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Characteristics of electroless copper-deposited activated carbon fibers for antibacterial action and adsorption–desorption of volatile organic compounds

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Microorganisms collected on filter surfaces could affect the integrity of the filters and the release of microorganisms [1], so antibacterial treatment has to be applied to the air filter media in order to improve the air quality. Park and Jang [2], Tamai et al. [3] and Li et al. [4] have reported that bacteria preferably adhere to the solid carbon material. Moreover, Cecchini et al. [5] and Verdenelli et al. [1] reported that bacteria can adhere to glass acrylic fiber. Previous studies [6,7] have shown that antibacterial formulations only in the form of fine particles could be used as effective antibacterial materials. In this paper, we chose activated carbon fibers (ACFs) made of a type of highly microporous carbon material [2], as the air filter medium. Fine copper particles were selected as the antibacterial material [8]. The particles were forced to deposit on the ACFs to prevent bacteria from breeding on the surface

of the ACFs. Previous studies [6,7] have focused on the preparation and characterization of antibacterial materials rather than the method of deposition of antibacterial materials on the ACFs.

Recently, electrolytic metal deposition on carbon surfaces in an aqueous solution of metal has been proposed as a useful method for introducing metal onto carbon surfaces and into the micropores of carbons [9]. Electroless metal deposition is a kind of electrolytic metal deposition and it can be effective for coating ACFs [10]. Electroless metal deposition refers to the deposition of metal on a substrate, without external electric current, by an oxidation–reduction reaction [11]. This procedure can yield mechanically durable fine metal layers with high-specific surface areas. With the electroless deposition technique, filter material in some channels with complex configuration can be easily and uniformly deposited, provided that the deposition solution is in contact with the walls [12].

In this study, we prepared copper fine particles supported by rayon-based ACFs through electroless copper

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deposition. Then we characterized the particles and ACFs by field emission scanning electron microscopy (FESEM), inductively coupled plasma (ICP) analysis, and X-ray diffractometry (XRD). Next, we determined the antibacterial characteristics of prepared copper-deposited ACFs by varying copper deposition time. Finally, we studied the adsorption and desorption characteristics for removing volatile organic compounds (VOCs) via the prepared copper-deposited ACFs.

The rayon-based ACFs studied in this work were manufactured by Toyobo (KF-1500, Japan). Electroless copper depositions onto the ACFs were performed in our laboratory by using commercial electroless copper deposition solutions [13]. Details of the copper deposition procedure are presented in the Supplementary data. A field emission scanning electron microscope (FESEM, JSM-6500F, JEOL, Japan) was used to observe the surface morphology of the ACFs and the distribution of the copper particles. The amount of copper particles on an ACFs sample was determined by inductively coupled plasma (ICP, Elan 6000, Perkin–Elmer, US). About 0.1 g of the sample was inserted to 50 mL of nitric acid solution, which was then diluted with 50 mL of DI water. After 3 h, the sample was filtered and a part of the remaining mixture was placed in a volumetric flask for ICP analysis. To study the surface structures of the ACFs, wide-angle X-ray diffraction (XRD) patterns of the ACFs were obtained with a Rigaku Model D/MAX-Rint 2000 diffraction meter (Japan) and using $\text{CuK}\alpha$ radiation ($\lambda = 0.15418$ nm) at 30 kV and 20 mA. A thin powder sample of the ACFs was placed onto an oriented monocrystalline quartz plate; it was scanned from 10° to 80° (2θ) at a speed of $4^\circ/\text{min}$.

The antibacterial activity trend of these prepared ACFs samples was determined by using the modified Kirby-Bauer agar diffusion method [1]. Four experimental bacterial strains were used, i.e. two Gram-negative strains (*Escherichia coli*, ATCC 11775 and *Pseudomonas fluorescens*, ATCC 13525) and two Gram-positive strains (*Bacillus sub-*

tilis, ATCC 6633 and *Micrococcus luteus*, ATCC 10240). Samples of the pristine and copper-deposited ACFs were cut into discs (diameter: 10 mm) and sterilized with UV light. A constant volume (100 μL) of culturing solution containing the bacteria concentration of 10^8 cells/ml was injected on a 50 mm diameter nutrient agar plate (composition in g l^{-1} : beef extract 3, peptone 5 and agar 15 at pH 6–8 (DIFCO Laboratories, US)). Each copper-deposited ACFs disc was placed on the lawn of bacteria of the agar plate and incubated for 72 h at 303 K. The antibacterial activity was first examined by observing the growth of bacterial colonization near the prepared ACFs sample. The diameter of the inhibition zone of the bacterial colonization was then measured. The experiments were repeated four times and the same procedure was applied to the other bacterial strains. The concentrations of VOCs gases [14] were continuously measured (see the Supplementary data) by a photoionization detection (PID) gas analyzer (Kinsco Inc., Sniffer II, Korea), which monitored the TVOCs at a sampling flow rate of 0.5 L/min. The TVOCs gas analyzer has a performance range of 0–10 ppmv and a lower detection limit (LDL) of 0.01 ppmv. The PID output was measured and recorded at 1 Hz by using a data logger.

Fig. 1 shows the FESEM micrographs of the prepared ACFs samples. The particles were found to be copper particles as determined by EDX analyzes (see the Supplementary data). Copper particles having a “snowflake” shape or aggregates of 50 nm–1 μm are displayed in the copper-deposited ACFs sample. Fig. 1 also shows the results of ICP analyzes. Cu-10, Cu-20, and Cu-30 represent the samples obtained at deposition times of 10, 20, and 30 min, respectively. As the deposition time increased, there were more particles on the surface of the fiber and the particles grew larger (see the Supplementary data). In Fig. 2, the surface structures of the copper particles obtained by the wide-angle XRD method show that the sharp peaks found at approximately $2\theta = 43^\circ$, 50° , and 74° correspond to the

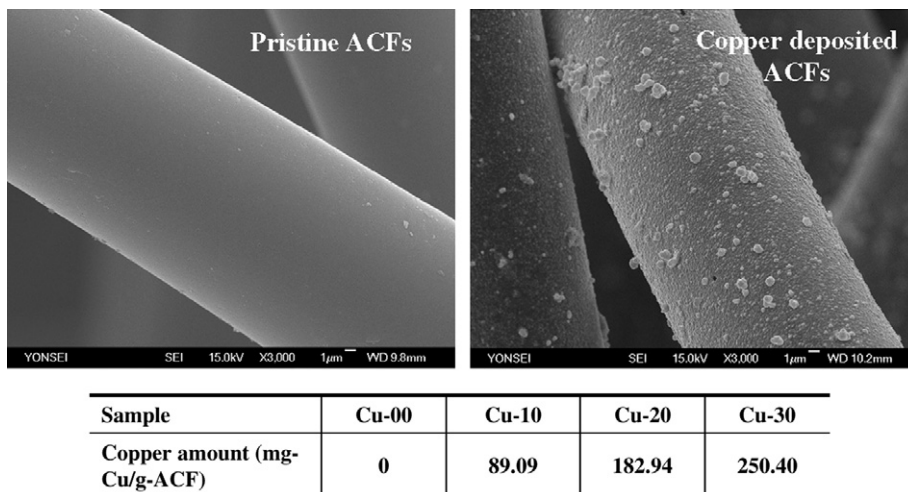


Fig. 1. SEM and ICP results of the pristine and copper-deposited ACFs.

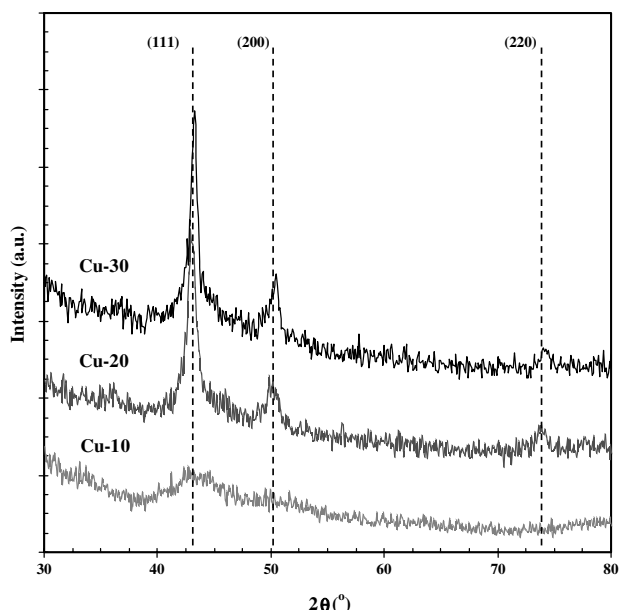


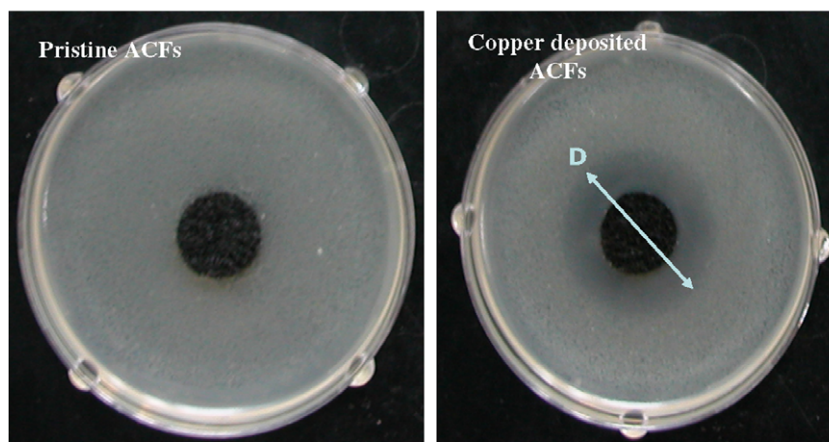
Fig. 2. X-ray diffraction patterns of the copper-deposited ACFs.

111, 200, and 220 planes of the copper (JCPDS 4-836) on the ACFs surfaces, respectively. The average crystallite sizes, estimated from the XRD line broadening of the 111 peak according to the Scherrer's equation, were 1.99 nm, 10.37 nm, and 12.98 nm for the copper deposition times of 10 min, 20 min, and 30 min, respectively. The sharpness of the copper peaks proves that the copper particles are of nearly perfect crystal structure. The intensity of the copper

peaks and the crystallinity in the copper-deposited ACFs were strengthened with increased deposition time.

Antibacterial tests were conducted once the copper particles were characterized. Fig. 3 shows the images of the inhibition zones for *B. subtilis*, which were formed in the areas surrounding the prepared ACFs samples. The inhibition zone is defined as the area where the bacteria can no longer diffuse towards the sample. The size of bacterial colonies grown on a plate with copper-deposited ACFs was significantly reduced. The diameters of the inhibition zones of four bacterial strains are also summarized in Fig. 3. For any bacterial strain, this diameter is proportional to the copper-deposition time. While *E. coli* and *P. fluorescens* (Gram negative) were less susceptible to the action of the samples, Gram-positive bacteria such as *B. subtilis* and *M. luteus* were highly responsive to the amount of copper that was deposited on the ACFs sample. One possible explanation for the lower sensitivities of the two Gram-negative bacterial strains is that the outer membrane of Gram-negative bacteria consists mainly of tightly packed lipopolysaccharide (LPS) molecules, which effectively resist against fine copper particles [8,15].

After the stability of copper particles deposited on the ACFs samples was checked (see the Supplementary data), experiments on the adsorption and desorption of VOCs were conducted. For adsorption tests, the inlet concentration of VOCs was kept constant at 1 ppmv. After obtaining a complete breakthrough for adsorption, desorption tests were then performed in the absence of VOCs gas injection. In all the test runs, the weight and face velocity of each



Samples	Inhibition Zone Diameter (D, mm)			
	Gram-positive		Gram-negative	
	<i>B.subtilis</i>	<i>M.luteus</i>	<i>E.coli</i>	<i>P.fluorescens</i>
Cu-00 (Control)	10.0	10.0	10.0	10.0
Cu-10	16.5	17.5	10.0	10.0
Cu-20	23.0	27.5	11.5	12.5
Cu-30	30.0	32.5	15.0	16.0

Fig. 3. Results for antibacterial tests.

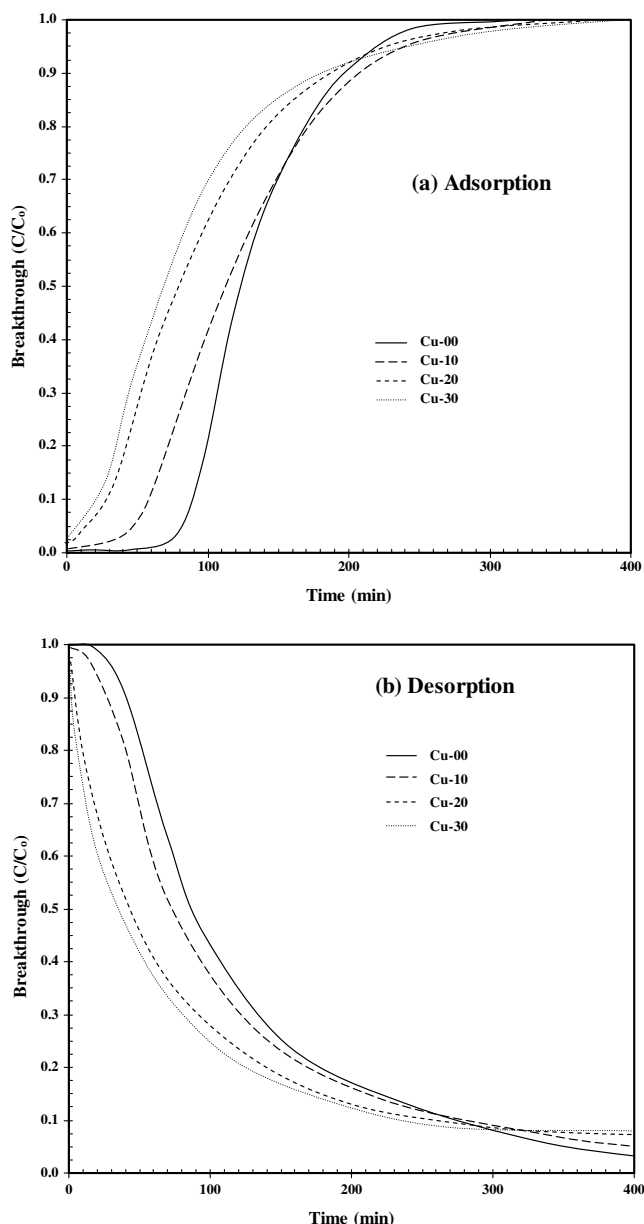


Fig. 4. VOCs adsorption and desorption characteristics of the pristine and the copper-deposited ACFs: (a) adsorption; and (b) desorption.

ACFs sample was 750 ± 50 mg (pristine ACFs) and 0.5 m/s, respectively. The VOCs concentration profiles of each test were recorded for duration of 400 min. Fig. 4 describes the breakthrough curves during adsorption and desorption for four different ACFs samples. For the adsorption of Cu-00, the breakthrough was almost zero (complete adsorption) until 70 min. After it rose sharply at about 80 min, then it became unity (zero adsorption) at 250 min. The tailing effect was more significant as the copper deposition time increased, due to the blockage of micropores by copper particles in the ACFs. The results for desorption tests can be explained similarly. The amounts and effective diffusivities of VOCs adsorption and desorption and textural

properties of the ACFs samples are expressed in the Supplementary data.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.carbon.2007.06.026.

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