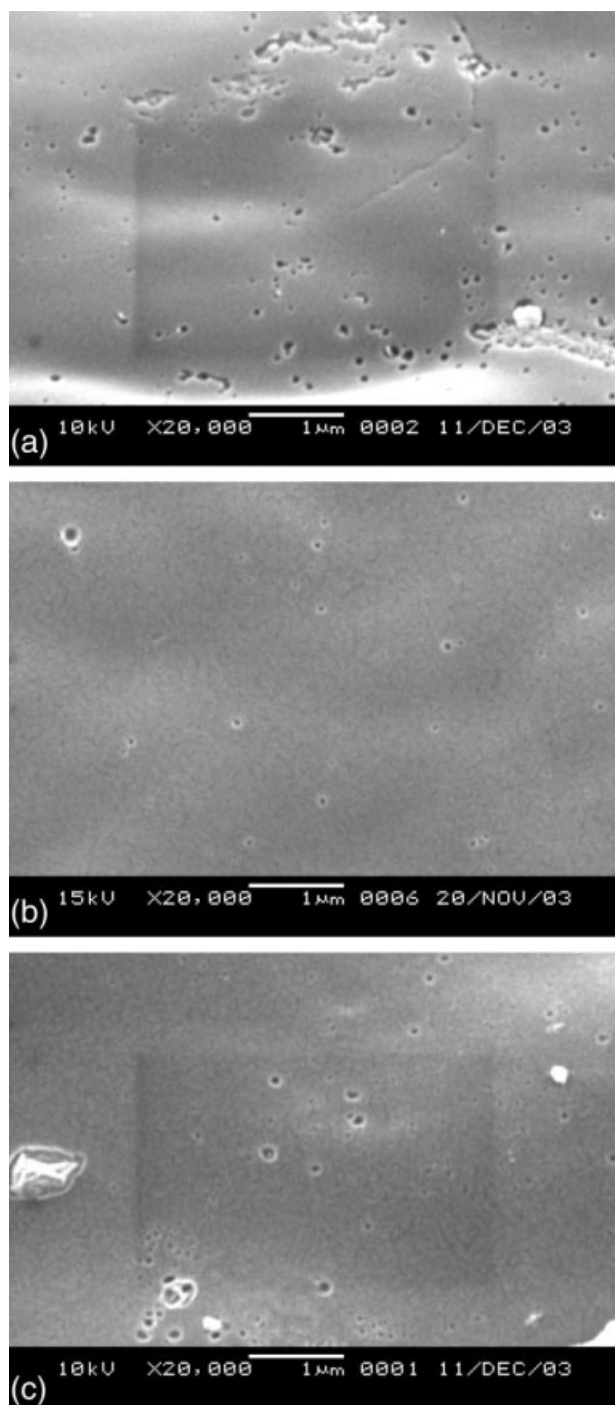
ACHF and primarily adsorb the matter of micromolecules. According to their molecule sizes, creatinine < VB<sub>12</sub>, the molecule size of creatinine are less than 2 nm and primarily adsorbed by micropores (<2 nm). However, the molecule size of VB<sub>12</sub> is larger than 2 nm and primarily adsorbed by mesopores (2–50 nm).

Figure 5 shows the variation in adsorption ratio of PAN-ACHF with concentration of ammonium dibasic phosphate aqueous solution. Initial concentrations of creatinine and VB<sub>12</sub> aqueous solutions are 20 mg/L. As shown in Figure 5, the adsorption ratios to creatinine are all higher than 90% over the whole concentration of ammonium dibasic phosphate aqueous solution. The adsorption ratios to VB<sub>12</sub> gradually increase with the concentration of ammonium dibasic phosphate aqueous solution and reach a maximum (86%) when concentration of ammonium dibasic phosphate aqueous solution is 4% (wt %), then decreases slowly. It is suggested that the number of mesopores in PAN-ACHF increases with the concentration of ammonium dibasic phosphate aqueous solution increasing, and reaches the highest value when concentration of ammonium dibasic phosphate aqueous solution is 4% (wt %). This conclusion is coincident with that concluded after Figure 4.

### Morphology of PAN-ACHF

Figure 6 shows the external surface of the PAN-ACHF made of the fiber pretreated with ammonium dibasic phosphate aqueous solution of three different concentration with 0, 4% (wt %), 8% (wt %), respectively. For the PAN-ACHF made of the fiber which is not dipped, there are some pores on the surface of ACHF. However, the size and distribution of pore diameter are not uniform, as shown in Figure 6(a). After dipping with ammonium dibasic phosphate aqueous solution of 4% (wt %) concentration, there are some pores of uniform size, but the number of pores on the surface is few, as shown in Figure 6(b). As shown in Figure 4, BET surface area of PAN-ACHF and surface area of mesopores in PAN-ACHF reach the maximum (513 m<sup>2</sup>g<sup>-1</sup> and 66 m<sup>2</sup>g<sup>-1</sup>, respectively) when the concentration of ammonium dibasic phosphate aqueous solution is 4% (wt %). It is suggested that the use of ammonium dibasic phosphate results in the development of porosity. After dipping in ammonium dibasic phosphate aqueous solution of 8% (wt %) concentration, the number of pores on the surface changes little compared with Figure 6(b). and there are more solid ammonium dibasic phosphate on the surface of membrane, as shown in Figure 6(c). As shown in Figure 4, BET surface area of PAN-ACHF and surface area of mesopores in PAN-ACHF are small when the concentration of ammonium dibasic phosphate





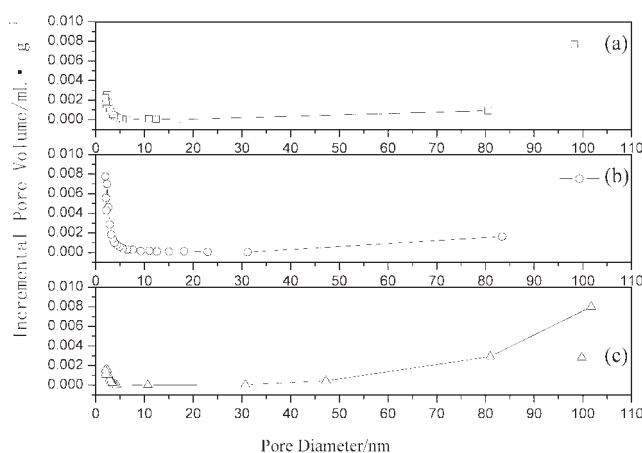
**Figure 6** SEM micrographs of the external surface of PAN-ACHF( $\times 20,000$ ) The concentration of ammonium dibasic phosphate aqueous solution of a, b, c is 0, 4%, 8% respectively.

aqueous solution is 8% (wt %). It is suggested that excessive ammonium dibasic phosphate in PAN-ACHF decomposes and more macropores produce when the concentration of ammonium dibasic phosphate aqueous solution is 8% (wt %), which results in low adsorption rate of PAN-ACHF to  $\text{VB}_{12}$ , as shown in figure 5.

### Pore size distribution of PAN-ACHF

PAN-based ACFs are amorphous graphitic carbon, consisting of  $\text{sp}^2$  hexagonal carbon layers with different pore sizes ranging from micropores to macropores.<sup>25</sup> PAN fibers activated by different methods are quite different either in graphitic microcrystallite, surface chemistry and pore size distribution.

Figure 7 shows the pore size distribution of the PAN-ACHF made of fiber pretreated with ammonium dibasic phosphate aqueous solution of three different concentration with 0, 4% (wt %), 8% (wt %), 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 by Figure 7. As shown in Figure 7, the maximum of incremental pore volume increases with the concentration of ammonium dibasic phosphate aqueous solution, and reaches  $0.0078 \text{ mL g}^{-1}$ , when the concentration of ammonium dibasic phosphate aqueous solution is 4% (wt %). Figure 7 shows the incremental pore volume of mesopores gradually decreases with average diameter, and dominant pore sizes of mesopores in PAN-ACHF range from 2 to 5 nm. As shown in Figure 4, the surface areas of mesopores in PAN-ACHF are much lower than that of BET surface area of PAN-ACHF when the concentration of ammonium dibasic phosphate aqueous solution is lower than 4% (wt %). It indicates that the pores in PAN-ACHF are mainly formed by micropores and just has a small quantity of mesopores over the whole concentration of ammonium dibasic phosphate aqueous solution. As shown in Figure 4, both of surface areas of mesopores in PAN-ACHF and BET surface area are very low when the concentration of ammonium dibasic phosphate aqueous solution is higher than 4% (wt %). It indicates that there are a small quantity of micropores and mesopores in PAN-ACHF



**Figure 7** Pore size distribution of PAN-ACHF The concentration of ammonium dibasic phosphate aqueous solution of a, b, c is 0, 4, 8% respectively.

when the concentration of ammonium dibasic phosphate aqueous solution is higher than 4% (wt %).

P-containing additives are frequently used as inhibitors for the oxidation of carbon materials. Imamura et al.<sup>26</sup> reported an increase in the steam activation rate of P-containing phenolic resin-based carbon fibers relative to equivalent samples without P in their structures; Suarez-Garcia<sup>27</sup> reported an increase in the CO<sub>2</sub> activation rate of P-containing Nomex [poly(*m*-phenylene isophthalamide)]. Nomex impregnation with phosphoric acid enhanced the reactivity during activation by an almost sevenfold factor. Our results are in better agreement with those from Imamura et al. and Suarez-Garcia et al. The characterization data available in this work indicate that chemical factors can enhance the reactivity of PAN hollow fibers by preimpregnation with ammonium dibasic phosphate.

### CONCLUSIONS

Ammonium dibasic phosphate is a beneficial activating agent during pyrolysis and activation of PAN hollow fiber with CO<sub>2</sub>. It greatly promotes pores including micropores, mesopores, and macropores to produce in PAN-ACHF by dipping PAN hollow fiber in ammonium dibasic phosphate aqueous solution. The concentration of ammonium dibasic phosphate aqueous solution has little influence on the weight loss and shrinkage of resultant PAN-ACHF. After PAN hollow fibers are dipped in ammonium dibasic phosphate aqueous solution of 4% (wt %) concentration for 30 min, because of decomposing of ammonium dibasic phosphate, the number of pores within and on the surface of the resultant PAN-ACHF reaches maximum and BET surface area of PAN-ACHF and surface area of mesopores in PAN-ACHF also reach the maximum (513 m<sup>2</sup>g<sup>-1</sup> and 66 m<sup>2</sup>g<sup>-1</sup>, respectively). The adsorption ratios to creatinine are all higher than 90% over the whole concentration of ammonium dibasic phosphate aqueous solution. The adsorption ratios to VB<sub>12</sub> gradually

increase with increasing of concentration of ammonium dibasic phosphate aqueous solution and reach a maximum (86%) when the concentration of ammonium dibasic phosphate aqueous solution is 4% (wt %), then decreases slowly. The dominant pore sizes of mesopores in PAN-ACHF range from 2 to 5 nm.

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