

# Heavy Metal Adsorption of Anodically Treated Activated Carbon Fibers in Aqueous Solution

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## Abstract

In this work, the effect of anodic oxidation treatment on Cr(VI) ion adsorption behaviors of activated carbon fibers (ACFs) was investigated. The aqueous solutions of 10 wt% H<sub>3</sub>PO<sub>4</sub> and NH<sub>4</sub>OH were used for acidic and basic electrolytes, respectively. Surface characteristics and textural properties of ACFs were determined by XPS and N<sub>2</sub> adsorption at 77 K. The heavy metal adsorption of ACFs was conducted by ICP. As a result, the adsorption amount of the anodized ACFs was improved in order of B-ACFs > A-ACFs > pristine-ACFs. In case of the anodized treated ACFs, the specific surface area was decreased due to the pore blocking or pore destroying by acidic electrolyte. However, the anodic oxidation led to an increase of the Cr(VI) adsorption, which can be attributed to an increase of oxygen-containing functional groups, such as, carboxylic, lactonic, and phenolic groups. It was clearly found that the Cr(VI) adsorption was largely influenced by the surface functional groups, in spite of the reduced specific surface area of the ACFs.

**Keywords :** anodic oxidation, activated carbon fibers, adsorption, heavy metal ion, surface properties

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## 1. Introduction

It has been well known for many years that activated carbon fibers (ACFs) have been widely used as an excellent adsorbent because of their large surface area, microporous character, and high adsorption/desorption rate [1-3].

The adsorption/desorption rate of carbonaceous adsorbents is greatly depended on the microporous structure and the surface properties [4, 5]. The microstructure of ACFs is developed during activation, and influenced by many factors, such as the degree of activation and the conditions used for carbonization. Oxidized carbons possess some unique properties caused by oxygen-containing functional groups, such as carboxylic, lactonic, and phenolic groups on their surfaces [6, 7]. That is, the surface functional groups make the hydrophilic carbon surface, and increase its adsorption capacity and rate in the liquid phase so that these carbons can be potential adsorbents for the removal of metal ions from industrial and domestic wastewater.

Meanwhile, the anodic oxidation of carbon in the electrolytes used can produce microstructure and surface changes in the carbon surfaces [8]. The major purpose of anodic oxidation of ACFs is obtaining a more hydrophilic surface structure with a relatively large number of oxygen-containing surface groups [4, 9, 10].

In this work, ACFs were modified by anodic oxidation with acidic or basic electrolyte to obtain oxygen-containing functional groups, and the effect of anodic oxidation treat-

ment on ACFs was studied in the context of Cr(VI) ion adsorption behaviors.

## 2. Experimental

### 2.1. Materials and Sample preparation

The pitch-based carbon fibers were supplied from Kureha (Japan), and they were activated by steam diluted with nitrogen at 900°C. These ACFs were washed with deionized water and dried for 24 h at 80°C (pristine-ACFs). The ACFs were subjected to electrolytic reaction in the aqueous solutions of 10 wt% H<sub>3</sub>PO<sub>4</sub> (A-ACFs) and NH<sub>4</sub>OH (B-ACFs), whereby negative ions were attracted to the surface of the ACFs acting as an anode, thereby modifying the ACF surfaces. A cathode graphite plate was also submerged in the electrolyte solution, and the conditions of the surface treatment were processed in an electro-bath at 7 A for 10 min.

### 2.2. Surface characteristics and textural properties

The surface properties of ACFs were measured by XPS (X-ray photoelectron spectroscopy, ESCA LAB MKII). The XPS was collected using a MgK<sub>α</sub> X-ray source (1253.6 eV) and the pressure inside the chamber was held below 1 × 10<sup>-9</sup> torr.

Specific surface area was calculated from the Brunauer-Emmett-Teller (BET) equation for N<sub>2</sub> adsorption at 77 K (Micromeritics, ASAP 2010) [11]. The t-method of de Boer

was used to determine the micropore volume [12]. The pore size distribution curves of micropores were obtained by the Horvath-Kawazoe (H-K) method [13].

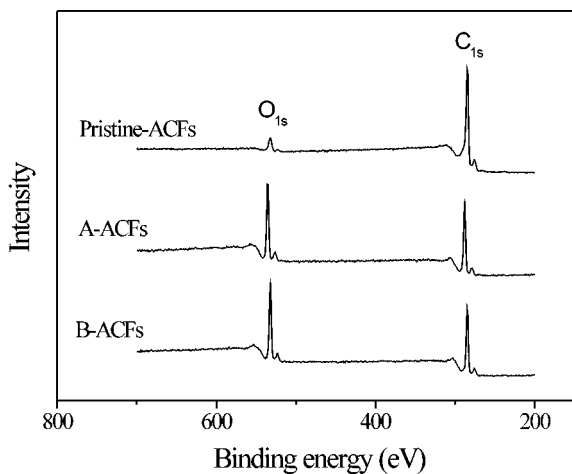
### 2.3. Adsorption of heavy metal ion

0.05 g of each of the activated carbon fibers were placed in 150 ml of 20 ppm sodium chromate ( $\text{Na}_2\text{CrO}_4 \cdot 4\text{H}_2\text{O}$ ) solution for the adsorption of Cr(VI) ion. The initial pH of the Cr(VI) solution was adjusted to pH 3 with 0.1 N HCl and NaOH, respectively. The bottles were sealed with paraffin film and then shaken on a time sequence of 10, 20, 30, 40, 50, 90, and 180 min at 25°C at a frequency of 100 strokes/min using a shaking bath. At the end of the reaction time, each reaction mixture was filtered to separate the supernatant and activated carbon fibers. The adsorbed amount of Cr(VI) was measured by ICP-AES (Jovin-Yvon Ultima-C). The amount of adsorbed heavy metal ions was obtained by calculating the difference of each concentration of heavy metal ions before and after adsorptions.

## 3. Results and Discussion

### 3.1. Surface characteristics and textural properties

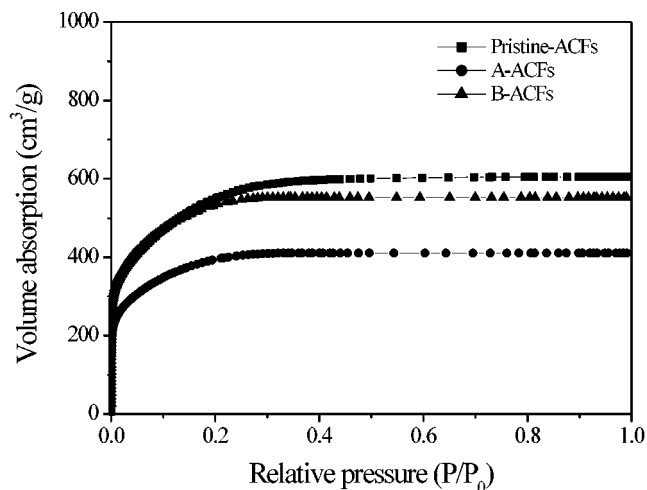
XPS is used to determine the elemental composition on ACF surfaces. Figure 1 shows the XPS survey scan spectra of the non-treated and the anodically treated ACFs. The  $\text{C}_{1\text{S}}$  and  $\text{O}_{1\text{S}}$  peaks of ACFs are found at the binding energy of about 284.6 and 532.8 eV, respectively [14]. As seen in Figure 1, the intensity of  $\text{O}_{1\text{S}}$  peak of anodically treated ACFs is increased and the intensity of  $\text{C}_{1\text{S}}$  peak of the treated ACFs is decreased. Also, Table 1 represents the XPS results of the chemical compositions of the treated ACF surfaces. The content of oxygen and the  $\text{O}_{1\text{S}}/\text{C}_{1\text{S}}$  ratio were increased by the anodic oxidation. This is clearly attributed to the increase



**Fig. 1.** XPS survey scan spectra of activated carbon fibers before and after anodic oxidation.

**Table 1.** Results for the  $\text{O}_{1\text{S}}/\text{C}_{1\text{S}}$  Ratio of Anodically treated ACFs

	Elemental analysis		
	$\text{C}_{1\text{S}}$ (mol.%)	$\text{O}_{1\text{S}}$ (mol.%)	$\text{O}_{1\text{S}}/\text{C}_{1\text{S}}$
Pristine-ACFs	92.5	6.5	0.070
A-ACFs	53.7	26.6	0.495
B-ACFs	53.5	26.7	0.499



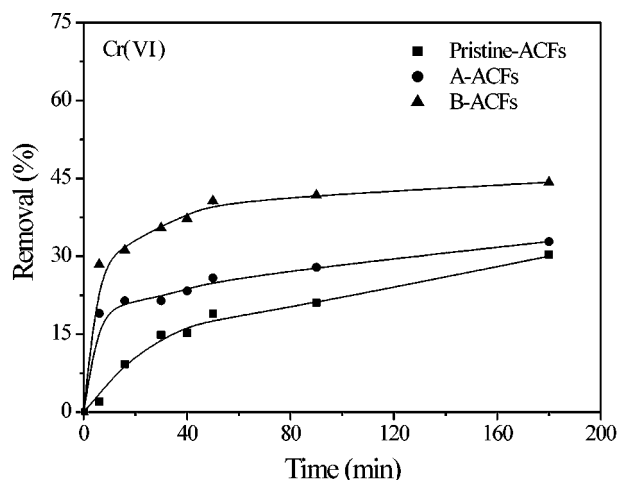
**Fig. 2.** Adsorption isotherms of  $\text{N}_2$  at 77 K on activated carbon fibers.

of oxygen-containing functional groups on the ACF surfaces. The result can also be explained by that the anodic oxidation treatment produces various oxygen-containing functional groups, *i.e.*, carboxylic, lactonic, and phenolic groups on the ACF surfaces.

The nitrogen adsorption isotherms of anodically treated ACFs are shown in Figure 2, and the pore structure of the treated ACFs is summarized in Table 2. As expected, the adsorption isotherms studied are typical type I, according to the IUPAC classification [15]. This means that all the modified ACFs are systematically microporous. Also, the specific surface area of the Pristine-ACFs, A-ACFs, and B-ACFs were 1944, 1430, and 1757  $\text{m}^2\text{g}^{-1}$ , respectively. That is, the BET's specific surface area was decreased by 26% for A-ACFs compared to the pristine-ACFs. This might be explained by that the micropores of A-ACFs were destroyed by the acidic electrolyte. The destroyed micropores of A-

**Table 2.** Textural Characteristics of Anodically Treated ACFs

	BET surface area [ $\text{m}^2\cdot\text{g}^{-1}$ ]	Micropore volume [ $\text{cm}^3\cdot\text{g}^{-1}$ ]	Total pore volume [ $\text{cm}^3\cdot\text{g}^{-1}$ ]
Pristine-ACFs	1944	0.787	1.027
A-ACFs	1430	0.243	0.560
B-ACFs	1757	0.660	0.781



**Fig. 3.** Adsorption of metal ions onto activated carbon fibers as a function of reaction time.

ACFs led to a decrease of specific surface area or micropore volume. Also, total pore volume and micropore volume of anodically treated ACFs were decreased. This was due to the increase of oxygen-containing functional groups, which were attributed to the block of the micropores.

### 3.2. Adsorption of heavy metal ion

The results of percentage adsorption of Cr(VI) ion on the ACFs from aqueous solution are presented in Figure 3. It was clearly observed that the initial adsorption rate of Cr(VI) ion on the ACFs increased rapidly, especially due to the molecular sieve structures of ACFs. The percentage adsorption of Cr(VI) ion increases with increasing the reaction time and the percentage adsorption of Cr(VI) ion of anodically treated ACFs was superior to that of pure-ACFs. It was probably accounted that the anodic oxidation of ACF surfaces led to an increase of oxygen-containing functional groups, resulting in improving the adsorption capacity of ACFs. Also, A-ACFs show lower percentage adsorption of Cr(VI) ion than that of B-ACFs. It seems to be due to the destruction of micropores by acidic electrolyte, resulting in decreasing the specific surface areas.

## 4. Conclusions

In this work, the anodically treated ACFs were used to

investigate the adsorption characteristics in terms of the microstructures and surface functional groups. In the results of XPS and BET measurements, the specific surface area of the anodized ACFs was decreased by the pore blocking of surface functional groups and the treatment of acidic electrolyte. However, the oxygen-containing functional groups of the treated ACFs were significantly increased, which could be attributed to the increasing of the Cr(VI) adsorption of ACFs. It was concluded that the heavy metal adsorption was greatly influenced by the surface functional groups, in spite of the reduced specific surface area of the ACFs.

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