Ammonia Adsorption on Bamboo Charcoal with Acid Treatment

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The effect of ammonia adsorption in aqueous solutions was examined for bamboo charcoal carbonized at 400, 700 and 1000°C, and activated carbon. Furthermore, the change of the ammonia adsorption in aqueous solutions was also examined by treatment of each sample with diluted sulfuric acid. Bamboo charcoal carbonized at 400°C and treated with diluted sulfuric acid was the most effective for removing ammonia from aqueous solutions. Although the ammonia adsorption of the bamboo charcoal carbonized at 400°C in gas phase hardly changed by the treatment with diluted sulfuric acid, that in aqueous solutions significantly increased by the treatment.

Key words —— bamboo charcoal, activated carbon, ammonia, ammonium ion, adsorption

INTRODUCTION

Chlorination in water forms chloramines in presence of ammonia.[1)] The chloramine formed by the chlorination has an odor and makes the water taste bad. Furthermore, chloramine has been found to cause the formation of methemoglobin[2)] and is a weak mutagen.[3)] Activated carbon is known to remove chloramines.[4,5)] However, in actual water purification plant, the chloramines can not remove by the activated carbon, because the chloramines are generated by the chlorination which is usually conducted after the activated carbon treatment. Therefore, removing the ammonia that forms chloramine during water treatment is an effective method. Although activated carbon is widely used in water treatment processes, chloramine is formed in tap water due to the insufficient removal of ammonia by the activated carbon that cannot adequately adsorb the ammonia. The biological activated carbon treatment can remove ammonia in water, while it is generally believed that the rate drops sharply at temperatures below 288 K.[6)] Particularly, bacterial activities decrease in winter because of the low temperature. Consequently, the adsorbent simply and easily produced and removing ammonia all year around is needed.

Many reports have describes the adsorption of ammonia gas by activated carbon and charcoal.[7–19)] The charcoal carbonized from 400 to 500°C is found effective for the adsorption of basic ammonia gas due to many acidic functional groups on its surface.[7–11)] It is also described that the adsorption amount of the ammonia gas on activated carbon increases by modifying the acidic functional groups on the surface of the activated carbon with an oxidizing reagent.[20,21)] In aqueous solutions, properties differing from the gas phase are expected because ammonia with a high solubility in water is easily soluble and NH_4^+ is formed on the basis of the solution of pH. However, the properties of the ammonia adsorption in aqueous solutions have not been reported except for ammonia adsorption in the gas phase on activated carbon and charcoal. In this study, the relation between the carbonization temperature and ammonia adsorption was examined in order to effectively remove ammonia from aqueous solutions. Furthermore, the improvement of the adsorption capacity of ammonia by treatment with dilute acid was examined.

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MATERIALS AND METHODS

Sample Preparations —— Giant timber bamboo (*Phyllostachys bambusoides*) dried at 115°C for

24 hr was carbonized at the final temperature of 400, 700 and 1000°C for 1 hr with cutting off the air supply using an electric charcoal kiln KTC (Kankyo Thechno Consal, Japan). For the bamboo charcoal (BC) carbonized at 400°C (hereafter referred to BC400), the bamboo was heated for 2 hr from room temperature to 400°C, the temperature of the charcoal kiln were maintained at 400°C for 1 hr, and then the charcoal kiln was allowed to reduce to the room temperature. For the bamboo charcoal carbonized at 700 and 1000°C (hereafter referred to BC700 and BC1000), the bamboo was heated for 2 hr from the room temperature to 500°C, and then the increasing temperature rate was 2°C/min from 500 to 700 and 1000°C. After the temperature of the charcoal kiln was maintained at 700°C and 1000°C for 1 hr, the charcoal kiln was allowed to cool to the room temperature.

Commercial activated carbon (AC) (Wako Pure Chemical Industries, Japan) (hereafter referred to AC) was used for comparison with the bamboo charcoal. The obtained bamboo charcoal and AC were crushed and sieved, producing powders with a particle diameter under 125 μm.

When the bamboo charcoal powders and AC powders were treated with diluted sulfuric acid, a 0.1 g sample of the powders was put in 100 ml of a 20 mmol/l sulfuric acid solution for 8 hr, and then test samples obtained by filtration were washed 6 times with 10 ml each of purified water. The test samples were dried at 115°C for 3 hr before the experiments.

Brunauer Emmett Teller (BET) Surface Area and Total Pore Volume —— The surface area and total pore volume were determined by nitrogen adsorption. The nitrogen adsorption isotherms were measured at relative pressures from 0.01 to 1.0 and at a 77.4 K adsorption temperature using an Autosorb 1C-VP-2 (Quantachrome, U.S.A.). The surface area was calculated from the BET plots in the relative pressure range from 0.01 to 0.15, and the total pore volume was determined from the amount of nitrogen adsorption at a 0.98 relative pressure.

Measurements of Ammonia Adsorption Isotherms in Aqueous Solutions —— The 0.1 g test samples were placed in 100 ml of ammonia solutions prepared with various concentrations and the test solutions were shaken in an incubator at 20°C for 24 hr. The adsorption amounts of ammonia were calculated from the difference between the initial ammonia concentrations and the equilibrium concentrations of final concentrations after 24 hr. These ammonia concentrations were determined using an ion chromatograph Basic IC 792 (Metrohm, Switzerland) equipped with a conductivity detector and non-suppressor. An eluent of 3 mmol/l nitric acid + 1.5 mmol/l 18-crown-6 was flowed at 1.0 ml/min into a column of Shodex IC YK-421 (Shoko Co., Japan). All samples were injected using a 20 μl sample loop.

Measurements of Ammonia Adsorption Isotherms in Gas Phase —— A ammonia adsorption isotherms were measured using an Autosorb 1C-VP-2 (Quanthachrome, U.S.A.). The combined adsorption isotherm was first measured from 20 to 800 mmHg at 298 K after vacuum treatment at 473 K for 3 hr. After the combined adsorption isotherm was obtained, the same sample was vacuum treatment at 298 K and then a weak adsorption isotherm was measured. A strong adsorption isotherm was calculated from the difference in the combine adsorption isotherm and the weak adsorption isotherm. The combined adsorption isotherm is the adsorption isotherm for the total adsorbed site. The weak adsorption isotherm is the adsorption isotherm for the adsorbed site with a weak adsorption potential such as physical adsorption desorbing at 298 K. The strong adsorption isotherm is the adsorption isotherm for the adsorbed site of the strong adsorption potential such as chemical adsorption not desorbing at 298 K.

Elution of Cation from Samples —— The concentration of cations eluting from each charcoal sample was determined using an ion chromatograph, when the each sample was immersed in purified water. The conditions of the ion chromatograph were the same conditions used for the measurements of the ammonia adsorption isotherms in aqueous solutions. Each 0.1 g sample was immersed in 100 ml of purified water, and then the test solution was shaken for 24 hr at 20°C. Filtrated test solution was measured using the ion chromatograph after 24 hr.

RESULTS AND DISCUSSION

BET Surface Area and Total Pore Volume

The BET surface area and total pore volume of each sample are shown in Table 1. The BET surface area and total pore volume increased as the carbonization temperature of the bamboo charcoal increased, and those of BC1000 were the highest. Furthermore, those of AC were about four times as high as those of BC1000. This result is the same as the

Table 1. BET Surface Area and Total Pore Volume

	BC400		BC700		BC1000		AC	
	Without treatment	H_2SO_4 treatment	Without treatment	H_2SO_4 treatment	Without treatment	H_2SO_4 treatment	Without treatment	H_2SO_4 treatment
BET Surface Area (m^2/g)	2.17	2.80	367	367	451	447	1670	1610
Total Pore Volume (ml/g)	<0.01	<0.01	0.19	0.19	0.21	0.21	1.62	1.53

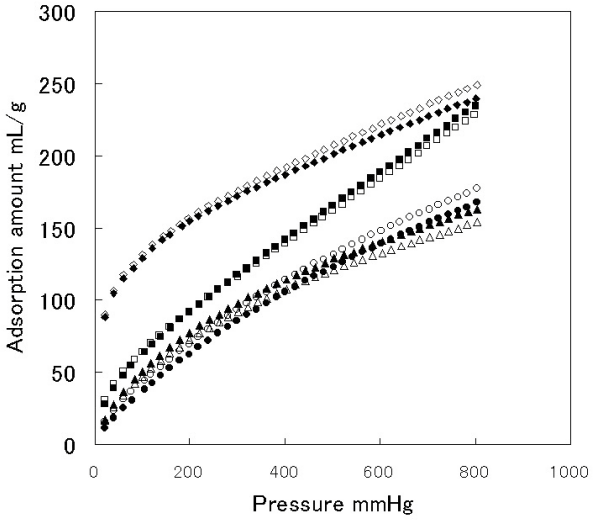

Fig. 1. Combined Adsorption Isotherms of Ammonia Gas
◆, BC400 without treatment; ◇, BC400 with H_2SO_4 treatment; ▲, BC700 without treatment; △, BC700 with H_2SO_4 treatment; ●, BC1000 without treatment; ○, BC1000 with H_2SO_4 treatment; ■, AC without treatment; □, AC with H_2SO_4 treatment.

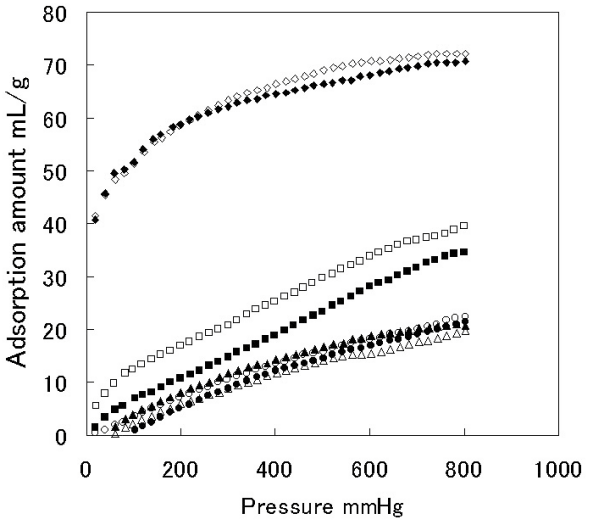

Fig. 2. Strong Adsorption Isotherms of Ammonia Gas
◆, BC400 without treatment; ◇, BC400 with H_2SO_4 treatment; ▲, BC700 without treatment; △, BC700 with H_2SO_4 treatment; ●, BC1000 without treatment; ○, BC1000 with H_2SO_4 treatment; ■, AC without treatment; □, AC with H_2SO_4 treatment.

results from our previous study.[22] The treatment with diluted sulfuric acid did not influence pore structure, because the BET surface area and total pore volume hardly changed by the treatment with diluted sulfuric acid. In the study by Maruyama *et al.*,[21] the BET surface area and pore volume decreased due to the loading of many acidic functional groups by the liquid phase oxidation using $(NH_4)_2S_2O_8$. However, in this study, a few acidic functional groups were loaded and the BET surface area and pore volume hardly changed due to using diluted sulfuric acid as a weak oxidizing agent.

Adsorption of Ammonia Gas

The combined adsorption isotherms and strong adsorption isotherms of ammonia are shown in Figs.1 and 2, respectively. The adsorbed amount on BC400 and AC in the combined adsorption isotherms was higher than that of BC700 and BC1000, and that of BC400 was highest. The pore volume of AC from the results of the nitrogen adsorption isotherms was highest, but the chemisorbed amount on BC400 from the results of the strong adsorption isotherms was the highest. The reason for the high chemisorbed amount on BC400 was due to the presence of more carboxyl groups and phenolic hydroxyl groups as described in previous studies.[7–9,22] Although the chemisorbed amount on bamboo charcoal hardly changed by treatment with diluted sulfuric acid, that on AC slightly increased by this treatment. The increase of chemisorbed amount on AC was considered because of occurring by oxidation of the surface. The AC has an especially high surface area as compared with that of BC, and this result had the same tendency as reported by Maruyama *et al.*[21] Therefore, the treatment with diluted sulfuric acid slightly increased the amount of acidic functional groups for AC but hardly influence that for bamboo charcoal.

Table 2. Components and Total Equivalents of Ion Eluting from Each Sample

	BC400		BC700		BC1000		AC	
	Without treatment	H_2SO_4 treatment	Without treatment	H_2SO_4 treatment	Without treatment	H_2SO_4 treatment	Without treatment	H_2SO_4 treatment
Na (mg/l)	0.07	0.11	0.07	<0.06	<0.06	<0.06	0.30	<0.06
K (mg/l)	2.87	0.30	0.74	0.06	0.89	0.10	<0.05	<0.05
Mg (mg/l)	<0.03	<0.03	0.05	<0.03	0.18	0.03	<0.03	<0.03
Ca (mg/l)	0.08	0.08	0.06	0.04	0.06	0.07	0.04	0.06
Total Equivalent (mEq/l)	0.08	0.02	0.03	0.004	0.04	0.01	0.02	0.003

Elution of Cation from Sample in Aqueous Solutions

The components and total equivalents of ions eluting from each sample are shown in Table 2. A high amount of potassium ion was eluted from the non-treated bamboo charcoal, and much sodium ion was eluted from non-treated AC. However, the amount of ions eluted from each sample treated with diluted sulfuric acid decreased. Therefore, the treatment with diluted sulfuric acid was found to remove the minerals from each sample.

Adsorption of Ammonia in Aqueous Solutions

The adsorption isotherms of ammonia in aqueous solutions for each sample are shown in Fig.3. The amount of ammonia adsorption in the aqueous solutions increased as the carbonization temperature of the bamboo charcoal decreased, and that of AC was the highest. The ammonia adsorption amount on BC400 clearly increased by treatment with the diluted sulfuric solution, and that of BC400 with this treatment was higher than that of AC. Furthermore, the treatment with diluted sulfuric acid slightly influenced the samples except for BC400. This is because the acidic functional groups, such as carboxyl and phenolic hydroxyl groups on the surface of BC400 function as cation exchangers. Although cations such as sodium, potassium, calcium, magnesium eluting from the bamboo charcoal in aqueous solutions interfered with the adsorption for the acidic functional groups as the cation exchangers, the amount of NH_4^+ adsorption on BC400 having many acidic functional groups was found to increase due to the decrease in the amount of cations eluting from bamboo charcoal by the treatment with diluted sulfuric acid.

BC400 treated with diluted sulfuric acid can suppress the formation of chloramine to remove ammonia from aqueous solutions. A manufacturing process of AC needs activation of charcoal, while that of BC400 is only carbonization and simple. Therefore, it is expected that the use of BC400 treated with diluted sulfuric acid suppresses the odor of chloramine in a filtration plant.

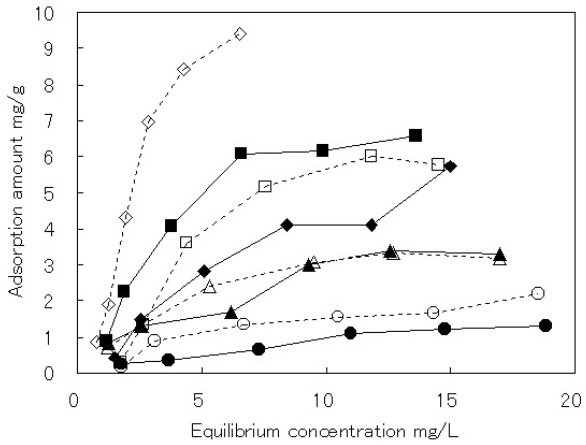

Fig. 3. Adsorption Isotherms of Ammonia in Aqueous Solutions
◆, BC400 without treatment; ◇, BC400 with H_2SO_4 treatment; ▲, BC700 without treatment; △, BC700 with H_2SO_4 treatment; ●, BC1000 without treatment; ○, BC1000 with H_2SO_4 treatment; ■, AC without treatment; □, AC with H_2SO_4 treatment.

In conclusion, BC400 treated with diluted sulfuric acid was the most effective for removing ammonia from aqueous solutions. Although the pore volume of BC400 was hardly influenced by the treatment with diluted sulfuric acid, the treatment removed minerals from BC400. Furthermore, the adsorption amount of ammonia gas on BC400 hardly changed by the treatment with diluted sulfuric acid. However, the adsorption amount of ammonia in an aqueous solution on BC400 significantly increased by this treatment. The interference, *i.e.*, acidic functional groups affecting the ammonia adsorption by absorbed minerals expect for ammonia, was suppressed by treatment with the diluted sulfuric acid.

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