Surface Transition by Solvent Washing Effects and Biological Properties of Metal Treated Activated Carbons

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Metal treated activated carbons are prepared using various metals. Adsorption behaviors, morphologies, as well as antibacterial effects of metal treated samples are compared before and after solvent washing. Adsorption isotherms are used to characterize the porous structure of metal treated activated carbons before and after the solvent washing with acetone or ethyl alcohol. From these data, it is noticed that the changes in physicochemical properties of metal treated activated carbons depend on the solvents employed. Similar results are observed from BET data obtained from nitrogen adsorption isotherms. From scanning electron microscopy (SEM) studies, the changes in shape and size of metal particles are observed after the samples are washed with solvents. These changes result in different blocking effects, which, in turn, affect the adsorption behavior of metal treated activated carbons. X-ray diffraction (XRD) patterns of the samples treated with different metals are different each other. High intense sharp peaks attributed to metals are observed from silver treated samples, while the peaks are not observed from copper treated samples. To compare thermodynamic behavior of metal treated activated carbons washed with different type of solvents, differential scanning calorimetric (DSC) analysis is carried out. The analysis shows similar endothermic curves for all of the samples. Finally, antibacterial effects of metal treated activated carbon against *Escherichia coli* are discussed. Comparing the effects among the metals employed, highest effects are obtained from Cd, while lowest effects are obtained from Cu. Antibacterial activity becomes higher with the increase of the amount of metals treated, Optimum concentrations of metals to treat activated carbons, obtained from a shake flask test, are known to be 0.4, 0.1, and 0.6 moles for Ag, Cd, and Cu, respectively.

Key Words : Activated carbon, SEM, XRD, DSC, Antibacterial effect

Introduction

Activated carbons have received considerable attention in the area of environmental science[1,2] such as the removal of various types of organic and inorganic pollutants from waters. Wide application of activated carbons on the removal of pollutants have been attributed to their unique physicochemical properties such as high surface area, variety of pore size, and high adsorption capacity. In addition, the chemical natures of surface or the adsorption properties of activated carbon have been modified to meet its application. Supported metal catalyst has been an example of modification of activated carbon. To prepare supported metal catalysts, metallic ions have been either adsorbed or impregnated on activated carbons. Metal treated activated carbons have been known as an excellent material for the removal of toxic species such as hydrocarbons, halogenated hydrocarbons, alcohols, phosgene, hydrogen cyanides.[2] Diversity of raw materials has been known as another advantage of activated carbon. Therefore, high adsorption capacity and multifunctional properties have been easily achieved by the selection of the appropriate raw materials and their chemical and physical treatments. Although many studies on the physicochemical properties of the non-treated active carbon have been carried out, few studies on the properties of the metal treated carbon have been reported.[3-6] Therefore, the physical view of the metal treated carbon has not been clearly revealed. For the treatment of metals onto carbon supports, it has been reported that both uptake and final dispersion of metals depend on oxygenated functional groups on the carbon surface, since the groups serve as adsorption sites. To increase the uptake and dispersion of supported metals, such methods to generate more number of functional groups on the carbon as partial oxidation, and/or chemical treatment with oxidizing regents[8] have been employed. But, the effects of heat treatment or solvent washing on the physicochemical properties of metal treated activated carbons have not been fully understood.

In this study, the changes in physicochemical properties of metal treated activated carbons before and after the solvent washing were compared by adsorption isotherms and surface area. Surface morphologies were investigated by scanning electron microscopy (SEM) to explain the changes in adsorption properties. The structural and thermal properties of metal treated activated carbons were also examined by X-ray diffraction and DSC analysis, respectively. Finally, antibacterial effects of metal treated activated carbon against *Escherichia coli* were discussed. The metals employed to compare antibacterial effects were Ag, Cu, and Cd.

Experimental Section

Materials and Preparation of Metal-ACs. The activated carbon used as a starting material was prepared from

coconut shell based granular type. The carbonized coconut shell was heated first at 500 °C for burn off, then physically activated with water vapor at the temperature range of 750-780 °C. $AgNO_3$, $CdCl_2$ and $CuCl_2$ were obtained from Aldrich (99+ %, ACS reagent) and used as received. In order to be free from impurities, doubly distilled water was used. For metal treatment, 30 g of activated carbons were dipped into 100 mL of metal dissolved aqueous solution and stirred for 24 h at room temperature. Then, air and bubbles in the solutions were removed under the pressure of about 1.33 Pa for 20 min, and then discarded the solution. Finally, these samples were dried at 110 °C for 48 h in air atmosphere. For the study of solvent washing effects, acetone (Aldrich, 99+ %, ACS reagent) and ethyl alcohol (Aldrich, 99+ %, ACS reagent) were used without further purification. Metal treated samples were soaked in a solvent and stirred for 24 h. Then, solvent washed samples were dried completely in the oven.

Analysis and Measurement. Digisorb 2500 (Micrometrics Instruments Co., USA) volumetric adsorption analyzer were employed to measure Nitrogen adsorption isotherms. The isotherms obtained at 77 K were used to characterize the porous structure of metal treated activated carbons. BET specific surface areas were also calculated from nitrogen adsorption isotherms. Scanning electron microscopy (SEM, Topcon sm-300, Japan) was used to observe the surface state and structure of metal treated activated carbons. X-ray diffraction patterns were taken using an X-ray generator (Shimatu XD-D1, Japan) along with Cu Kα radiation. Differential Scanning Calorimeter (DSC) analyzer (NETZSCH, Germany) was used to confirm the thermal stability and reactivity under N_2 of the metal-ACs. Al_2O_3 was used as a standard material and a Pt crucible was used for the reaction. The range of the measuring temperature of the DSC analyzer was from room temperature to 200 °C. The metal salts contents before and after solvent washing were taken using gravimetric analytical method by JIS specification.[9] The results of analysis are listed in Table 1 and 2.

Antibacterial Test. Employing the method proposed by Berman,[10] antibacterial activity against *Escherichia coli* was examined in cultivated culture medium. For the test, the solution was sterilized first. Then, *Escherichia coli* was cultivated for 24 h under the conditions of constant humidity and temperature of 37 °C. Finally, the cultivation was carried out again for 24 h under the constant humidity and temperature, after metal treated activated carbons were dropped on to the cultivated culture medium. After the cultivation, size of dots caused by antibacterial activity was measured. For quantitative analysis of antibacterial effects, shake flask method was employed. Detailed procedures were described elsewhere.[6]

Table 1. Comparison of Metal Salt Contents for Metal-ACs

Sample	Metal salts Contents (%)	Sample	Metal salts Contents (%)	Sample	Metal salts Contents (%)
$Ag_{0.1}$-AC	1.23	$Cd_{0.1}$-AC	1.17	$Cu_{0.1}$-AC	1.21
$Ag_{0.2}$-AC	1.76	$Cd_{0.2}$-AC	1.21	$Cu_{0.2}$-AC	1.37
$Ag_{0.4}$-AC	2.58	$Cd_{0.3}$-AC	1.66	$Cu_{0.3}$-AC	1.76
$Ag_{0.6}$-AC	3.02	$Cd_{0.4}$-AC	1.68	$Cu_{0.4}$-AC	2.02
$Ag_{0.8}$-AC	3.33	$Cd_{0.6}$-AC	1.81	$Cu_{0.6}$-AC	2.24
		$Cd_{0.8}$-AC	1.79	$Cu_{0.8}$-AC	2.23

Results and Discussion

Modification of activated carbons by Ag(I), Cd(II), or Cu(II) salts is carried out to provide the antibacterial effects. To compare the adsorption properties before and after the metal treatment, adsorption isotherms of series of metal-treated activated carbons prepared from various amounts of Ag, Cd and Cu salts are obtained and shown in Figure 1. All carbons show similar shape of isotherms. The isotherms of original carbons were shown in the reference.[11] The isotherms of original carbons are also similar to these, although they are not shown here. Upon the metal treated carbons, Molina-Sabio *et al.*[12] reports similar shape of isotherms obtained from the impregnation of chromium or copper salts on activated carbon. From the isotherms in Figure 1, it is 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 amount is nearly constant once the pressure becomes higher than 0.2. According to BET (Brunauer, Emmett, and Teller) classification,[13] these isotherms can be assigned to typical Type-I, which is known to be related to typical characteristics for microporous solids.[14] Therefore, it can be concluded that metal-treated activated carbons as well as original carbons have micropore structure rather than mesopore structure. In these isotherms, the cross point between sharp knee band and plateau region can be postulated as the point where the micropore filling is completed. Since all of the carbons are consisted only with very fine micropore, adsorption mechanism of N_2 can be explained by pore filling rather than surface coverage. And it is also recognized that the shape of the isotherms is not dependant on the amounts as well as the types of metal treated. As shown in Figure 1, the amounts of adsorbed N_2 (mL/g) decrease as the amounts of the treated-metal increase. It is probably due to the loss in

Table 2. Comparison of Metal Salt Contents for Metal-ACs after Solvent Washing

Sample	Metal salts Contents (%)		Sample	Metal salts Contents (%)		Sample	Metal salts Contents (%)	
	Acetone	Ethanol		Acetone	Ethanol		Acetone	Ethanol
$Ag_{0.1}$-AC	0.36	0.24	$Cd_{0.1}$-AC	0.28	0.23	$Cu_{0.1}$-AC	0.31	0.32
$Ag_{0.8}$-AC	1.55	1.51	$Cd_{0.8}$-AC	1.13	0.98	$Cu_{0.8}$-AC	1.78	1.66

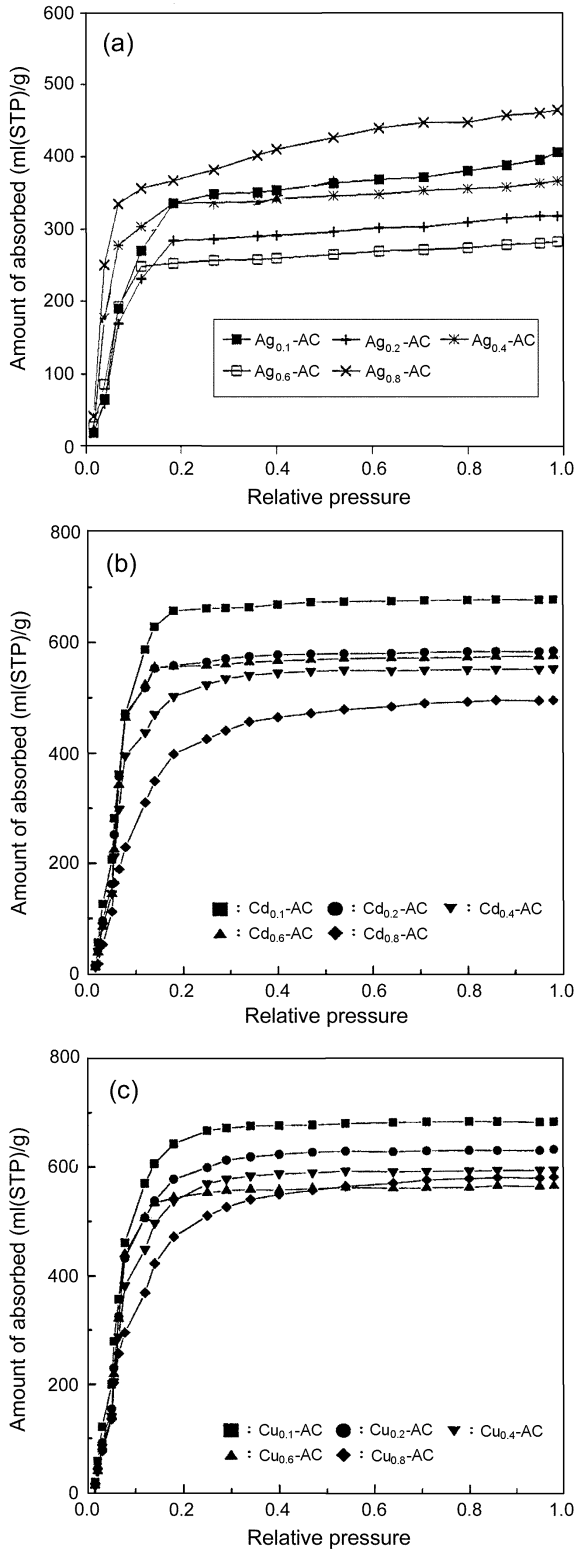


Figure 1. Adsorption isotherms of metal-treated activated carbon; (a) Ag-treated, (b) Cd-treated, and (c) Cu-treated Activated Carbons.

porosity of the carbons caused by the metal treatment. Comparing the effects of treated-metal on the amounts of adsorbed N_2 observed at the plateau region of the isotherms, the Cd or Cu-treated carbons show relatively higher value

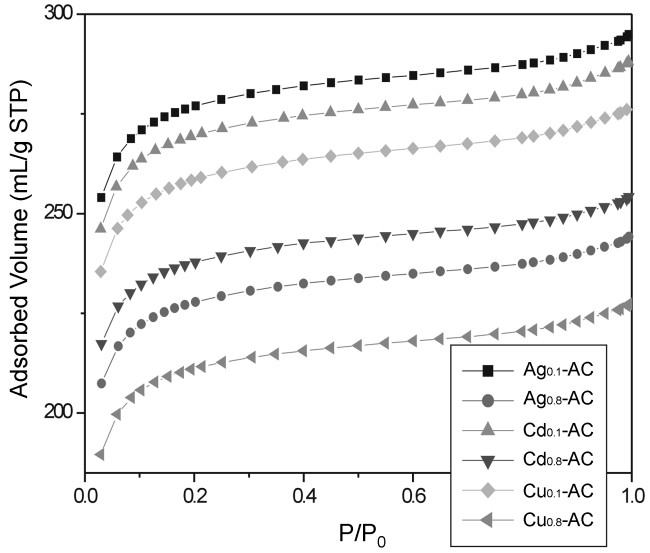


Figure 2. Nitrogen adsorption isotherms of the metal treated activated carbons washed with acetone.

(400-700 mL/g) than the Ag-treated carbons (250-400 mL/g), which means that silver shows more significant effects on the loss of adsorption capacity. Pore blocking can be postulated as a possible cause of the adsorption capacity loss.[11,15] Upon the effects of metal contents treated on the carbons, adsorption capacity loss becomes more significant as the contents of loaded-metal increase in the case of Cd and Cu, while it is not true in the case of Ag. A possible explanation for these phenomena is differences in blocking effects of metals.

In order to examine solvent washing effects on adsorption capacity of metal treated carbon, isotherms are obtained. As shown in Figure 2, the type of isotherms is not altered even after washing with acetone. As mentioned before, the isotherms of non-washed metal treated activated carbons show typical type I. But, it is recognized that the adsorbed volume of N_2 decreases after the metal treated activated carbons are washed with acetone. Cd treated and Cu treated activated carbons shows significant reduction of adsorbed volume, while Ag treated samples shows less significant reduction. Upon the samples treated with low concentration of metal (treated with 0.1 mole of metal solution), the adsorbed volume of nitrogen is decreased in the order of Ag, Cd, and Cu treated sample after the samples are washed with acetone. When the amounts of metal treated on the activated carbons are relatively high (treated with 0.8 mole of metal solution), the value is decreased in the order of Cd, Ag, and Cu treated sample. These phenomena are probably due to the interaction between acetone and metals treated on activated carbons. The interaction may change physico-chemical properties of metals such as oxidation state, shape, and size of particles. Figure 3 shows nitrogen adsorption isotherms of metal treated activated carbons after the samples are washed with ethyl alcohol. It is also noticed that the adsorbed volume of N_2 decreases after the metal treated activated carbons are washed with ethyl alcohol. When the

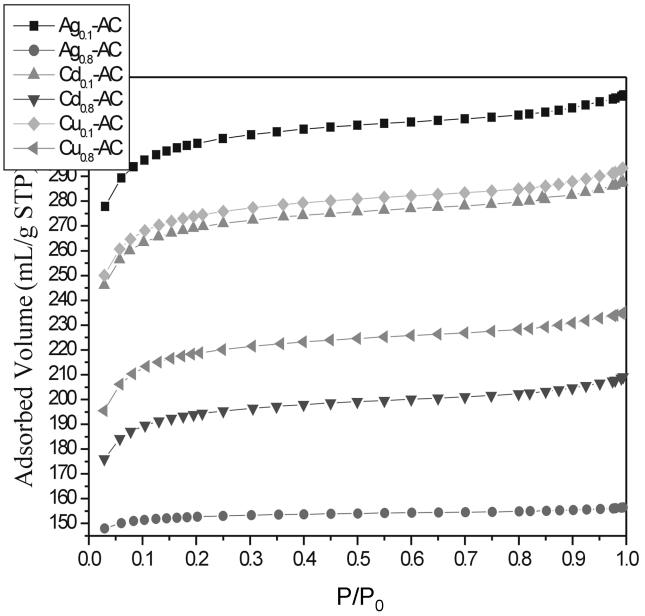
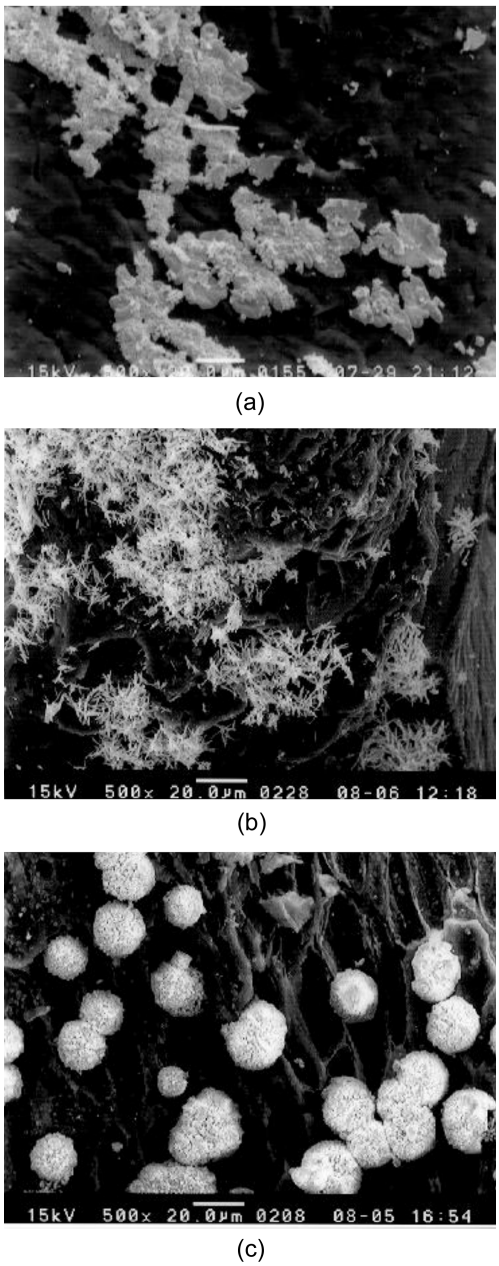


Figure 3. Nitrogen adsorption isotherms of the metal treated activated carbons washed with ethyl alcohol.

amounts of treated metal are low (treated with 0.1 mole of metal solution), adsorbed volume is decreased in the order of Ag, Cu, and Cd treated sample after the samples are washed with ethyl alcohol. When the amounts of metal are relatively high (treated with 0.8 mole of metal solution), the value is decreased in the order of Cu, Cd, and Ag treated sample. As a conclusion, it is recognized that ethyl alcohol washed samples show different behavior in adsorbed volume from the samples washed with acetone. From these results, it can be postulated that the changes in physicochemical properties of metals treated on activated carbons depend on the solvents employed. Similar results are obtained from the BET data shown in Table 2. Specific surface areas of all of the samples appear to decrease after solvent washing. The reduction of the areas is more significant when the samples are washed with ethyl alcohol. Among the samples treated with different metals, silver treated samples show most significant reduction in specific surface areas.

To reveal the causes of the differences in adsorption capacity and specific surface area after the samples are washed with solvents, surface morphology and pore structure are investigated by scanning electron microscopy. Figure 4 shows the surface morphologies of the metal treated activated carbons before solvent wash. In Figure 4, one can clearly see the highly developed porous structure and homogeneous distribution of metals on the surface of activated carbon. It is also noticed that a number of micropores are blocked by metals after the treatment. Differences in the degree of blocking effects depend on the type of treated-metals. In the case of silver, as reported by Wang *et al.*,[16] silver ion (Ag^+) adsorbed on the activated carbon is known to be initially reduced to form silver metal nuclei which are migrating and aggregating to form silver particles, and then greater size of silver is obtained as the reduction is continued. Figure 5 and Figure 6 show the surface morphologies of metal treated activated carbons after the samples are washed with two different kinds of solvents, acetone and ethyl alcohol. It is noticed that the size of aggregated particles obtained from washed samples is smaller than that obtained from non-washed samples. Before the samples are washed with solvents, most of the aggregated metal salts particles form island and are deposited on external surface of the activated carbon, while remaining small particles block the pores. After the samples are washed with solvents, aggregated particles become smaller. From SEM results, it is observed that more number of small metal salts particles are heterogeneously dispersed both inside of micropores and on



(a)

(b)

(c)

Figure 4. SEM photographs of the metal treated (0.1 mole) activated carbons before solvent washing; (a) Ag-treated, (b) Cd-treated, and (c) Cu-treated Activated Carbons.

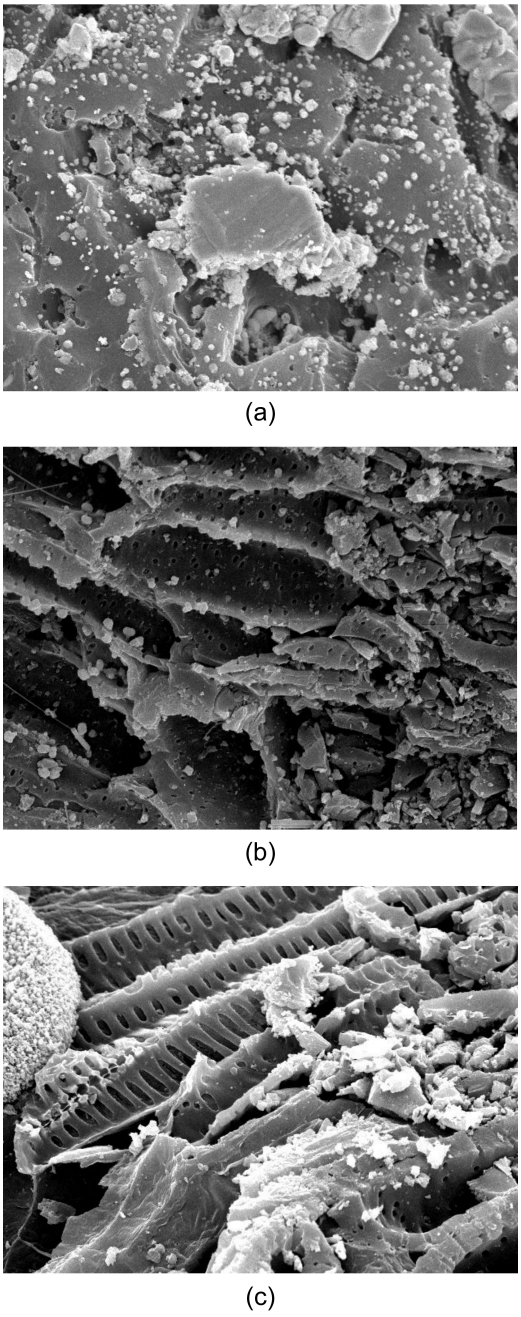


Figure 5. SEM photographs of the metal treated activated carbons after the samples are washed with acetone; (a) Ag-treated, (b) Cd-treated, and (c) Cu-treated Activated Carbons.

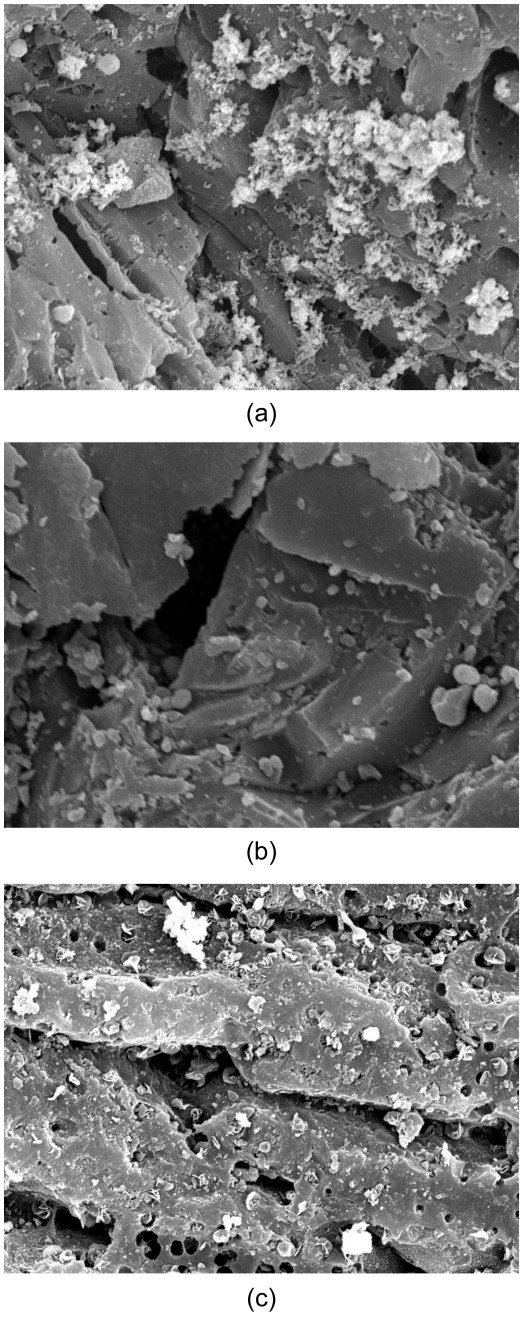


Figure 6. SEM photographs of the metal treated activated carbons after the samples are washed with ethyl alcohol; (a) Ag-treated, (b) Cd-treated, and (c) Cu-treated Activated Carbons.

the surface of metal treated activated carbons after washing with solvents. Therefore, it can be postulated that the differences in adsorption properties before and after the solvent washing are mainly due to different blocking effects. And the effects depend on the way of distribution, shape of metal salts particles, and the pattern of aggregates. It is believed that the solvent wash alters not only morphologies of metal salts on the carbon surface but chemical properties of surface of the carbon itself.

X-ray diffraction patterns are shown in Figure 7. The samples treated with different metals show different diffraction patterns. From the sharp XRD peaks, existence of metals on the surface is confirmed. The X-ray diffraction peaks of metal treated activated carbons are very similar to those of non treated raw activated carbons except sharp peaks obtained by metals. Generally, the peak of amorphous carbon like activated carbon, cokes and carbon black is determined from large and broad lower X-ray diffraction peak.

The DSC thermal data are shown in Figure 8 and 9. The enthalpy and entropy formation were calculated by the confirmation of the thermodynamic endothermic reaction,

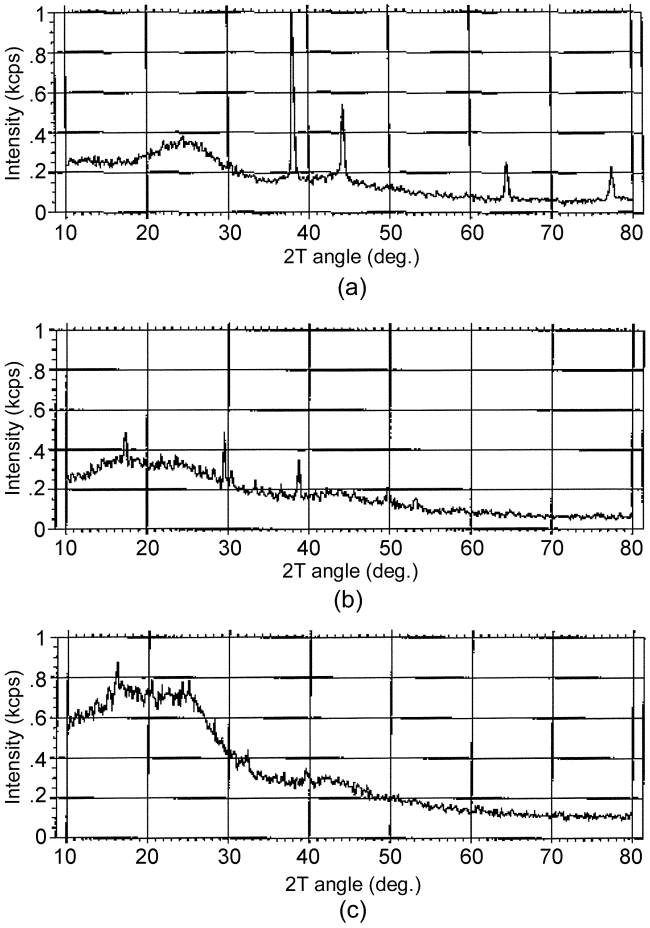


Figure 7. XRD analysis of the metal treated activated carbons; (a) Ag-treated, (b) Cd-treated, and (c) Cu-treated Activated Carbons.

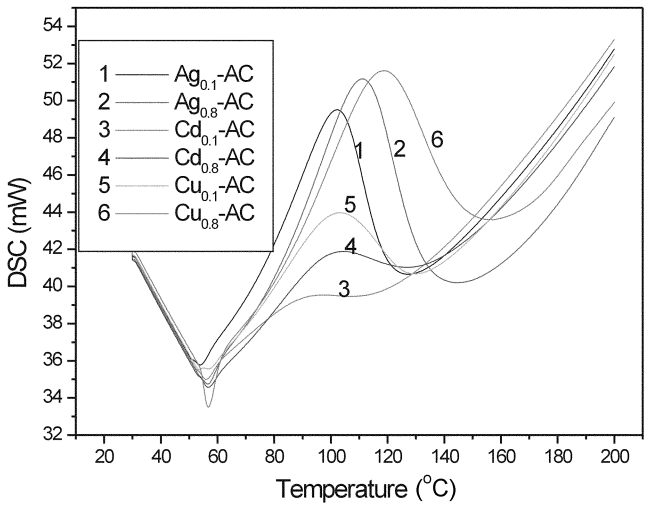


Figure 8. DSC analysis of the metal treated activated carbons after the samples are washed with acetone.

depending on the kind of treated metal and their concentration. From the Figure 8 and 9, these curves show the biggest absolute values for the enthalpy formation. The enthalpy and entropy formation for metal treated activated carbon after solvent washing that resulted for one set of

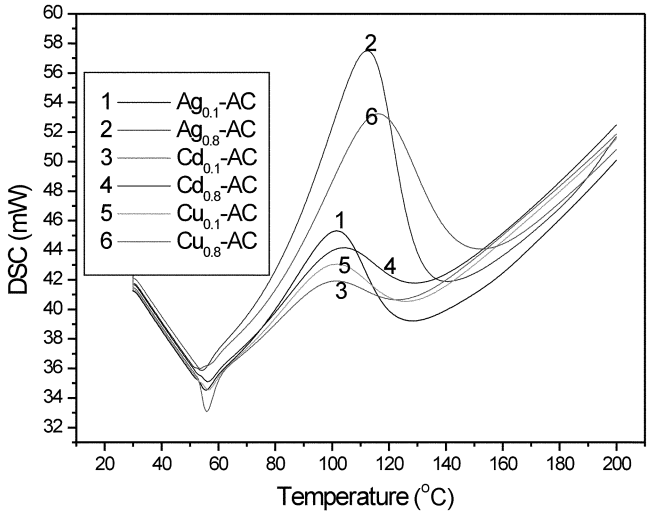


Figure 9. DSC analysis of the metal treated activated carbons after the samples are washed with ethyl alcohol.

Table 3. Comparison of BET specific surface area (m^2/g) for the solvent washed metal treated activated carbons

Sample \ Solvent	Non	Acetone	Ethyl alcohol
$Ag_{0.1}$-AC	1122.1	1020.6	931.93
$Ag_{0.8}$-AC	1062.0	877.32	767.11
$Cd_{0.1}$-AC	1418.0	898.72	895.90
$Cd_{0.8}$-AC	1196.8	648.40	631.73
$Cu_{0.1}$-AC	1361.3	915.20	862.17
$Cu_{0.8}$-AC	1212.5	734.34	702.98

samples are listed in Table 4. This work demonstrated that surface chemistry after solvent washing becomes important to maintain adsorption properties as a function of treated metal concentration at high temperature. From Table 4, one notes that the entropy of metal treated activated carbons after solvent washing increases with increasing metal content as a function of mole concentration. As well as, the quantities of enthalpy of metal treated activated carbons after solvent washing increase with increasing treated metal contents, respectively. The results of the DSC analysis for the metal treated activated carbon after solvent washing are shown very similar endothermic curves for all samples. It is postulated that differences in adsorption properties before and after the solvent wash are mainly due to different blocking effects of carbon surface. It is consider that the formations of enthalpy are results of thermal behavior between the metal salts by heat treatment.

Although many studies on catalytic effects of metal have been reported,[17] very few studies on the antibacterial effects of metals treated on the activated carbon have been reported. In this study, various types of metals are employed to compare antibacterial effects. For the test, *E. coli* known as a kind of colon bacillus is employed. Antibacterial activity against *E. coli* is examined in cultivated culture medium for 24 h. The test is carried out under constant humidity and

Table 4. Thermodynamic data for the solvent washed metal treated activated carbons

Sample \ Solvent	Acetone			Ethyl alcohol		
	Temp. (°C)	ΔH ($J \cdot g^{-1}$)	ΔS ($J \cdot g^{-1} \cdot K^{-1}$)	Temp. (°C)	ΔH ($J \cdot g^{-1}$)	ΔS ($J \cdot g^{-1} \cdot K^{-1}$)
$Ag_{0.1}$-AC	53.93 - 128.1(101.4)	137.8	1.36	55.33 - 131.9(100.4)	110.4	1.10
$Ag_{0.8}$-AC	54.86 - 143.1(111.8)	260.7	2.33	54.86 - 143.1(111.8)	260.9	2.20
$Cd_{0.1}$-AC	57.20 - 117.9(86.55)	23.67	0.27	62.33 - 130.0(97.23)	43.41	0.45
$Cd_{0.8}$-AC	56.73 - 138.4(98.12)	55.04	0.56	56.73 - 134.2(100.4)	79.93	0.80
$Cu_{0.1}$-AC	55.80 - 133.3(100.4)	80.95	0.80	56.71 - 134.1(98.13)	71.52	0.73
$Cu_{0.8}$-AC	60.93 - 162.2(116.9)	204.9	1.75	56.72 - 156.1(114.6)	210.0	1.83

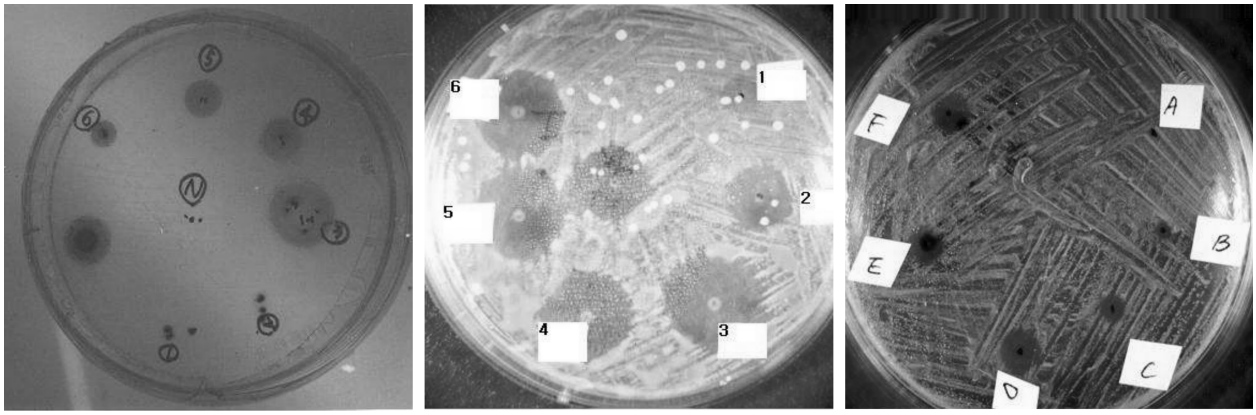


Figure 10. Photograph of antibacterial test for metal-treated activated carbons against *E. coli*; (a) Ag (① : $Ag_{0.1}$-AC, ② $Ag_{0.2}$-AC, ③ $Ag_{0.4}$-AC, ④ $Ag_{0.6}$-AC, ⑤ $Ag_{0.8}$-AC, N: Non-treated AC), (b) Cd (1: $Cd_{0.1}$-AC, 2: $Cd_{0.2}$-AC, 3: $Cd_{0.4}$-AC, 4: $Cd_{0.6}$-AC, 5: $Cd_{0.8}$-AC), and (c) Cu (A: $Cu_{0.1}$-AC, B: $Cu_{0.2}$-AC, C: $Cu_{0.4}$-AC, D: $Cu_{0.6}$-AC, E: $Cu_{0.8}$-AC).

temperature through out whole experiments. In Figure 10, black circles (sometimes shown as transparent circles) are resulted from antibacterial activity of metal-treated activated carbon against *E. coli*. The radii of black circles are reported in Table 5. From these results, it is recognized that non-treated activated carbon (N) dose not have antibacterial activity, while all of the metal-treated activated carbons show the activity. Comparing antibacterial effects among the metals, highest effects are obtained from Cd, while lowest effects are obtained from Cu. No matter what type of metal is employed, the area of black circles becomes larger with the increase of the amount of metal treated. In other words, antibacterial effects depend on the amount of metal. But the antibacterial activity is not increased much, once the amount of impregnated metal is in certain level, in this case 1.0 M. For the quantitative analysis of antibacterial activity, shake flask method is employed. Similar results are obtained from both methods. The order of antibacterial effects is Cd, Ag, and then Cu as shown in Figure 11. In the case of Cd, 100% of the effects are observed even with the lowest concentration of metals treated. From the results, it is possible to

Table 5. Comparison of the radius of black and clean circle obtained from the antibacterial test of metal (Ag, Cd, and Cu) treated activated carbons

Sample	Radius (mm)	Sample	Radius (mm)	Sample	Radius (mm)
$Ag_{0.1}$-AC	4	$Cd_{0.1}$-AC	6	$Cu_{0.1}$-AC	2
$Ag_{0.2}$-AC	6	$Cd_{0.2}$-AC	9	$Cu_{0.2}$-AC	2
$Ag_{0.4}$-AC	7	$Cd_{0.4}$-AC	19	$Cu_{0.4}$-AC	4
$Ag_{0.6}$-AC	11	$Cd_{0.6}$-AC	18	$Cu_{0.6}$-AC	8
$Ag_{0.8}$-AC	15	$Cd_{0.8}$-AC	18	$Cu_{0.8}$-AC	9

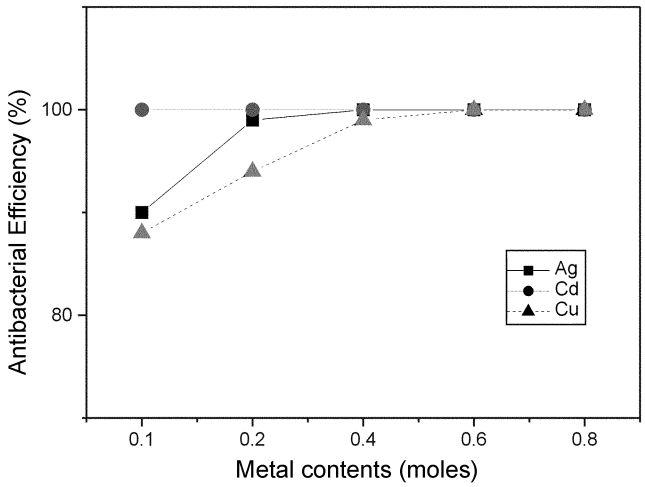


Figure 11. Antibacterial effects of the metal-treated activated carbons examined by Shake flask method.

determined the optimum amounts of treated-metal. In this study, optimum concentrations of metals are known to be 0.4 mole for Ag, 0.1 mole for Cd, and 0.6 mole for Cu. But, the antibacterial effects of metal treated activated carbons are not affected by solvent wash.

Conclusion

Metal treated activated carbons are prepared using various metals. Adsorption behavior, morphologies, and antibacterial effects of metal treated activated carbons are examined before and after solvent wash. From the studies of nitrogen adsorption isotherms of metal treated activated carbons before and after the samples are washed with acetone or ethyl alcohol, the changes in physicochemical properties of metals treated on activated carbons are recognized probably due to interaction between solvents and metals. It is also recognized that ethyl alcohol washed samples show different behavior in adsorbed volume from the samples washed with acetone. From these results, it can be postulated that the changes in physicochemical properties of metals treated on activated carbons depend on the solvents employed. Similar results are obtained from the BET surface areas data. From SEM study, it is observed that the shape and size of metal particles are changed after the samples are washed with solvents. Due to these change, different blocking effects will be caused. The results of the DSC analysis for the metal treated activated carbon are shown very similar endothermic curves for all samples. It is postulated that differences in adsorption properties before and after the solvent wash are mainly due to different blocking effects. To test the antibacterial effects against *E. coli.* two different techniques, Bermans and shake flask method, are employed. From the studies, it is noticed that non-treated activated carbon (N) dose not have antibacterial activity, while all of the metal-treated activated carbons show the activity. Comparing antibacterial effects among the metals, highest effects are obtained from Cd, while lowest effects are obtained from Cu. From all of the metals, it is observed that antibacterial activity becomes higher with the increase of the amount of metal treated. From the shake flask test employed for quantitative analysis of antibacterial activity, optimum concentrations of metals are known to be 0.4 mole for Ag, 0.1 mole for Cd, and 0.6 mole for Cu. It is also concluded that the antibacterial effects of metal treated activated carbons are not affected by solvent wash.

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