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SHORT COMMUNICATION

Adsorption characteristics of bamboo activated carbon

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Abstract−Dye is difficult to remove from aqueous solution with common adsorbents due to its large molecular size. Mesoporous bamboo activated carbon is utilized in the adsorption of Black 5, Red E and phenol. The adsorption performance of the carbon is experimentally examined along with the characterization of the adsorbent. The comparison of adsorption capacity of the bamboo activated carbon with that of coconut activated carbon and carbon cryogel indicates that the large volume of mesopore in the carbon helps the expansion of adsorption capacity. Microscopic observation, the measurement of pore characteristics and fitting to the adsorption isotherms are conducted in the characterization of the bamboo activated carbon.

Key words: Bamboo Activated Carbon, Dye Adsorption, Mesoporous Adsorbent, Black 5

INTRODUCTION

Dye in wastewater is difficult to treat due to its large molecular size and stability, and common treatment techniques of wastewater have proven to be ineffective for the substance. Activated carbon is widely used in water treatment because of its large capacity and wide applicability of adsorption and ready availability. However, the adsorption capacity is significantly affected by the pore size and structure of the carbon and the molecular size and chemical nature of adsorbates. The coconut-based or coal-based activated carbon is widely utilized in the adsorption of small molecules, because it has a large volume of micropore. The utilization includes various applications of water treatment.

On the other hand, large molecules, such as dye, are not treated with the common activated carbon due to its pore characteristics. Because the large molecular size and stability of dye prevent from applying conventional removal techniques from water, various alternative methods have been proposed and tested for the dye removal. Using a simple adsorption treatment, food and wood wastes have been utilized for the dye treatment [1-3]. On top of the treatment, an electrochemical processing [4] and photocatalytic technique [5] were added for the improvement of treatment effectiveness. Also, the photocatalytic decomposition was enhanced by using titanium oxide catalyst in Mohamed and Al-Esaimi [6]. Due to the large molecular size of dye, several studies have used mesoporous adsorbents for the dye removal. Hydrogel is readily designed with its pore size in the preparation process, and it has been utilized with various modifications of its surface [7,8]. Though conventional activated carbon contains mostly micropores, the activated carbon produced from some raw materials has large volume of mesopores. Various adsorbents, such as natural zeolite [9], mesoporous silica [10] and the activated carbon from apricot waste [11] have been used for the dye removal from water.

In this study, the dye was removed with bamboo activated carbon having mostly mesopores. The activated carbon was characterized for the dye adsorption through microscopic observation, pore size determination and adsorption isotherm fitting, and its removal performance was examined with three different sizes of molecules.

EXPERIMENTAL

1. Materials

The bamboo activated carbon used in this study was obtained from a local company (Eulji Chemical Co., Korea), and the coconut activated carbon was obtained from Sinkwang Chemical, Korea. The carbon cryogel micro-particles (CCM 600) were yielded from gel carbonation as described below. The reactants (RF solution) were prepared from resorcinol, formaldehyde (37% in methanol), sodium carbonate as a basic catalyst and distilled water. The molar ratio of resorcinol to catalyst was 600, the resorcinol concentration in water was 0.25 g/cm^3, and the molar ratio of resorcinol to formaldehyde was 0.5. The mixed RF solution in an Erlenmeyer flask was kept at 25 °C for 32 hours to allow sol-gel transition. All the chemicals were from the Wako Chemical Co., Japan and used as received. The gel was dispersed into an organic phase of cyclohexane containing surfactant Span 80 with a molar ratio of the RF solution to cyclohexane of 0.25, and the molar ratio of Span 80 to RF solution was also 0.25. An inverse emulsion was made with a homogenizer agitating at 15,000 rpm for three minutes. Then, the emulsified solution was stirred at room temperature for a week in order to complete the sol-gel polycondensation producing ultra-fine hydrogel particles. The particles were separated from the solution with a centrifuge rotating at 12,000 rpm for ten minutes. The separated particles were immersed in *t*-butanol for 24 hours to replace the water contained in the particles with *t*-butanol and then centrifuged at 12,000 rpm for 15 minutes. The whole process of water removal and particle separation was repeated three times. The particles were placed at a temperature of −30 °C for a day for freezing-drying, and dried under vacuum at a temperature of −10 °C for four days. Finally, the dried particles were pyrolyzed at a temperature of 1,000 °C. The pyrolysis was conducted with a constant flow of argon at a rate of

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Table 1. Pore characteristics of adsorbents

Adsorbent	BET area (m^2/g)	V_{micro} (cm^3/g)	V_{meso} (cm^3/g)
Bamboo activated carbon	1,329	0.23	0.85
Coconut activated carbon	1,199	0.39	0.42
Carbon cryogel	639	0.22	1.23

100 mL per minute. The particles were initially heated to 250 °C at a heating rate of 250 °C per hour, and were kept at the temperature for two hours. Then, the particles were heated to 1,000 °C at the same heating rate for three hours, followed by being maintained at the temperature for four hours. The pore characteristics of the adsorbents are listed in Table 1.

In the performance evaluation of dye removal, Black 5 (Sigma-Aldrich, U.S.A., No. 306452) and Red E (Nippon Kayaku Ltd., Japan) were utilized for large molecule substances, and phenol (Sanko Kagaku Ltd., Japan) was for small molecule ones. All the materials were used as received.

2. Equipments

The dye concentration in water was measured with a UV-VIS spectrophotometer (Varian, Inc., U.S.A., Model Cary 50), and pore size distribution was determined with an adsorption analyzer (Micromeritics Instrument Co., U.S.A., Model TriStar 3000). The surface of adsorbents was observed with a scanning electron microscope (JEOL Ltd., Japan, Model JSM 6700F).

3. Procedures

The dye solutions used in the experiment were prepared for concentrations between 6.25 ppm and 1,000 ppm. The solution up to 100 ppm was diluted from the standard solution of 200 ppm, which was prepared by dissolving 0.2 g of dye into 1 L of water. For instance, the 6.25 ppm solution was obtained by diluting 6.25 mL of 200 ppm solution into the solution of 200 mL. Higher concentration solution than 100 ppm was directly prepared without dilution. Bamboo activated carbon was sieved to separate the particle size between 150 μm and 250 μm.

The dye solution of 100 mL was placed in a 300 mL Erlenmeyer flask, and 50 mg of the bamboo activated carbon was put into the

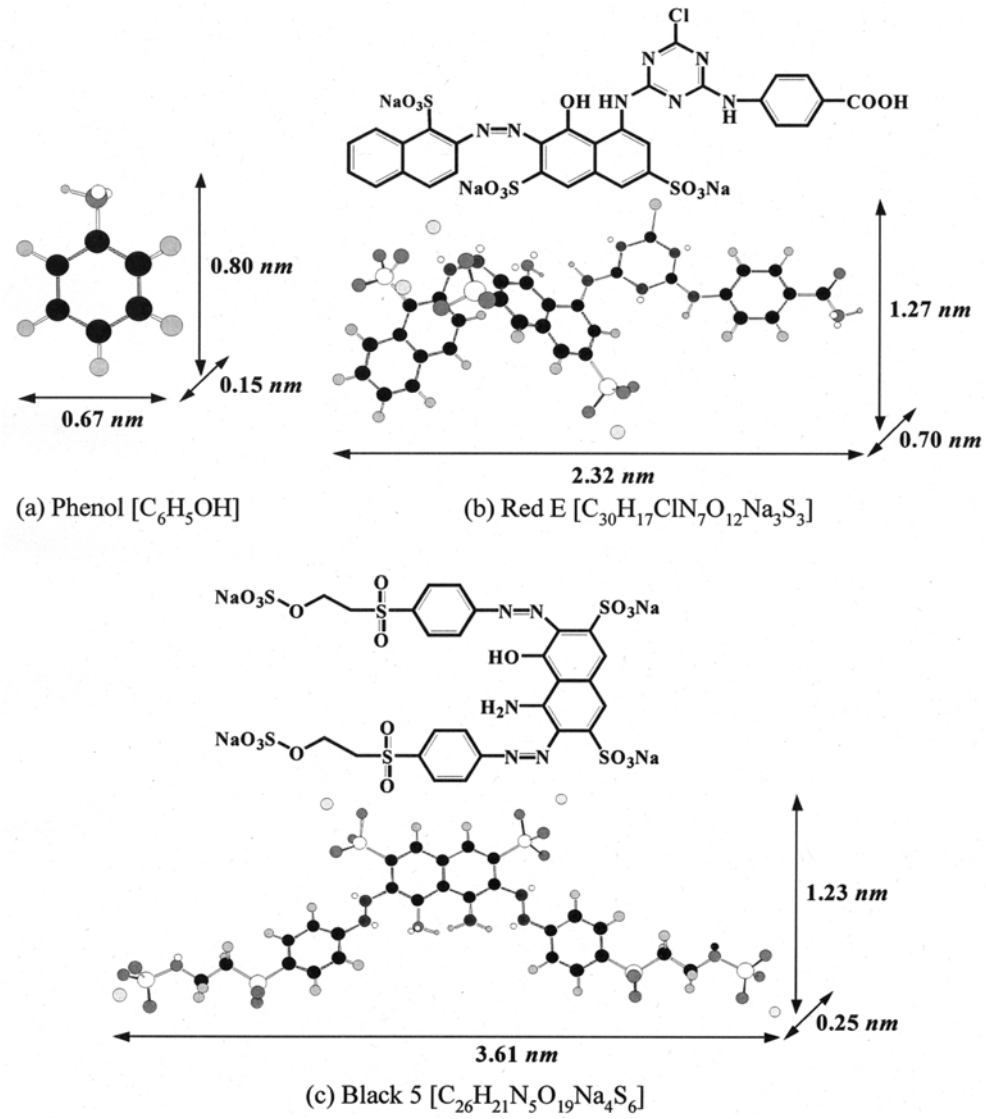

Fig. 1. Molecular structures of phenol, Red E and Black 5.

flask. The solution in the flask with a lid was stirred by a magnetic stirrer at room temperature for 48 hours. The solution concentration after 48 hour treatment was measured with a spectrophotometer. The wavelength was set at 599.5 nm, 545 nm and 269.9 nm for Black 5, Red E and phenol, respectively.

RESULTS AND DISCUSSION

Unlike common activated carbon made from coconut shell or coal, bamboo activated carbon has relatively large pores suitable for the adsorption of large molecules. Fig. 1 compares the molecules of Black 5, Red E and phenol. Phenol is about 1/25 of Red E in volume. How the difference of the molecules affects the adsorption in the mesoporous bamboo activated carbon is examined here.

The surfaces of bamboo activated carbon, coconut activated carbon and carbon cryogel were observed with a scanning electron microscope as illustrated in Figs. 2 through 4, respectively. The SEM photograph of bamboo activated carbon shows much larger holes than coconut activated carbon due to the coarse texture of the raw bamboo. The photograph of carbon cryogel demonstrates homogeneous distribution of tiny holes because the particles are prepared from chemicals instead of natural raw material. The pore structure of the bamboo activated carbon was investigated with the measurement of pore size distribution plotted in Fig. 5. The distribution shows a large peak of 30 Å in diameter with the bamboo activated carbon. The coconut activated carbon gives small distribution at the diameter, and the carbon cryogel has large distribution with larger pores.

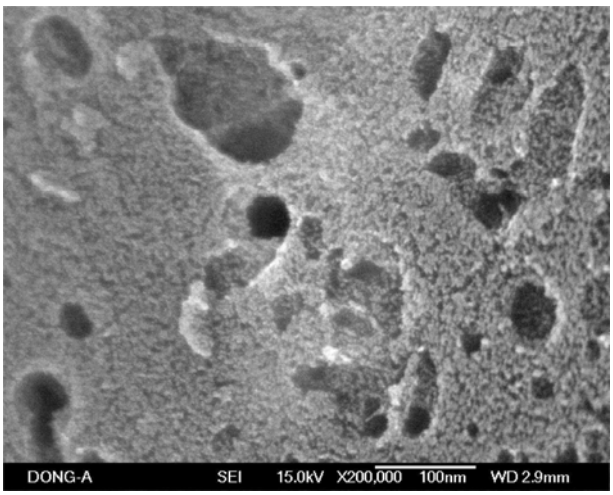

Fig. 2. An SEM photograph of bamboo activated carbon.

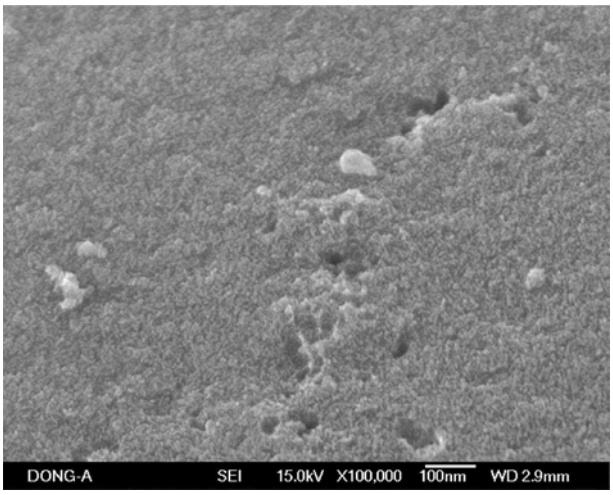

Fig. 3. An SEM photograph of coconut activated carbon.

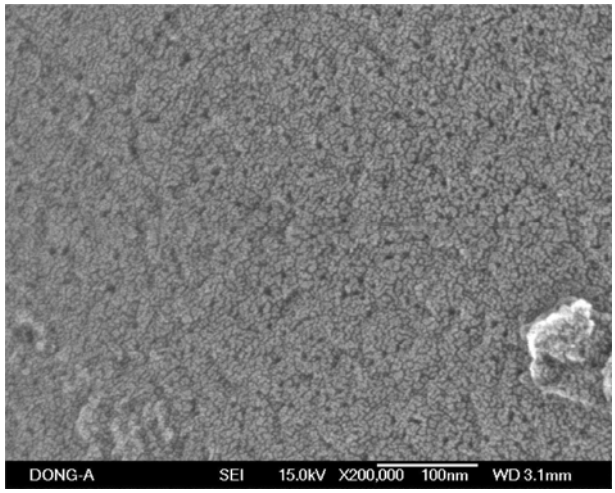

Fig. 4. An SEM photograph of carbon cryogel micro-particles.

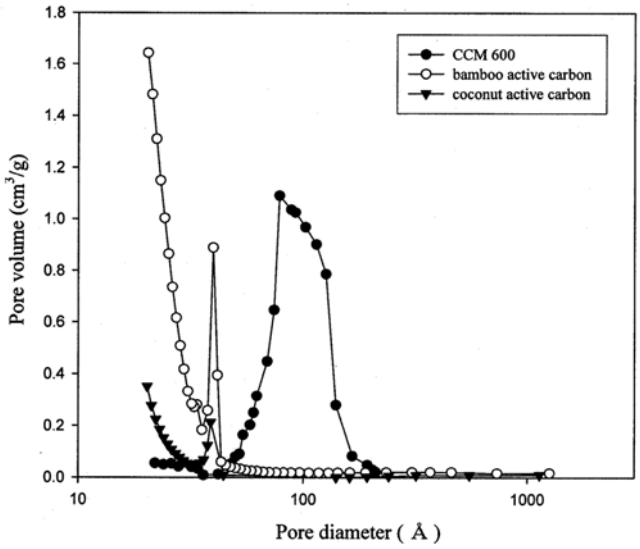

Fig. 5. Pore size distributions of bamboo active carbon, coconut active carbon and bamboo charcoal.

The adsorption capacity of bamboo activated carbon was compared with that of coconut activated carbon and carbon cryogel through batch adsorption tests. In the adsorption of Black 5, the bamboo activated carbon gives a comparable capacity with carbon cryogel as found in Fig. 6. The cryogel is known to have a large volume of mesopore similar to the bamboo activated carbon. Because coconut activated carbon has low volume of mesopore, the adsorption capacity is much less than the mesoporous adsorbents. However, the adsorption capacity is very low with all three adsorbents in the adsorption of Red E as demonstrated in Fig. 7. Note that the scale

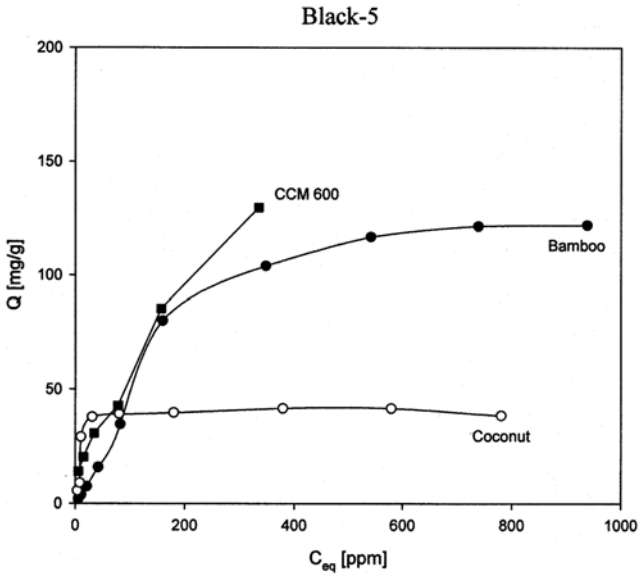

Fig. 6. Comparison of Black 5 adsorption capacity of bamboo activated carbon, coconut activated carbon and carbon cryogel at different equilibrium concentrations.

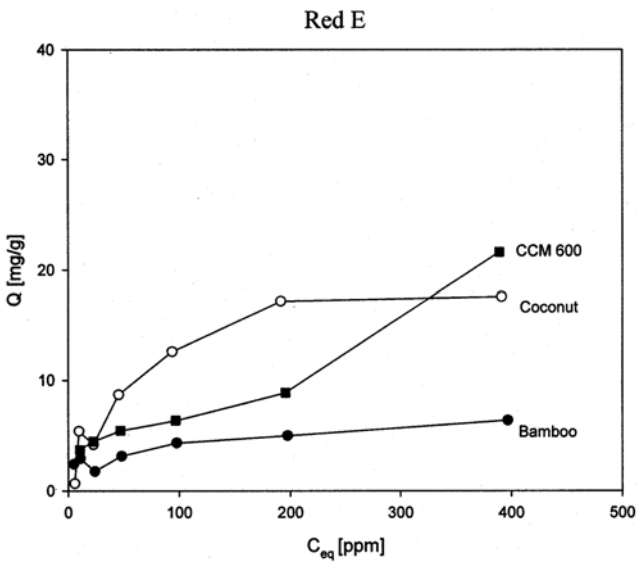

Fig. 7. Comparison of Red E adsorption capacity of bamboo activated carbon, coconut activated carbon and carbon cryogel at different equilibrium concentrations.

of the ordinate is much smaller than in the previous figure. The difference in the adsorption capacities between two dyes can be explained with the structure and chemical nature of the adsorbates. As shown in Fig. 1, Black 5 has a symmetric molecular structure in two dimensions, while Red E is an unsymmetric, three-dimensional molecule. In addition, Red-E has -COOH group at one end of the molecule giving a weaker interaction between Red E and the hydrophobic surface of the adsorbent compared with Black 5 having no such a hydrophilic group [12]. In case of phenol adsorption as shown in Fig. 8, coconut activated carbon illustrates the highest capacity due to its large volume of micropore suitable for the adsorption of small sized phenol molecules.

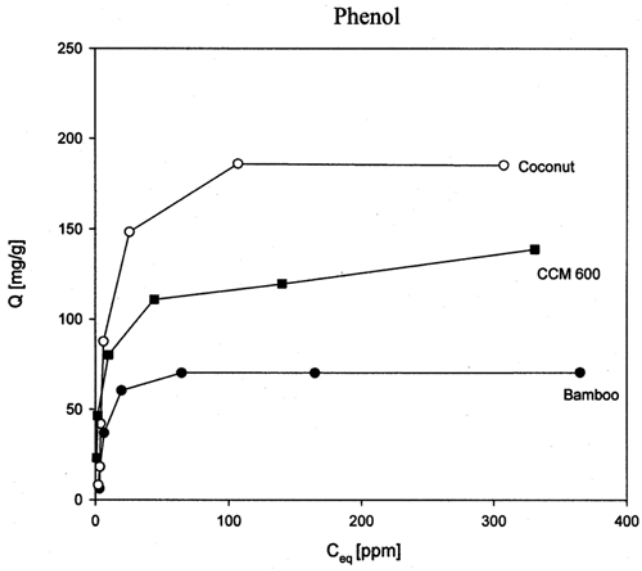

Fig. 8. Comparison of phenol adsorption capacity of bamboo activated carbon, coconut activated carbon and carbon cryogel at different equilibrium concentrations.

Table 2. The Freundlich and Langmuir parameters and correlation coefficients of adsorption isotherms

Adsorbate	Freundlich			Langmuir		
	K_f	1/n	r	Q_0	b	r
Black 5	0.338	1.025	0.957	1,216	0.00031	0.966
Red E	1.366	0.238	0.927	6.777	0.0236	0.878
Phenol	6.305	0.655	0.867	97.55	0.0454	0.937

The adsorption capacity of bamboo activated carbon is fitted in two adsorption isotherms of Freundlich and Langmuir, and their parameters are summarized in Table 2. Because good adsorption is yielded with Black 5, relatively good correlation is found with it. The adsorptions of Red E and phenol are poor, resulting in relatively poor correlation as given in the table.

CONCLUSION

Bamboo activated carbon was implemented in the removal of dye substances from aqueous solution, which is difficult to separate with common adsorbents. The bamboo activated carbon was characterized by surface observation and the measurement of pore size distribution. The adsorption capacity of the bamboo activated carbon was also examined and compared with different adsorbents. From the adsorption experiments with Black 5, Red E and phenol, it is found that the mesoporous activated carbon is suitable for the removal of large dye molecules, but a thick molecule with a hydrophilic functional group is difficult to separate. The adsorption capacity was explained with the result of characterization of the carbon and fitting to adsorption isotherms.

ACKNOWLEDGMENT

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NOMENCLATURE

b : equilibrium constant in the Langmuir isotherm
k_f : adsorption capacity related constant in the Freundlich isotherm
n : inverse exponent in the Freundlich isotherm
Q_0 : saturation related constant in the Langmuir isotherm
r : correlation coefficient

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