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The physicochemical properties and the antibacterial effects of Ag-treated activated carbon

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은이 처리된 활성탄의 물리화학적 특성과 항균 특성

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Abstract We studied the physicochemical properties and the antibacterial effects of the Ag-treated activated carbon. The adsorption isotherms for the series of Ag-impregnated activated carbons represented typical Type-I. The surface area of the impregnated carbon was in the range of 740~1110 m^2/g, while the surface area of starting materials was 1440 m^2/g. Using t-plot, α_s-plot as well as DR-plot, and the volume of micropore was obtained. From the SEM study, the highly developed porous structure and the homogeneous distribution of Ag on the surface of activated carbon were confirmed. Finally, antibacterial effects of Ag-treated carbon against *E. coli* was discussed.

요 약 본 연구에서는 은이 처리된 활성탄에 물리화학적 특성과 항균성에 대하여 연구하였다. 은이 처리된 활성탄에 대한 흡착등온곡선은 대표적인 Type-I 형태를 나타내었다. 출발물질의 비표면적은 1440 m^2/g를 나타낸 반면에 금속이 처리된 활성탄은 740~1110 m^2/g에 범위에 분포하였다. 또한 이들 시료에 대하여 t-plot, α_s-plot와 DR-plot로부터 미세 동공부피를 구하였다. SEM 연구로 부터 활성탄의 표면에 은의 균일한 분포와 상당히 균일한 동공 분포를 확인하였다. 그리고 최종적으로 은이 처리된 활성탄에 대하여 *E. coli*에 대한 항균효과에 대하여 토론하였다.

1. Introduction

The adsorption of metallic ions on activated carbon is an impotant process in preparation of supported metal catalysts with increasing usage and application [1, 2]. The use of activated carbons to remove organic and inorganic pollutants from waters has been widely extended due to their unique properties such as high surface area, porous structure, high adsorption capacity, and surface chemical nature. The chemical nature of carbon surface can be appropriately modified by physical and chemical treatments to meet its application. It has been proposed that the adsorption of metal precursor ions or metal ions in aqueous solutions would be achieved by the interaction with functional groups on carbon surface [3-5].

It is well known that the physicochemical properties of the activated carbons depend on the manufacturing process. Therefore, many researches have been carried out to investigate their physicochemical properties such as pore size, surface area, pore volume [1-6]. As a promising application, activated carbon has been employed to get rid of bacteria in water. But we may need to consider the secondary pollution from bacteria due to their affinity with the carbon [7]. To solve the problem, activated carbons treated with metals have been employed because of their antibacterial effects. The carbons treated with metals have also been used to adsorb harmful gases in industrial and military application [8]. Various metals treated on the carbons

Table 1
Characteristics of the starting activated carbon

	Elemental analysis (%)					Volataile matter (%)	Ash content (%)	S_{BET} (m^2/g)
	C	H	S	N	O			
Starting activated carbon	93.98	1.55	0.39	0.75	3.33	4.21	1.12	1440.0

have been employed to study their purification and antibacterial effects [7, 9-11]. Among those metals, many researches have been focused on silver ions and fine silver particles because they have strong antibacterial activity [12-16].

In this study, we studied the physicochemical properties and the antibacterial effects of the Ag-treated activated carbon. In order to investigate the physicochemical properities, we obtained adsorption isotherms and surface area. Using t-plot, α_s-plot, and DR-plot, the volume of micropore was obtained. The variation of adsorption properties and surface structures after the impregnation was observed by SEM (scanning electron microscopy). Finally, antibacterial effects of Ag-treated carbon against *E. coli* was discussed.

2. Experimental

2.1. Materials

As a raw material, we employed home-made activated carbon. To prepare the carbon, coconut shell was burned off first at 450°C, then chemically activated at 800°C. Some of the characteristics of the starting activated carbon are shown in Table 1. We noticed its low sulfur contents and high surface area. $AgNO_3$ (Aldrich, 99 + %, ACS reagent) was used as a silver source for Ag treatment.

2.2. Preparation procedures

Silver nitrate was dissolved in doubly distilled water to prepare a series of solutions (mole concentrations of 0.1 to 1.0). For the treatment, 30 g of activated carbons were dipped into 100 m*l* of Ag dissolved aqueous solutions and stirred for 24 hours at room temperature. Then, we removed air and bubbles in the solutions under the pressure of about 10^{-1} torr for 20 minutes, and then discarded the solution. Finally, these samples were dried at 110°C for 48 hours. In order to reduce the experimental error, sample dryness was confirmed through the whole experiments prior use.

2.3. Measurements

Employing Sibata P-850 adsorption apparatus and liquid nitrogen method, we obtained adsorption isotherms. Samples were heated to 110°C by the heating mantle equipped under the sample bulb. In order to remove physically adsorbed materials on the surface of the micropores, the samples were degassed for several hours at this temperature under the vacuum state of 10^{-4}~10^{-5} torr. The experiments were performed at 77 K isotherm using liquid nitrogen bath. Scanning electron microscopy (SEM, Topcon sm-300, Japan) was used to observe the surface state and structure of Ag treated activated carbon and the physical state of the silver. Antibacterial activity against *E. coli* (*NB153-16, korea*) was examined in cultivated culture medium [17]. This test was carried out for 24 hours under the constant

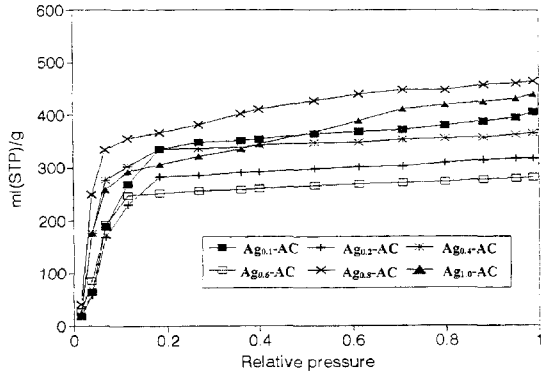

Fig. 1. Adsorption isotherms of nitrogen on the Ag treated activated carbon

Table 2
BET specific surface area of Ag-treated activated carbon

	Sample	S_{BET} (m^2/g)
1	$Ag_{0.1}$-AC	1017.11
2	$Ag_{0.2}$-AC	839.98
3	$Ag_{0.4}$-AC	1112.22
4	$Ag_{0.6}$-AC	740.89
5	$Ag_{0.8}$-AC	1102.14
6	$Ag_{1.0}$-AC	1062.61

Ag-AC : Ag-treated activated carbon.

humidity (about 60 %) and temperature (about 25°C).

3. Results and discussion

A series of Ag-treated activated carbons were prepared from various concentrations of $AgNO_3$ solutions. In Fig. 1, the adsorption isotherms for the series of Ag-treated activated carbons are shown as a function of relative pressure. According to BET (Brunauer, Emmett, and Teller) classification [18], these isotherms can be assigned to typical Type-I. From the isotherms,

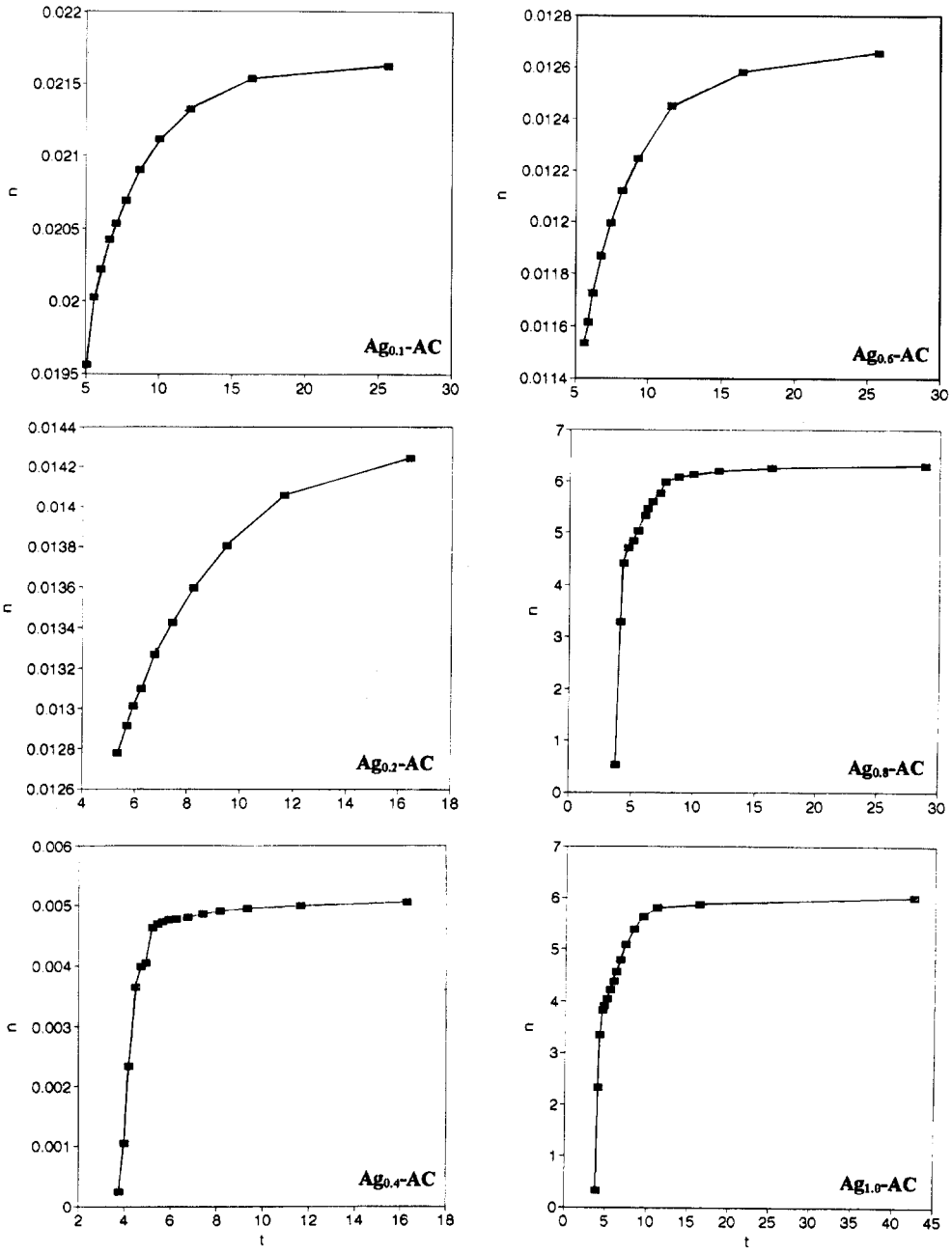

Fig. 2. t-plots of Ag-treated activated carbon.

we noticed that the amount of adsorbed N_2 is abruptly increased in the region where the relative pressure is lower than 0.2, but the volume is nearly constant once the pressure becomes higher than 0.2. This phenomenon is known as typical characteristics for microporous solids. Therefore, we can conclude that the Ag-treated activated carbon we prepared has micropore structure rather than mesopore structure. In these isotherms, the cross point between sharp knee band and plateau region could be the point where the micropore filling is completed. For the adsorbents consisted only with very fine micropore, the mechanism of adsorption can be explained by pore filling rather than surface coverage. Therefore, the increase of adsorbates could not affect the pore wall, but change the structure of the external surface. And we also noticed that the shape of the isotherms is not dependant on the amount of Ag treated.

For the activated carbon, it is important to get the information on the monolayer equivalent area known as the area of closed-packed monolayer of adsorbated molecules. The specific surface areas(S) of activated carbon can be determined from gas adsorption measurements. The BET equation can be employed to analyze adsorption isotherms. The S_{BET} value of activated carbon is calculated as :

$$S_{BET} = (V_m a_m N_m P)/RT$$

where V_m is the monolayer capacity and obtained from the BET plot, a_m is the specific surface area of nitrogen molecule at 77 K, N_m is the Avogadro's constant, and T is the absolute temperature. In our study, we obtained specific surface area of Ag-treated activated carbon from type-I isotherms using BET equation. The calculated S_{BET} values are shown in Table 2. The area of Ag-treated activated carbon is in the range of 740~1110 m^2/g, while the surface area of starting materials is 1440 m^2/g. The area obtained after Ag treatment is relatively higher than the value Oya *et al.* [19] reported. Oya *et al.* reported S_{BET} value of 500~750 m^2/g for Ag-treated activated carbon fiber. But, it is generally known that BET equation is valid only for meso and macropore [18, 20, 21]. We also noticed that surface area becomes smaller with $AgNO_3$ concentration increase.

For the further studies on the microporosity, we employed t-plot, α_s-plot as well as DR-plot. In t-plot as shown in Fig. 2, the amount adsorbed was plotted against t, the statistical thickness of the film, rather than relative pressure. We calculated the volume of micropore from the intercept on the adsorption axis of the extrapolated linear branch of the t-plot by the conversion of adsorbed amounts to the volume of the liquid nitrogen. The calculated pore volume is shown in Table 3. Using adsorption isotherm, α_s was calculated from the adsorbed amounts at the relative pressure of 0.4. Figure 3 shows α_s-plot (adsorbed amounts *vs.* α_s) of different concentrations of Ag-treated activated carbons. Pore volume calculated from α_s-plot is in the range of 0.38~0.67 $ml \cdot g^{-1}$ as shown in Table 3.

Table 3
The average pore radius and the micropore volume calculated from various methods

Sample	Micropore Volume(ml g^{-1})			Average pore radius (Å)
	from t-plot	from α_s-plot	from DR-plot	
Non-AC	0.88	0.80	1.86	11.1
$Ag_{0.1}$-AC	0.56	0.67	0.87	11.0
$Ag_{0.2}$-AC	0.44	0.42	0.77	11.0
$Ag_{0.4}$-AC	0.56	0.54	0.98	11.0
$Ag_{0.6}$-AC	0.41	0.38	0.62	11.4
$Ag_{0.8}$-AC	0.70	0.55	1.38	11.2
$Ag_{1.0}$-AC	0.59	0.46	1.42	11.3

If the activated carbon has micropore under the relative pressure of 0.1~0.2, DR-plot can be obtained from log V_a and $\log^2 (P_0/P_a)$ value. DR-equation is known as

$$\log V_a = \log V_t - D \log^2 (P_0/P_a)$$

where Va is adsorbed amounts (ml (STP) g^{-1}) at a relative pressure, D is a constant ($D = 2.303\ K\ (RT/\beta)^2$) determined by pore structure or type of adsorbent, and V_t is total micropore volume. Fig. 4 shows the DR-plot of Ag-treated activated carbon. In Table 3, the pore volumes obtained from three different methods are compared. We obtained similar value from t-method and α_s-method, while somewhat larger value from DR-method. The average pore size obtained from these method is in the range of 11.0~11.4 Å in radius.

To investigate surface state and pore structure of the activated carbon prior to and after the Ag impregnation, we obtained scanning electron microscopy (SEM). Figure 5 shows the pore distribution of non-treated activated carbon. It is confirmed that the starting material has micropore structure and the size of almost all the pores is distributed to 9~13 Å in radius. In Fig. 6, one can clearly see the highly developed porous structure and the homogeneous distribution of Ag on the surface of activated carbon. From the SEM

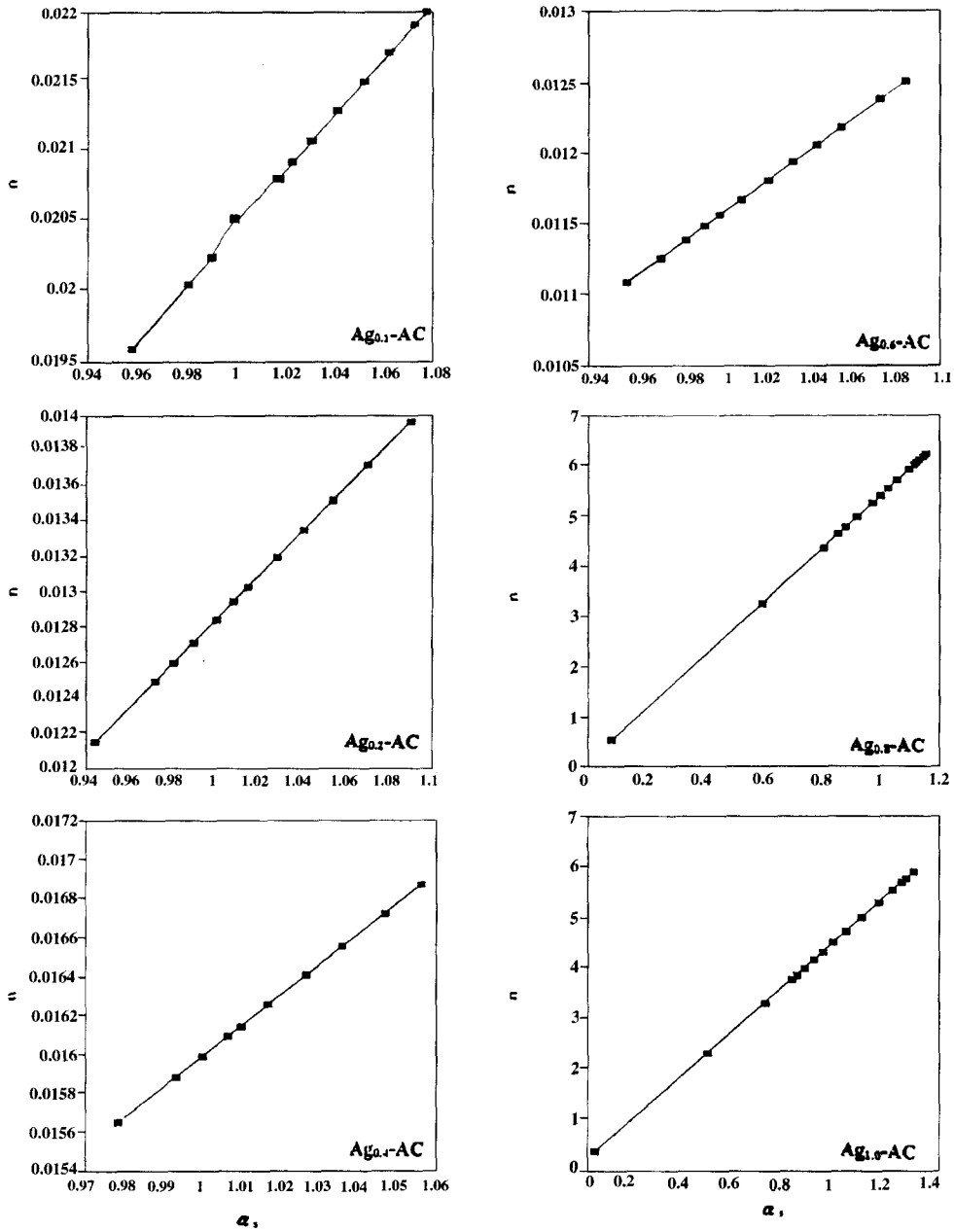

Fig. 3. α_s-plots of Ag-treated activated carbon.

results, it is observed that many of micropores in activated carbon are blocked by window blocking effect of Ag after the impregnation.

In order to test antibacterial effects of Ag-treated activated carbon, we employed *E. coli* known as a kind of colon bacillus. Antibacterial activity against *E. coli* was examined in cultivated culture medium for 24 hour. This test was carried out under the constant humidity and temperature. In Fig. 7, black circle part is due to antibacterial activity of Ag-treated activated carbon against *E. coli*. And the radii of black circle are shown in Table 4. From these results, we also observe that non-treated activated carbon (N) dose not have antibacterial activity, but the area of antibacterial activ-

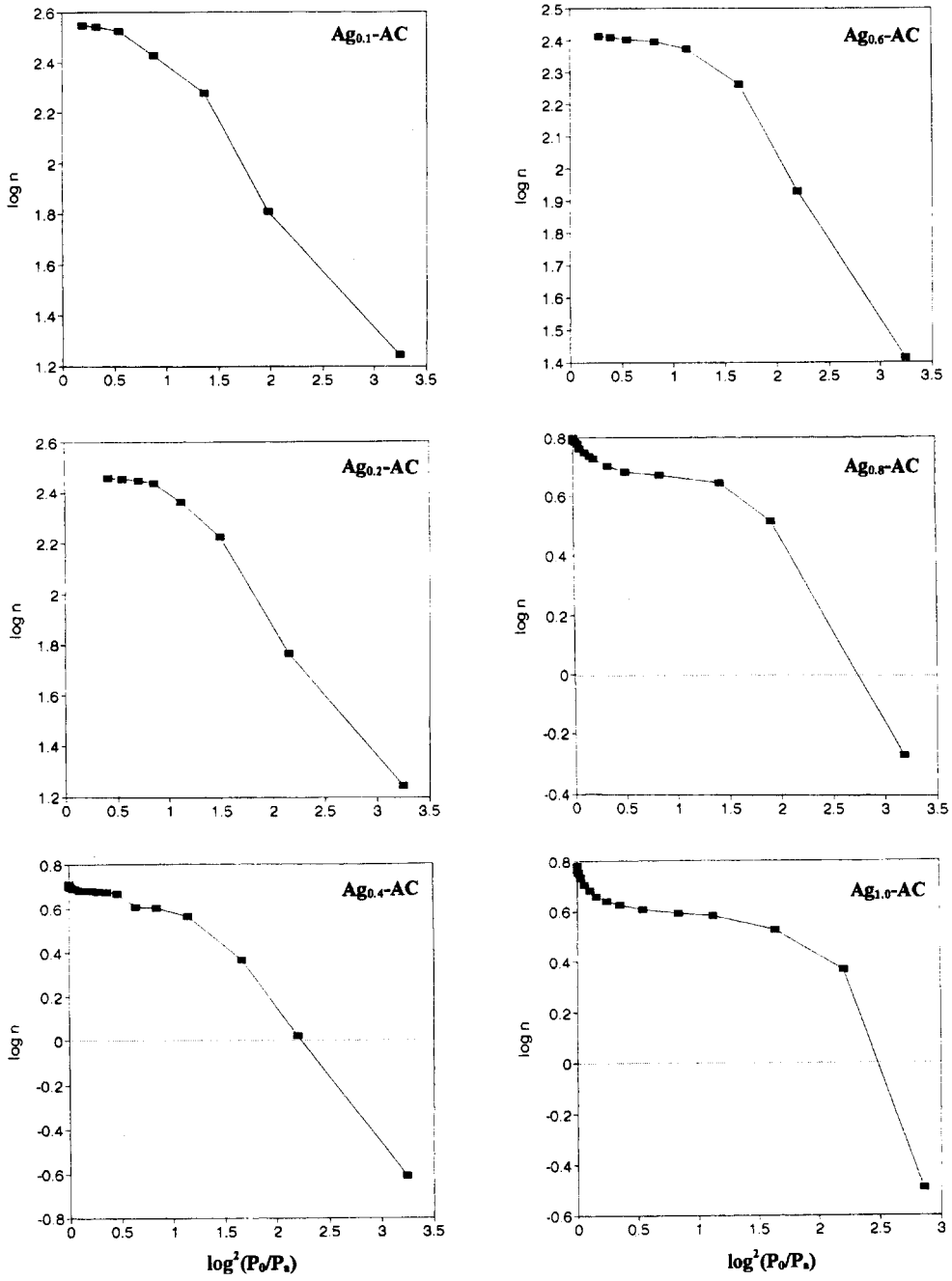

Fig. 4. DR-plots of Ag-treated activated carbon.

ity becomes larger with the increase of the amount of Ag treated. The effect is more prominent, when the amount of treated Ag is high enough (over 0.4 M). But the antibacterial activity is not increased much once the amount of treated Ag is in the certain level, in our case 1.0 M. We expected that the antibacterial effects would be affected by both the amount of treated Ag and the physicochemical properties of treated carbon such as surface area and pore volume of the activated carbon. When enough amount of Ag is treated, antibac-

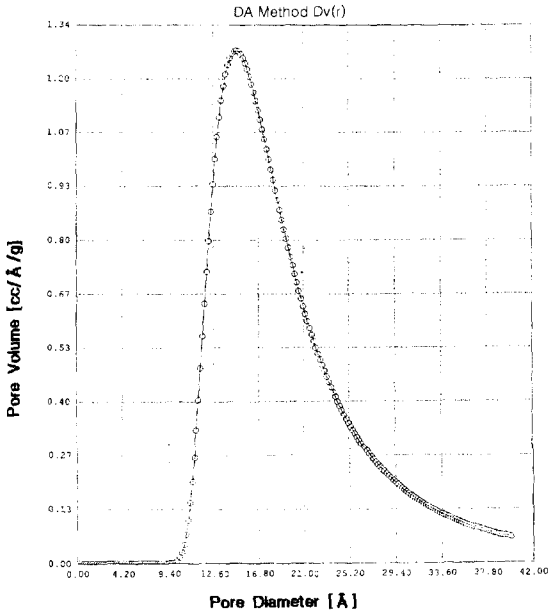

Fig. 5. Pore distribution of non-treated activated carbon obtained from liquid nitrogen method.

terial activity caused only by Ag would be increased, on the other hand, the surface area, *i.e.* adsorption would be decreased because most of pores are blocked by Ag. Therefore it may be necessary to optimize the amount of Ag treated.

4. Conclusions

The studies on the physicochemical properties and the antibacterial effects of the Ag-treated activated carbon were carried out. From the adsorption studies on the series of Ag-treated activated carbons, typical Type-I isotherm was observed. We also noticed that the Ag-treated activated carbon has micropore structure rather than mesopore structure. The surface area of the treated carbon obtained from BET equation was in the range of 740~1110 m^2/g, while the surface area of starting materials was 1440 m^2/g. Using t-plot, α_s-plot, as well as DR-plot, the volume of micropore was obtained. The volume obtained from t-method and α_s-method was similar, while the value obtained from DR-method was somewhat larger. The average pore size obtained from these method was in the range of 11.0~11.4 Å in radius. From the SEM study, the highly developed porous structure and the homogeneous distribution of Ag on the surface of activated

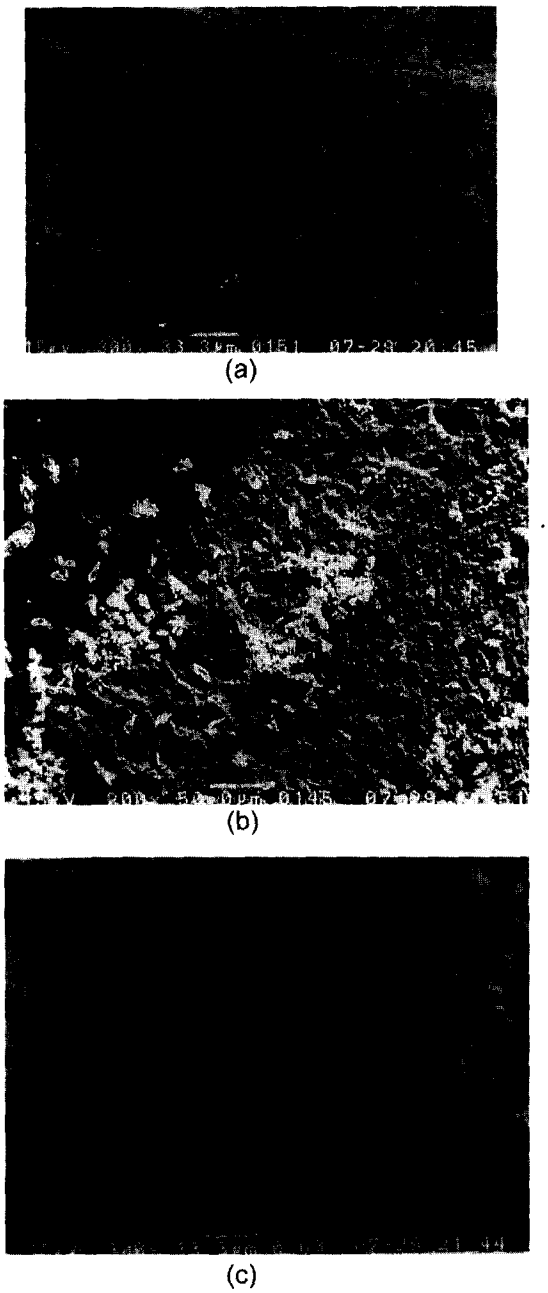

Fig. 6. SEM micrographs of Ag-treated activated carbon.

carbon were confirmed. It is also observed that many of micropores in activated carbon are blocked by window blocking effect of Ag after the treatment. Finally, antibacterial effects of Ag-treated carbon against *E. coli* was discussed. From the study, we observed that non-

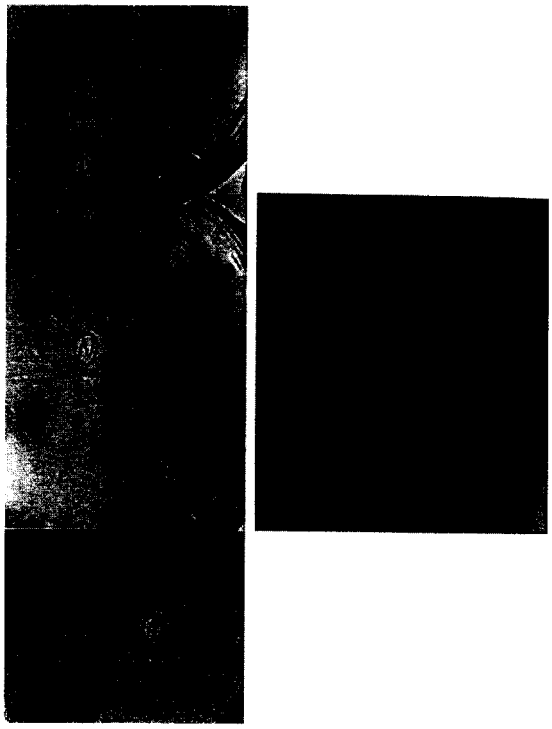

Fig. 7. Photograph of antibacterial test for Ag-treated activated carbon against Escherichia coli (N : non-treated activated carbon, ①②③④⑤⑥⑦ : Ag-treated activated carbon according to the $AgNO_3$ concentration).

treated activated carbon (N) dose not have antibacterial activity, but the area of antibacterial activity becomes larger with the increase of the amount of Ag treated.

Table 4
The diameter of antibacterial active area

	Sample	Diameter (mm)
1	Non-AC	0
2	$Ag_{0.1}$-AC	4
3	$Ag_{0.1}$-AC	6
4	$Ag_{0.1}$-AC	7
5	$Ag_{0.1}$-AC	11
6	$Ag_{0.1}$-AC	15
7	$Ag_{1.0}$-AC	15

Non-AC : Non-treated activated carbon. Ag-AC : Ag-treated activated carbon. The x-value of Ag_x-AC is mole ratio of treated $AgNO_3$.

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