

## Chloride ion removal effect for the ACF electrochemically treated with silver

Won-Chun Oh<sup>★1</sup> Choung-Sung Park<sup>2</sup> and Jang-Soon Bae<sup>3</sup>

<sup>1</sup>Department of Advanced Materials & Science Engineering, Hanseo University, Chungnam 356-706, Korea

<sup>2</sup>Department of Environmental Engineering, Hanseo University, Chungnam 356-706, Korea

<sup>3</sup>Department of Industrial Chemistry, Dankook University, Chungnam 330-714, Korea

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**Abstract :** The removal efficiencies of silver-ACFs were associated with their surface properties such as surface area, porosity, and the electro-chemical reaction time for the silver treatments. X-ray diffraction patterns of fibers electrochemically treated with silver display diffraction peaks for metallic silver and kinds of silver chloride complexes on the fiber surface after electrochemical adsorption. The results of SEM and EDX indicate that surface reaction motive of silver-ACF prepared by electrochemical reaction are depend on time function for the chloride ion removal efficiency. Finally, Cl ion adsorbed by the silver-ACFs from the ICP analysis seems to show an excellent removal effect.

**Key words :** silver-activated carbon fiber, surface area, SEM/EDX, XRD, ICP

### 1. Introduction

Activated carbons and their fiber have been extensively used not only as an adsorbent but also a catalyst support or even a direct catalyst. In particular, activated carbon fiber has often been used to support active metal for removal of air or water pollutants. There are various techniques for removing small amounts of organic or inorganic compounds from aqueous solution, including electrolysis, precipitation, and ion exchanges. On the other hand, activated carbon fiber is a carbon-based material with a developed pore structure that is widely used as an adsorbent for gas purification, solvent recovery, and removal of other pollutants. It has also been used for adsorption of organic or inorganic ions from the

standpoint of environmental problems, many studies have appeared regarding the removal of heavy metals utilizing electrochemical methods based on activated carbon and their fibers.<sup>1-3</sup> The unique adsorption characteristics of activated carbon and its fiber were found to depend on the specific surface area, pore structure, surface functional groups. Moreover, the surface functional groups anchored on carbon were found to be responsible for the variety in physico-chemical and catalytic properties of the matter considered. In the past few years, research to study the removal of metal ions from aqueous solution using carbon electrodes has been carried out.<sup>4,5</sup> The proposal was to capture the various ions and compounds in the activated carbon pores by transport of the ions or interaction of dipole moments using electrostatic

★ Corresponding author

Phone : +82-(0)41-660-1337 Fax : +82+(0)41-688-3352

E-mail: wc\_oh@hanseo.ac.kr

force. The technique of electro-chemical adsorption, which is an added electrical driving force to the traditional adsorption or ion exchange mechanism, has reversible properties of purifying waste solution by adsorption and concentrating pollutants by desorption. The using of metal-ACFs for an efficient removal of trace components from liquid system is of highly homogeneous distribution of metal in the electro-catalytically designed device.

The purpose of this study is to propose for the preparation of homogenous silver treatment by electro-chemical method, to effectively remove trace amounts of  $\text{Cl}^-$  from aqueous solution using highly porous carbon materials homogenous distributed with metal and to develop a method to regenerate the silver-ACFs. The  $\text{Cl}^-$  removal capacities of silver-ACFs were related to physical properties such as surface area, pore volume and pore size. XRD spectra provided information on the nature of bonds formed between Ag-ACFs and removed  $\text{Cl}^-$ : it provides information on the intermediates and products formed on the surface. The morphologies on carbon surfaces were observed by SEM to explain the changes in removal properties. And, quantitative properties in the ACFs were also studied by EDX. Finally, ICP for the elemental analysis in chloride ion solutions after column removal was used to study the quantitative properties.

## 2. Experimental

### 2.1. Preparation procedures of raw materials

Felt typed ACFs were heated first at 823 K for sizing removal, and the ACFs were reactivated for obtaining large surface area by steam diluted with nitrogen in a cylinder quartz glass tube in the temperature range of 1053~1073 K for 30 min. The characteristics for the ACF were listed in further study.<sup>6</sup> For electrochemically metal treatments,  $\text{AgNO}_3$  (Aldrich, 99+%, ACS reagent) was used as an Ag source.

### 2.2. Electro-chemical treatment

The test electrodes were fabricated as follows. A working electrode consisted of a size of 20(b)×

50(h)×5(t) mm for the felt type activated carbon fiber, while the counter electrode of same size was artificial graphite (TCK, Korea). The electrolyte was 0.1M silver nitrate solution for 1, 30 and 60 min. The electrode properties were investigated by electrochemically adsorbed metal ion measurements at  $0.5 \text{ mAcm}^{-2}$  at room temperature. The measured voltage was set to 4.5V. All the measurements were conducted in a glove box containing dry argon at room temperature.

### 2.3. Bed column experimental methods

The authors<sup>7</sup> describe the equipment used during these fixed bed column studies previously. It consisted of a PE (Polyethylene) make-up tank in which the process effluent added at a concentration of 156 ppm NaCl. The solution was then gravity fed to a feed tank, having a volume of 100 liters and from which the effluent was pumped using a peristaltic pump at constant flow rate of  $10 \text{ mL} \cdot \text{min}^{-1}$ . The effluent solution was fed through a bed of silver-ACFs in up-flow mode. The silver-ACF beds were contained in glass columns with diameter 30 mm to which a both end plate with inlet and outlet nozzle was attached. The columns gave a standard bed height of 250 mm which resulted in beds with silver-ACFs mass of approximately 200 g of 2 mm thickness size.

### 2.4. Measurement

For measurements of the physical adsorption properties of the activated carbon fiber felts electrochemically treated with silver ions, Degisorb 2500 (Micrometrics Instruments Co., USA) volumetric adsorption analyzer was used to study the nitrogen adsorption measurements at 77K. During the process of adsorbed volume measurements, nitrogen gas of 99.99999% (Nippon Oxygen Gas Co., Japan) was used as an adsorbent. BET specific surface area, pore volumes and pore diameter for the felts were investigated from the measurements. Before the measurements, all of the felts were heated to 350°C in a high vacuum (ca.  $1.33 \times 10^{-3} \text{ Pa}$ ) for 5 h as a degassing condition. Scanning electron microscopy (SEM,

Table 1. Physical Parameters of Ag-ACF before and after NaCl Solution Treatments

Sample	BET Surface area (m <sup>2</sup> /g)	Micropore Volume (cm <sup>3</sup> /g)	Adsorption Average Pore Diameter (Å)	Micropore Surface Area(m <sup>2</sup> /g)	
As-received	1582	0.45	16.65	1015.2	
Before	0.1Ag-1M-ACF	1005	0.34	15.24	882.1
	0.1Ag-30M-ACF	998.5	0.32	15.22	863.1
	0.1Ag-60M-ACF	967.7	0.30	15.21	837.8
	0.1Ag-120M-ACF	936.9	0.29	15.21	810.2
After	0.1Ag-1M-ACF	935.4	0.29	15.22	812.3
	0.1Ag-30M-ACF	869.2	0.28	15.18	789.2
	0.1Ag-60M-ACF	852.1	0.26	15.10	762.8
	0.1Ag-120M-ACF	828.7	0.25	15.11	723.5

Ag : Silver nitrate concentration(M)

M : Silver treatment time (min.)

JSM-5200 JOEL, Japan) was used to observe the surface state and structure of silver treated ACFs and the formation of silver compounds on the surfaces. For the elemental analysis in chloride ion solutions after column removal, Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP-AES, Jovin Yvon Ultima-C) was used.

### 3. Results and Discussion

Generally, electrochemical studies on the deposition of metal ions to the activated carbon fibers indicated that such a process consists of several consecutive steps<sup>8,9</sup>: transfer of the metal ions from the bulk solution to the proximity of the fiber surface, surface diffusion of metal ions towards active sites, adsorption of the metal ions, growth of metals on the fiber surface, reduction of metal ions on the fiber surface, and incorporation of the metals into the fiber lattice. This method for the electrochemical treatment of metal has the merit of a homogeneous distribution of metal on the fiber surface without impurities like metal oxide compounds.

The N<sub>2</sub> isotherms at 97 K were determined using a conventional volumetric apparatus. From the isotherms, which are omitted for the sake of brevity, the BET surface area ( $S_{\text{BET}}$ ) was obtained as usual. Table 1 shows the values of  $S_{\text{BET}}$ , external surface area ( $S_{\text{ext}}$ ), volume of micropores ( $V_{\text{m}}$ ), and average pore

diameter (APD) of silver-ACFs before and after NaCl solution treatment. As shown in Table,  $S_{\text{BET}}$ s were distributed between 936.9 and 1005 m<sup>2</sup>/g before column filtration. Increasing electro-chemical reaction time in silver solution leads to a decrease in micropore volume, external surface area and APD. That is, the number of pores decreases with electro-chemical reaction times. And also, the blocking of pore with NaCl solution filtration is more significant as silver compound formation with decreasing of  $S_{\text{BET}}$ s. The values of  $S_{\text{BET}}$  were decreased nearly 36.0-40.9% for the non-treated Ag-ACFs, but the values decreased 40.9-47.6% at NaCl solution treatments. The subsequent filtration with Cl<sup>-</sup> at the levels employed in this study led to additional, though less significant, decreases in those parameters.

Electrochemical reductive adsorption is one mechanism which could lead to increasing Ag<sup>+</sup> adsorption. Reductive adsorption with ACF removes Ag<sup>+</sup> from solution by deposition of Ag<sup>0</sup> onto the surface. Meanwhile, it is well known that XRD technique for knowing the detailed and precise microstructure, such as the metal salts formation and their crystalline on the fiber surface (Fig. 1). X-ray diffraction patterns of fibers electrochemically treated with silver display diffraction peaks for metallic silver on the fiber surface after electrochemical adsorption.<sup>1)</sup> When the activated carbon fibers were treated with silver, major peaks were observed;  $2\theta = 38.021$

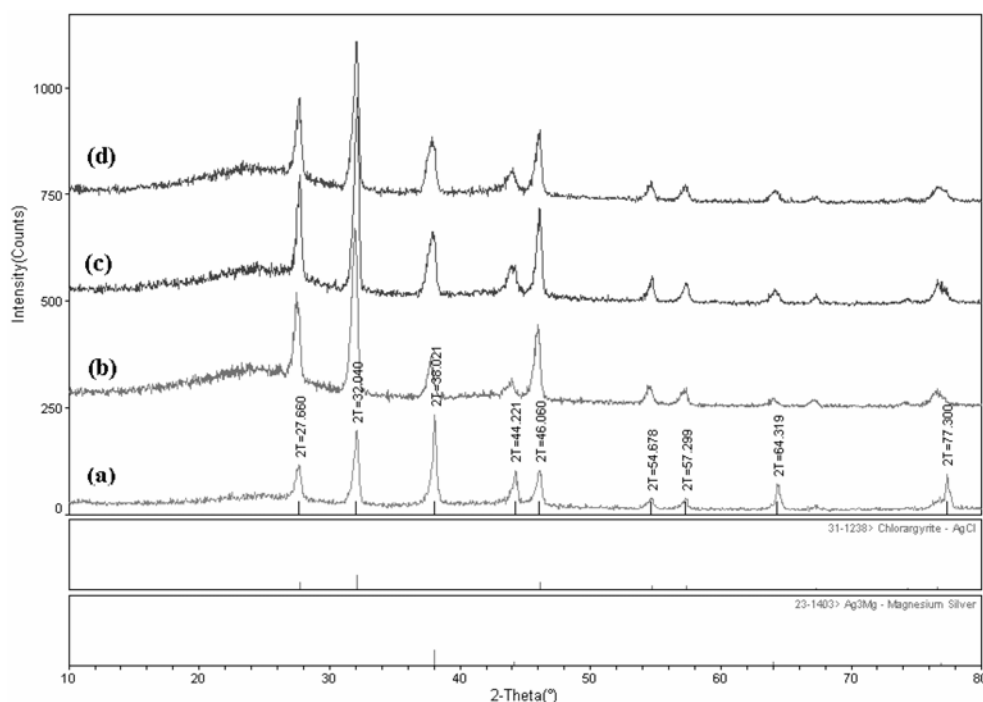


Fig. 1. X-ray diffraction patterns of activated carbon fibers electrochemically adsorbed with silver and their chloride ion removal effect; (a) 0.1Ag-1M-ACF (b) 0.1Ag-30M-ACF (c) 0.1Ag-60M-ACF (d) 0.1Ag-120M-ACF.

(Ag(111)),  $2T = 44.221$  (Ag(200)) and  $2T = 64.319$  (Ag(220)). Minor peaks were also observed as kinds of silver chloride complexes on the carbon surfaces. The complexes formed on the surface through the filtration of the solution including chloride ion exhibits silver chloride complex for the carbon active sites. We found that chloride ions are removed and adsorbed due to capturing of silver-ACFs by physicochemical attraction forces.

Fig. 2 shows the SEM micrograph of Ag-ACFs after filtration of NaCl solution. SEM observation of numerous surfaces and cross-section of silver and its complexes containing ACFs show that the particles and agglomerates are evenly distributed and irregular in shape and size. Comparison of these micrographs shows that the transformation of the carbon surface by removal chloride does significantly change the surfaces of the matrix of the Ag-ACF. These figures showed the surface morphology and silver complexes attached on the activated carbon fiber surface. Analyzing texture, the modification by silver treat-

ment on the ACFs, which are clogged by the adsorbed silver molecules. Various levels of brightness indicate differences in the surface chemistry, a consequence of the time function. This also explains the reasons for the reduction in the surface of silver-ACFs as compared with non-treated ACFs.<sup>6</sup> From these results, it was shown that the number of silver compounds on the surface increase with increasing of function time. In addition to, external surface polluted with dendrite and frost formation could be observed. Samples treated with higher operation time like 0.1Ag-60M-ACF and 0.1Ag-120M-ACF, which are also observed much aggregated particles and agglomerated silver chlorides.

The EDX spectra of silver-ACFs transformed by chloride ion containing solution are shown in Fig. 3. These spectra showed the presence of C, O and Ag with strong Cl peak. The results of EDX elemental microanalysis of Ag-ACFs are listed in Table 2. In the most of the samples, carbon and chloride are present as major elements in the Ag-ACFs after

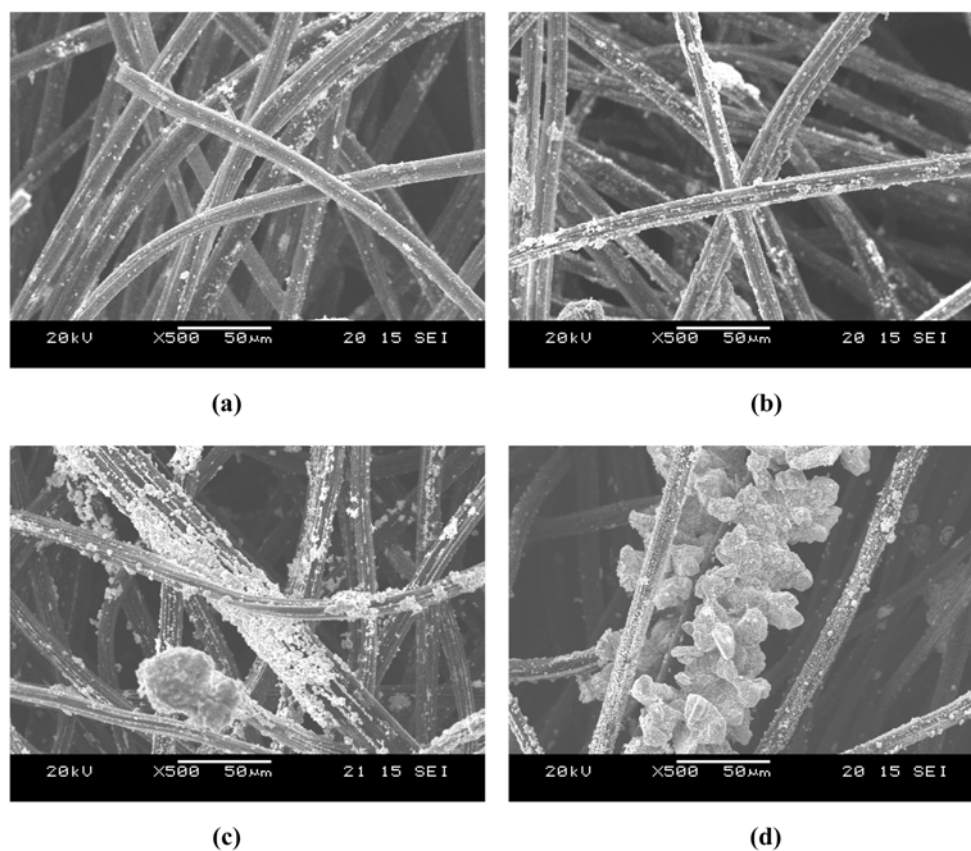
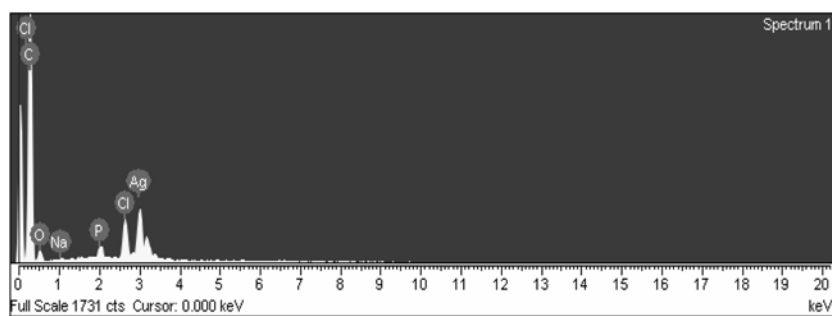


Fig. 2. SEM images of 0.1Ag-ACF series after NaCl solution treatments; (a) 0.1Ag-1M-ACF (b) 0.1Ag-30M-ACF (c) 0.1Ag-60M-ACF (d) 0.1Ag-120M-ACF.

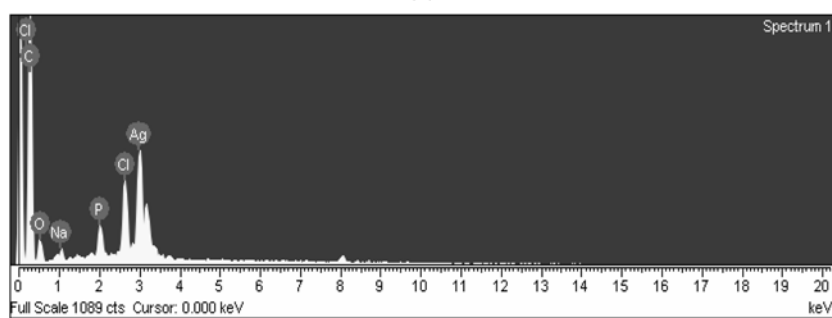
treatment of sodium chloride solution. These results were obtained that the spectra corresponding to almost all samples showed an increasing of the major elements like a silver and chloride according to operation time. It should be note that an increase of the Cl content with decreasing of the C content is observed for the over all sample series, which become more heterogeneous as the silver-carbon fiber surface adsorbs chloride ions. The results of SEM and EDX indicate that surface reaction motive of silver-ACF prepared by electrochemical reaction are depend on time function for the chloride ion removal efficiency. Oh *et al.*<sup>3</sup> reported that the removal efficiency of various metal elements from wastewater appeared to be very good from EDX results using primitive ACF.

Chloride ion removal efficiency for 0.1Ag-ACF

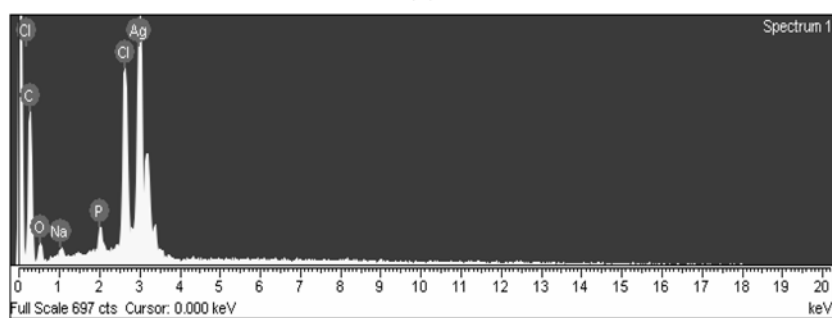
series after filtration of NaCl solution is shown Fig. 4. This application of Ag-ACFs for chloride compound removal is becoming more important because of the environmental aspects. Different metals, metal oxides and zeolites have been used in the selective catalytic reduction.<sup>10</sup> The removal of these Cl ions with Ag-ACFs treated with an electro-chemical method might be an attractive alternative to these traditional compound removal methods. Ag-ACFs can also be used as catalysts and catalytic supports in the ECR. The Cl ion in wastewater are transformed into an electron donor. The average concentrations of Cl ions in the primitive samples were over 156 ppm, while the final water purified by filtration was 4.9 ppm for the these Ag-ACF series. According to comparing test, Cl ions adsorbing and removing by the Ag-ACFs were an excellent effect in 0.1Ag-



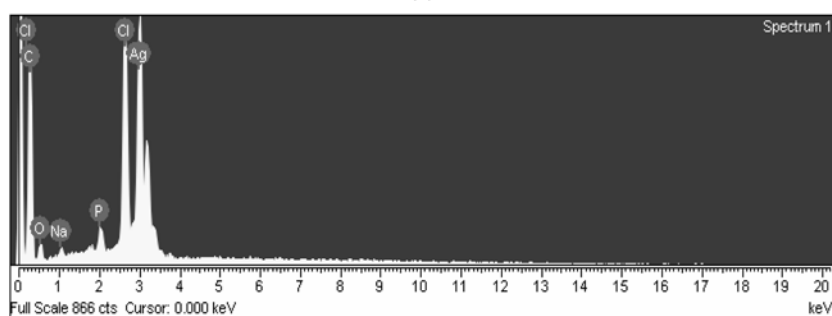
(a)



(b)



(c)



(d)

Fig. 3. Typical EDX microanalysis for 0.1Ag-ACF series after NaCl solution treatments; (a) 0.1Ag-1M-ACF (b) 0.1Ag-30M-ACF (c) 0.1Ag-60M-ACF (d) 0.1Ag-120M-ACF.

Table 2. EDX Elemental Micro-Analysis of Ag-ACFs after NaCl Solution Treatment

Sample	Elements (%)					
	C	O	Na	P	Cl	Ag
0.1Ag-1M-ACF	75.6	8.78	0.36	0.94	3.0	11.3
0.1Ag-30M-ACF	64.2	11.4	0.67	1.62	4.14	18.0
0.1Ag-60M-ACF	54.0	6.93	0.62	1.02	8.82	28.6
0.1Ag-120M-ACF	50.0	8.82	0.82	1.05	8.80	34.6

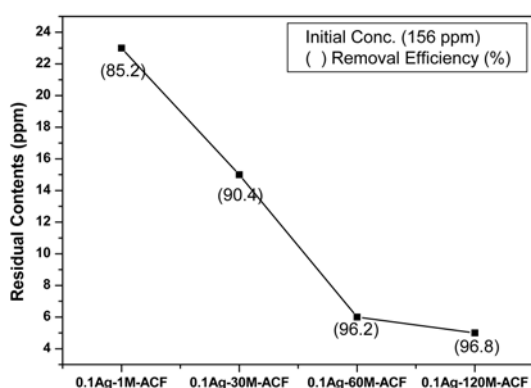


Fig. 4. Chloride ion removal efficiency for 0.1Ag-ACF series after filtration of NaCl solution.

129M-ACF case.

#### 4. Conclusions

The effectively remove of trace  $\text{Cl}^-$  from aqueous solution using highly porous carbon materials homogenous distributed with metal and a method to regenerate the Ag-ACFs were developed. The removal efficiencies of silver-ACFs were associated with their surface properties such as surface area, porosity and the electro-chemical reaction time for the silver treatments. X-ray diffraction patterns compared to the fibers electrochemically treated with silver display diffraction peaks for metallic silver and kinds of silver chloride complexes on the fiber surface after electrochemical adsorption. SEM micrographs showed that the silver complexes attached on the activated carbon fiber surface and transforma-

tion of the carbon surface by removal chloride does significantly change the surfaces of the matrix of the Ag-ACF. The results of EDX elemental microanalysis of Ag-ACFs showed that the presence of C, O and Ag with strong Cl peak. According to the ICP analysis, Cl ions adsorbed by the Ag-ACFs showed an excellent removal effect in 0.1Ag-129M-ACF case.

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