

# Studies on pore structures and surface functional groups of pitch-based activated carbon fibers

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## Abstract

The present study concerns the physical activation and chemical oxidation of pitch-based activated carbon fibers (ACFs) as ways to improve the adsorption properties. The surface oxides of the ACFs studied were determined by Boehm's titration and the pore structures were studied by the BET method with N<sub>2</sub>/77 K adsorption. Also, the adsorption properties of the ACFs were investigated with chromium ion adsorption by different adsorption models. As a result, it was observed that carboxyl groups were largely created after nitric acid treatment on ACFs. The affinity for chromium ions increases with increasing specific surface area, micropore volume, and surface functionalities of ACFs as the activation time increases.

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## 1. Introduction

Porous carbon materials have been widely used in separation, purification, and catalytic processes due to their extended specific surface area, high adsorption capacity, microporous structure, and special surface reactivity. The adsorption of ACFs depends on many factors, such as raw materials, activation process, pore structure, and surface functionalities [1–3].

Activated carbon can be made from various raw materials that have a high carbonaceous content, such as wood, charcoal, petroleum coke, sawdust, and coconut shells. The activation process can determine the performance of the carbon, as it can alter the physical and functional properties of the carbon surfaces [4,5]. Different methods of activation on the same raw material can yield totally different carbon characteristics. Chemical activation is performed in one step for carbonization and activation at low temperatures (e.g., 673–1073 K). Otherwise, physical activation involves the carbonization of a carbonaceous precursor followed by the gasification of the resulting char in the presence of a suitable

oxidizing gasifying agent such as CO<sub>2</sub> or steam at high temperatures (e.g., 1073–1373 K) [2].

It is well known that the adsorption behavior of activated carbons cannot be determined by their specific surface area or pore size distribution alone [6]. The porous structure of the carbon determines its adsorption capacity, while its surface functional groups affect its interaction with polar and nonpolar adsorbates. The existence of surface functional groups on carbons, such as carboxyl, phenol, lactone, and acid anhydride, has been postulated as constituting the source of surface acidity [7–11]. Active sites can determine the functional group interaction of the surface with other heteroatoms. Also, it is known that surface oxides on carbon surfaces are formed by thermal treatment at high temperatures, ozone treatment, and liquid treatment of the aqueous chemical solution [5]. Especially, surface treatments of carbons with chemical solutions are performed to give good functional groups, which improve adsorption capacity and selectivity on certain adsorbates in gaseous or liquid phase [3,12].

The main objectives of the present work were to prepare ACFs from pitch by physical activation with steam and to study the effect of the activation time and nitric acid treatment on the nanostructural properties and chromium adsorption of the final ACFs.

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## 2. Experimental

### 2.1. Materials and sample preparation

The precursor pitch was prepared by the reformation of petroleum naphtha cracker bottom (NCB) oil for 12 h at 633–663 K under nitrogen flow and then melt-spun through a nozzle ( $D = 0.3$  mm,  $L = 0.5$  mm) at 593 K. The as-spun fibers were stabilized for 6 h in an air convection oven at 553 K. Thereafter, the fibers were carbonized at 1273 K with a heating rate of 10 °C/min and held for 2 h under nitrogen flow. These carbonized carbon fibers were activated by steam diluted with nitrogen in a cylindrical quartz tube (I.D. = 50 mm,  $L = 500$  mm) at 1173 K for 30 min (ACF30M) and 45 min (ACF45M), respectively. At this time, the nitrogen flow rate was 1.6 lmin<sup>-1</sup> and the H<sub>2</sub>O/N<sub>2</sub> volume ratio was 0.44 in all cases, as previously reported [13]. These ACFs were washed with deionized water and dried overnight at ambient temperature. One gram of dry ACFs was added to a 1-l three-necked flask, equipped with stirrer, condenser, dropping funnel, and heating mantle. Thereafter, 1 M nitric acid was added slowly through the funnel. The reaction was carried out at the boiling temperature and stopped after 2 h and the oxidized ACFs (ACF30M–HNO<sub>3</sub>, ACF45M–HNO<sub>3</sub>) were washed as described above.

### 2.2. Characterization

The specific surface areas of the ACFs studied were measured by N<sub>2</sub> gas adsorption at 77 K with an automated adsorption apparatus (Micromeritics, ASAP 2400). The system and sample were outgassed at 573 K for 6 h to obtain a residual pressure of less than 10<sup>-3</sup> Torr prior to making determinations. The t-method of de Boer et al. [14] was used to determine the specific surface area and pore volume. The pore size distribution curves of micropores were obtained by the H–K method [15] from the low relative pressure region of the adsorption isotherm.

The titration method suggested by Boehm [16] was used to calculate the surface acidity of each ACF.

The adsorption of Cr(VI) from the dilute aqueous solution happens as follows: to a series of 250 ml glass bottles, various amounts of distilled water and solutions of sodium chromate (Na<sub>2</sub>CrO<sub>4</sub>·4H<sub>2</sub>O: 99.5%, Merck, USA) were fed, to a total volume of 100 ml. The initial pH of the Cr(VI) solution was adjusted with 1 N HCl to about pH 3. The bottles were sealed with paraffin film and then shaken for 24 h at 25 °C at a frequency of 240 rpm using a shaking bath. At the end of the reaction period, each reaction mixture was filtered to separate the supernatant and activated carbons. The adsorbed amount of Cr(VI) was measured using an atomic absorption spectrophotometer (HP3208).

Table 1

Textural properties of pitch-based activated carbon fibers treated with and without HNO<sub>3</sub> by nitrogen adsorption at 77 K

ACFs	$S_{\text{BET}}^{\text{a}}$ (m <sup>2</sup> g <sup>-1</sup> )	$V_{\text{m}}^{\text{b}}$ (cm <sup>3</sup> g <sup>-1</sup> )	$V_{\text{t}}^{\text{c}}$ (cm <sup>3</sup> g <sup>-1</sup> )	$D_{\text{AVR}}^{\text{d}}$ (Å)
ACF30M	1462	0.59	0.70	19.2
ACF30M–HNO <sub>3</sub>	976	0.39	0.48	19.7
ACF45M	1914	0.73	1.06	22.2
ACF45M–HNO <sub>3</sub>	1315	0.57	0.80	24.3

<sup>a</sup> BET specific surface area.

<sup>b</sup> Micropore volume.

<sup>c</sup> Total pore volume.

<sup>d</sup> Average pore diameter.

## 3. Results and discussion

### 3.1. Pore structural properties of pitch-based ACFs

The pore structural characteristics of activated carbon fibers determined by N<sub>2</sub> adsorption at 77 K are listed in Table 1. The specific surface areas of the ACF30M and ACF45M are 1462 and 1914 m<sup>2</sup> g<sup>-1</sup>, respectively, indicating that the ACF45M has a more developed pore structure. Also, activation of ACFs for relatively long times can obviously reduce the activation temperature and can overcome the defects of a high temperature of activation required to attain a larger specific surface area and offer higher potential to produce activated carbon fibers of greater adsorption capacity. As seen in Table 1, micropore volume and total pore volume are also raised with increasing activation time at 1173 K, due to the opening of blocked pores and the development of micropores due to reactions of crystallites on the opened walls with gasifying agents. As widely known, the porosity of the resulting chars can be effectively developed during the activation, and the specific surface area and pore volume commonly increase with soaking time and burn-off. The decrease of the micropore size of the activated carbons with increasing activation time agrees with the increase in micropore volume. In this work, using steam in N<sub>2</sub> with a volume ratio of 0.44 as the gasifying agent is favorable in producing an activated carbon with large micropores. Similar experimental results were reported by Rodriguez-Reinoso et al. [17] for olive stones with pure CO<sub>2</sub> and steam–N<sub>2</sub> mixture activation. They attributed the great development of micropores using steam activation to the low partial pressure of steam, which would produce a more selective attack on the carbon structure.

Figure 1 shows the N<sub>2</sub>/77 K adsorption isotherms on pitch-based activated carbon fibers. It is seen that the all adsorption isotherms are Type I according to the BDDT (Brunauer–Deming–Deming–Teller) classification, which shows the domination of micropores in the pore structure. The adsorption isotherms show a gradual adsorption increase up to relative pressure ( $P/P_0$ ) 0.3 for ACF30M and ACF45M, which can be attributed to the existence of larger micropores and/or small mesopores.

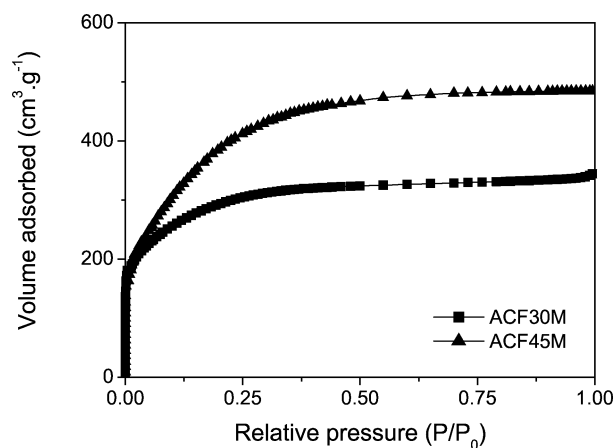


Fig. 1. N<sub>2</sub> adsorption isotherms at 77 K on pitch-based activated carbon fibers.

For better characterization of the changes, the microporous size of the pitch-based ACFs is studied, and the average micropore diameter of ACF30M and ACF45M is determined by the H–K method [15] in the low relative pressure region of the N<sub>2</sub> adsorption isotherm and summarized in Table 1. The data show, as expected, average micropore diameter decreases with increasing activation time.

Figure 2 shows the micropore size distributions of ACF30M and ACF45M. Pores within porous materials are classified as micropores (<2 nm), mesopore (2–50 nm), and macropores (>50 nm), in accordance with the classification adopted by the IUPAC [18]. It can be showed that the micropore size distribution curves of the ACF45M have multiple peaks including a maximum density at 10 Å, and the micropore size distribution is very wide; however, that of the ACF30M has only a peak with a maximum density at 15 Å, and the micropore size distribution is very narrow. As mentioned above, it is indicated that increasing activation time at the same temperature results in enhancement of micropore volume and broad range micropore size distribution.

Numerous studies on surface functionalities of carbon have already been described in the literatures [7–11]. The differences of the surface functionalities developed by activation on ACF30M and ACF45M are determined by Boehm's titration. The surface functionalities based on weight and on specific surface area of the pitch-based ACFs are listed in Table 2. The three bases used in the titration are regarded as approximate probes of acidic surface

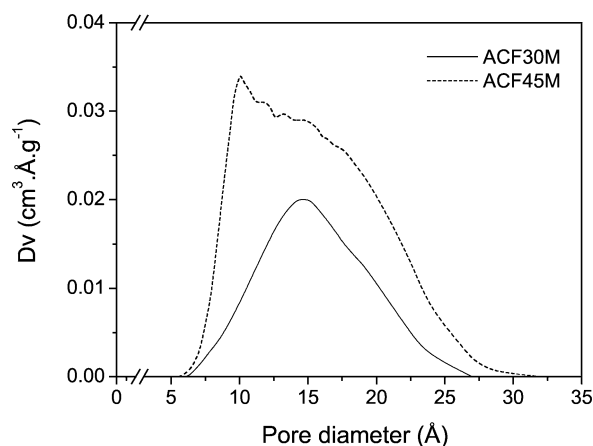


Fig. 2. Micropore size distributions of pitch-based activated carbon fibers.

functionalities: NaHCO<sub>3</sub> (carboxyl), Na<sub>2</sub>CO<sub>3</sub> (carboxyl and f-lactone), NaOH (carboxyl, f-lactonic, and phenolic). As seen in Table 2, phenol groups are enhanced, but carboxyl groups are extremely decreased with increasing activation time on pitch-based ACF surfaces. Table 2 clearly indicates that carboxyl groups on pitch-based ACF surfaces are extremely disappeared with increasing the activation time during activation.

### 3.2. Effects of nitric acid treatment on pitch-based ACFs

The surface treatment of activated carbon species with acidic chemical solutions gives functional groups, which improve adsorption capacity and selectivity on a certain adsorbate in gaseous or liquid phase [3,11]. In this work, pitch-based ACFs are modified by nitric acid in order to study changes of the nanostructural properties and surface functionalities due to acidic chemical treatment.

Figure 3 shows the N<sub>2</sub>/77 K adsorption isotherms on ACF30M–HNO<sub>3</sub> and ACF45M–HNO<sub>3</sub>. In particular, the isotherm of ACF45M–HNO<sub>3</sub> shows a sudden increase in pore volume at a high relative pressure. This implies that pore structures of ACF45M are more easily changed by nitric acid treatment. As already known from other studies [5,19], the stability of the graphite basal planes is high. Therefore, changes of pore structures on ACF45M are expected to be located at the prismatic edges of carbons, which are relatively weak and active sites of the carbon structure.

Table 2

Surface acidic functionalities of pitch-based activated carbon fibers treated with and without HNO<sub>3</sub> by Boehm's titration

ACFs	Surface acidic functionalities based on weight (meq g <sup>-1</sup> )			Surface acidic functionalities based on specific surface area (meq m <sup>-2</sup> , ×10 <sup>-3</sup> )		
	Phenol <sup>a</sup>	Lactone <sup>a</sup>	Carboxyl <sup>a</sup>	Phenol <sup>a</sup>	Lactone <sup>a</sup>	Carboxyl <sup>a</sup>
ACF30M	0.14	0.30	0.10	0.10	0.21	0.07
ACF30M–HNO <sub>3</sub>	0.26	0.60	0.90	0.27	0.62	0.93
ACF45M	0.58	0.28	0.02	0.30	0.15	0.01
ACF45M–HNO <sub>3</sub>	0.31	0.64	0.44	0.23	0.49	0.34

<sup>a</sup> NaHCO<sub>3</sub> (carboxyl), Na<sub>2</sub>CO<sub>3</sub> (carboxyl and f-lactone), NaOH (carboxyl, f-lactonic, and phenolic).

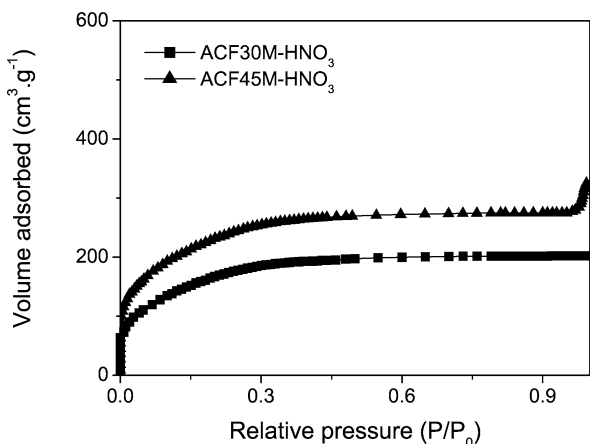


Fig. 3.  $N_2$  adsorption isotherms at 77 K on chemically modified pitch-based activated carbon fibers.

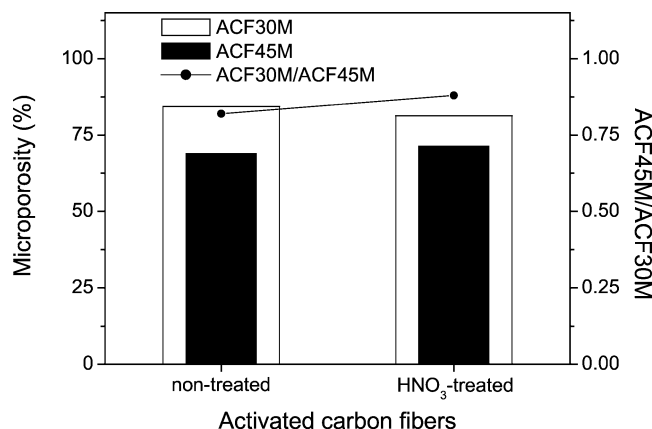


Fig. 4. Changes of microporosity on chemically modified pitch-based activated carbon fibers.

The characteristics of the resulting  $HNO_3$ -treated activated carbon fibers determined by  $N_2$  adsorption at 77 K are listed in Table 1. As seen in Table 1, the BET specific surface area, micropore volume, and total pore volume are decreased with  $HNO_3$  treatment at 1173 K.

Figure 4 shows the percentage of the microporous volume in the total pore volume of the pitch-based ACFs. After  $HNO_3$  treatment, the ACF45M/ACF30M ratio on microporosity is increased because the ACF30M and ACF45M were clearly decreased and increased on microporosity, respectively. This is also evidence that the basal panel of ACF45M is more easily changed by the nitric acid treatment than that of ACF30M.

The acid values of the modified carbons by  $HNO_3$  give a good indication of the surface properties and the electric surface changes developed by them [20]. The surface changes arise from the interaction between the carbon surface and the aqueous solution. Table 2 shows the experimental surface results of the ACFs modified by  $HNO_3$  treatment. As seen in Table 2, phenol groups are enhanced in ACF30M surfaces, but, reduced in ACF45M. Otherwise, carboxyl groups are enhanced in both ACF30M and ACF45M.

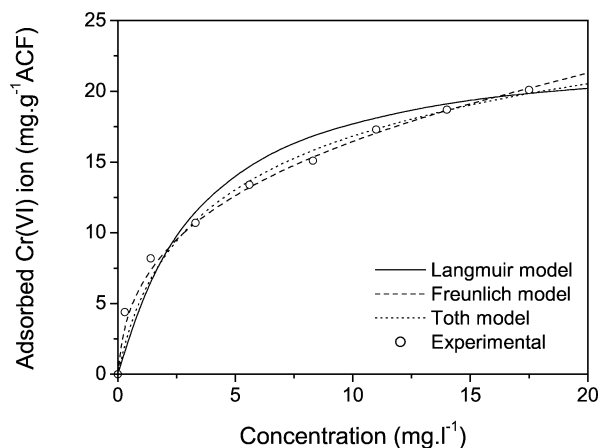


Fig. 5. Chromium ion adsorption isotherms at 298 K on ACF30M and various adsorption isotherm models.

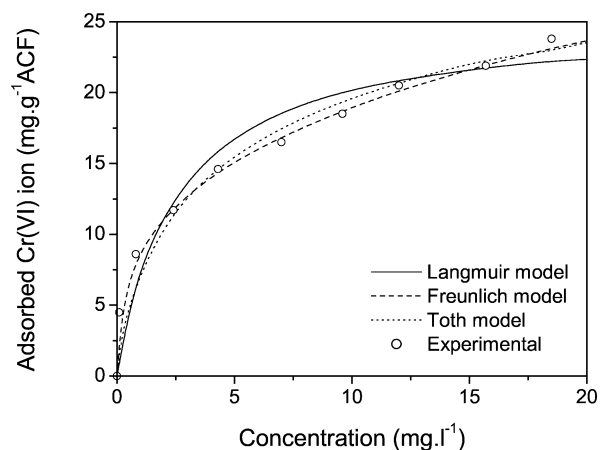


Fig. 6. Chromium ion adsorption isotherms at 298 K on ACF45M and various adsorption isotherm models.

### 3.3. $Cr(VI)$ adsorption properties on pitch-based ACFs

It is well known that the sorption of metal ions strongly depends on the surface functionalities of the carbon surfaces [9].  $Cr(VI)$  adsorption isotherms are carried out in order to study the pitch-based ACFs, which have various surface functionalities. Figures 5 and 6 are adsorption isotherms of chromium ions with various adsorption isotherm models on ACF30M and ACF45M, respectively, at 25 °C. As seen in Figs. 5 and 6, when we fitted the experimental adsorption data with various adsorption models, such as the Langmuir, Freundlich, and Toth model, we find that the model parameters varied with the activation period and there is a small trend on ACFs. The model that could best fit all sets of data is found to be the Freundlich and the Toth model.

The Langmuir equations given by

$$q_e = \frac{q_m b C_e}{1 + b C_e} \quad (\text{nonlinear form}), \quad (1)$$

$$\frac{C_e}{q_e} = \left( \frac{1}{q_m b} \right) + \left( \frac{1}{q_m} \right) C_e \quad (\text{linear form}), \quad (2)$$

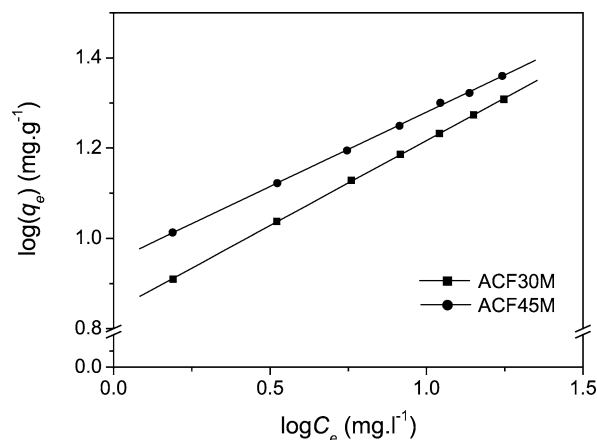


Fig. 7. Freundlich plot for the adsorption of chromium ions on ACF30M and ACF45M.

where  $q_e$  is the amount adsorbed ( $\text{mg g}^{-1}$ ),  $C_e$  is the equilibrium concentration of solute in the bulk solution ( $\text{mg l}^{-1}$ ),  $q_m$  is the monolayer adsorption capacity ( $\text{mg g}^{-1}$ ), and  $b$  is the constant related to the free energy of adsorption ( $b \propto e^{-\Delta G/RT}$ ). It is the value reciprocal of the concentration at which half saturation of the adsorbent is attained.

The Freundlich adsorption isotherm is applied to the removal of chromium ion on ACF30M and ACF45M. The Freundlich equation is given by

$$q_e = k C_e^{1/n} \quad (\text{nonlinear form}), \quad (3)$$

$$\log(q_e) = \log k + \left(\frac{1}{n}\right) \log C_e \quad (\text{linear form}), \quad (4)$$

where  $C_e$  is the equilibrium concentration in  $\text{mg l}^{-1}$  and  $q_e$  is the amount adsorbed ( $\text{mg g}^{-1}$ ). A plot of  $\log C_e$  vs  $\log(q_e)$  shows that the adsorption seems to follow the Freundlich isotherm model, as shown in Fig. 7. The constants  $k$  and  $n$  are found to be  $k = 7.01$  and  $n = 2.694$  for ACF30M and  $k = 8.85$  and  $n = 3.066$  for ACF45M, where  $k$  is a parameter of relative adsorption capacity of the adsorbent related to the temperature and  $n$  is a characteristic constant (intensity parameter of the adsorption) for the adsorption system under study. It is well known that values of  $n$  between 2 and 10 show good adsorption [21]. It is indicated that both ACF30M and ACF45M have good adsorption properties for chromium ions, ACF45M being better than ACF30M.

Parameter values of the Langmuir and Freundlich models for chromium ions on ACF30M and ACF45M are calculated and listed in Table 3. As seen in Table 3, the monolayer adsorption capacity ( $q_m$ ) and the free energy of adsorption ( $b$ ) are increased with increasing activation time for chromium ion adsorption in the Langmuir model, as well as the intensity parameter of the adsorption ( $n$ ) in Freundlich model, already seen in Fig. 7. It is indicated that the chromium ion has higher affinity for ACF45M than for ACF30M, because pore structures (nonpolar intermolecular attraction) and surface functional groups (polar intermolecular attraction between adsorbate and adsorbent) [4] of the ACF45M are more ef-

Table 3

Parameter values of Langmuir and Freundlich models for chromium ions on pitch-based activated carbon fibers

Equations	Parameters	ACF30M	ACF45M
Langmuir	$q_m^a$ ( $\text{mg g}^{-1}$ )	23.65	24.90
	$b^b$	0.305	0.419
	error	$\pm 0.03$	$\pm 0.03$
Freundlich	$k^c$	7.01	8.85
	$n^d$	2.694	3.066
	error	$\pm 0.01$	$\pm 0.04$

<sup>a</sup> Adsorption of monolayer.

<sup>b</sup> The constant related to the free energy of adsorption (constant in Langmuir).

<sup>c</sup> Constant in Freundlich.

<sup>d</sup> Characteristic constant for adsorption (Freundlich exponent).

fectively developed compared to those of ACF30M, as seen in Tables 1 and 2.

#### 4. Conclusion

The ACFs were prepared from pitch by physical activation with steam and then modified by nitric acid. The ACFs were studied with regard to microstructural properties, to surface properties, and to chromium adsorption properties. It is concluded that micropores increase with increasing activation time, due to reactions of crystallites on the opened walls with gasifying agents. After  $\text{HNO}_3$  treatment, the ACF45M/ACF30M ratio on microporosity is increased because the ACF30M and the ACF45M are decreased and increased in microporosity, respectively. The carboxyl groups on ACF surfaces are extremely disappeared during the activation. ACF30M has higher density than ACF45M on surface acidic functional groups. The chromium ion has higher affinity for ACF45M than for ACF30M, because pore structures of ACF45M are more effectively developed compared to those of ACF30M. And the adsorption models that could fit all sets of experimental data are the Freundlich and Toth models. Pore structures of the ACF45M are more effectively developed compared to those of ACF30M; otherwise ACF30M are superior to ACF45M in surface acidic functional group density.

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