

Influence of Pore Properties and Solution pH on Removal of Free Chlorine and Combined Chlorine by Porous Carbon

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The removal performance of free chlorine and combined chlorine by bamboo charcoals carbonized at 400°C (BC400), 700°C (BC700) and 1000°C (BC1000) and commercial activated carbon (AC) was examined. The removal performance of the free chlorine tended to increase with an increase in the total pore volume and the Brunauer Emmett and Teller (BET) surface area. However, the removal of the free chlorine was found to be related not only to the BET surface area and the total pore volume of the porous carbon, but also to the pH of the test solution. The removal performance of the combined chlorine by AC was the highest for all the porous carbons, and that by BC400 was the highest in the bamboo charcoal, opposite that of the removal performance of the free chlorine. The combined chlorine removal performance by BC1000 was greater than that by BC700. Although it is thought that a porous carbon having large surface area is effective for the removal of combined chlorine, the removal performance by BC400 with the smallest surface area was greater than that by BC700 and BC1000. The solution pH rather than the BET surface area and the total pore volume influenced the removal performance of the combined chlorine. Consequently, the removal performance of the free chlorine and combined chlorine by the porous carbon was effective under acidic conditions.

Key words — porous carbon, bamboo charcoal, free chlorine, combined chlorine, carbonization temperature

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INTRODUCTION

Hypochlorous acid is produced by dissolving Cl₂ in water with the water chlorination, and two forms of HClO and ClO⁻ exist.¹⁾ The forms change depending on the pH. Both HClO and ClO⁻ are called free chlorine. When ammonia, amine, and amino acid, *etc.*, exist, chloramines such as monochloramine, dichloramine, and trichloramine, are produced by a reaction between them and the free chlorine. This chloramine is called combined chlorine. The free chlorine and the combined chlorine are called the residual chlorine.

Chlorination is widely used in order to economically disinfect water. However, the tap water in some regions is unsuitable for drinking due to the strong smell of residual chlorine. Recently, many people drink water obtained from water purifiers or bottled water for this reason. Many water purifiers, which decompose the residual chlorine by an oxidation-reduction reaction with calcium sulfate or ascorbic acid, are widely used. The removal of the residual chlorine by a metal, such as copper, zinc, lead, and iron, has also been reported.²⁻⁴⁾ Furthermore, the removal of the residual chlorine by a porous carbon, such as an activated carbon and a charcoal, has been reported.⁵⁻⁸⁾ It has been described that the residual chlorine was removed by the oxidation-reduction reaction between the carbon on the porous carbon and the residual chlorine, and the pH and temperature of solution influenced the removal performance of the free chlorine.⁵⁾ These reports evaluated an activated carbon but have not systematically evaluated the relation between the pore properties and the removal performance. Especially about combined chlorine, there were a few reports,⁶⁾ and that have only been evaluated the relation between the pH and the removal performance of monochloramine and dichloramine by the activated carbon. In this study, the influence of the pore properties and solution pH on the removal performance of free chlorine and combined chlorine was systematically evaluated. Generally, when a porous carbon is added in water, pH of the water changes due to mineral eluting from the porous carbon. Therefore, the influence of the pH change with the porous carbon for the removal performance of free chlorine and combined chlorine was also considered as a part of the removal performance.

MATERIALS AND METHODS

Preparation of Porous Carbon — The bamboos (*Phyllostachys Bambusoides*) were carbonized using a KTC electric kiln (Kankyo Thechno Consul, Kobe, Japan) at the temperatures of 400 (BC400), 700 (BC700) or 1000°C (BC1000). One hr was maintained at each carbonization temperature, and the electric kiln was then cooled to room temperature. The obtained bamboo charcoal was crushed and sieved to obtain particles between 125 μm and 1000 μm . For comparison, commercial activated carbons (AC) (Wako Pure Chemicals, Osaka, Japan) were purchased. Prior to the experiments, the porous carbons were dried at 115°C for 3 hr.

Pore Properties — The specific surface area and the total pore volume were determined by a nitrogen gas adsorption analysis using an Autosorb 1-C-VP (Quantachrome, Boynton Beach, FL, U.S.A.). The adsorption isotherms of nitrogen were measured at -196°C in the relative pressure range of 0.01–1.0. Prior to the nitrogen gas adsorption analysis, each sample was out-gassed at 200°C for 3 hr. The specific surface area and the total pore volume were calculated by the BET (Brunauer Emmett and Teller) method and at the relative pressure of 0.98, respectively.

Removal Test of Free Chlorine and Combined Chlorine — The test solutions were prepared from a sodium hypochlorite solution (Wako Pure Chemicals) at the free chlorine concentration of 1.0 mg/l. For the removal tests of the combined chlorine, 16 μl of a 28% ammonia solution (Wako Pure Chemicals) was also added to the test solution at the combined chlorine concentration of 1.0 mg/l. The pH of the test solutions was adjusted with 1 mol/l HNO_3 and 1 mol/l NaOH . Each 0.50 g porous carbon was added to the 100 ml test solutions, and then shaken at 25°C. A portion of the test solution was removed to measure the concentration of the free chlorine and the combined chlorine after 5, 10, 20, 30 and 60 min. The blank tests were also carried out.

Measurement of Free Chlorine and Combined Chlorine — The concentrations of free chlorine and combined chlorine were determined using a Pocket colorimeter analysis system (Hach company, Loveland, CO, U.S.A.), which used the principal of a colorimetric method by oxidation of *N,N*-diethyl-*p*-phenyldiamine (DPD).⁹⁾ The free chlorine and total chlorine were measured, and the combined chlorine was calculated from the difference between

the total chlorine and the free chlorine. Prior to the measurements, the sample solutions were filtered using a DISMIC-25cs (ADVANTEC, Tokyo, Japan).

RESULTS AND DISCUSSION

BET Surface Area and Total Pore Volume

The BET surface area and the total pore volume are shown in Table 1. The BET surface area and the total pore volume increased with an increase in the carbonization temperatures of the bamboo charcoal. Those of BC400 were the lowest in all the samples and those of AC were the greatest. In previous reports,^{10–13)} the relationship between these two parameters and the carbonization temperatures has been described.

Removal Performance of Free Chlorine by Porous Carbon

The removal performance at pH 7 of the free chlorine by each porous carbon is shown in Fig. 1. The removal performance by AC was the highest for all the porous carbons. For the bamboo charcoals, the removal performance of the free chlorine tended to increase with an increase in carbonization temperature.

Table 1. BET Surface Area and Total Pore Volume of Bamboo Charcoal and Activated Carbon

	^{a)} S_{BET} [m^2/g]	^{b)} V_{pore} [ml/g]
BC400	6	0.006
BC700	312	0.189
BC1000	437	0.267
AC	981	0.595

^{a)} S_{BET} , BET surface area; ^{b)} V_{pore} , Total pore volume.

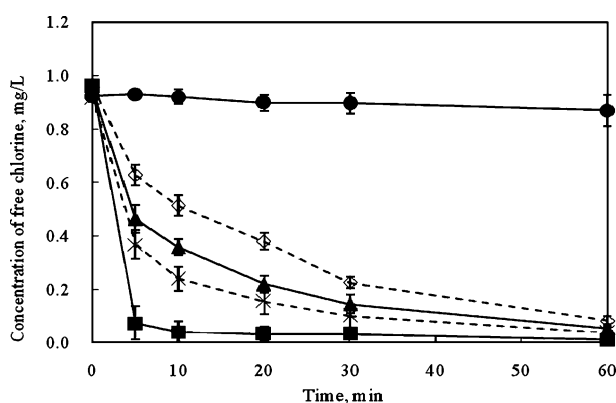
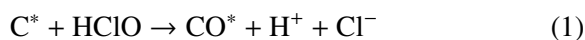


Fig. 1. The Change in Residue Concentration of Free Chlorine with Contact Time. The Mean and Standard Deviation Obtained from Five Replicate Results are Shown

●, blank; ◇, BC400; ▲, BC700; ×, BC1000; ■, AC.

The rate constants, which were calculated by regarding the removal rate of the free chlorine as a second-order reaction, and correlation constants are shown in Table 2. A slope was calculated as the rate constants of the second-order reaction, because the reciprocal of free chlorine concentration versus contact times was linear. The correlation constants of the all porous carbons obtained a linearity over 0.967. Therefore, this reaction looked the second-order reaction overall.

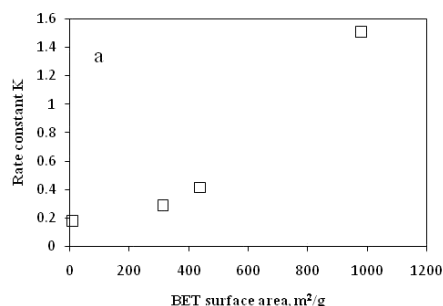
The relationship between the BET surface area or the total pore volume of each porous carbon and the rate constants is shown in Fig. 2. The rate constants of the free chlorine removal tended to increase with an increase in the BET surface area and the total pore volume. Therefore, the development of pores by increasing the carbonization temperature increased the removal performance of the free chlorine. Porous carbon having a large surface area was found to be effective, because the removal of the free chlorine is known to occur by the reaction represented by equation (1).⁵⁾



where C* represents a reactive site on the carbon surface.

Table 2. Rate Constant and Correlation Constant Which was Calculated by Regarding the Removal Rate of the Free Chlorine as a Second-order Reaction

	Rate constant (l/mg/min)	Correlation constant
BC400	0.180	0.972
BC700	0.288	0.981
BC1000	0.415	0.984
AC	1.52	0.967



Removal Performance of Combined Chlorine by Porous Carbon

The removal performance at pH 7 of combined chlorine by each porous carbon is shown in Fig. 3. The removal performance by AC was the highest for all the porous carbons, and that by BC400 was the highest in the bamboo charcoals, opposite that of the removal performance of the free chlorine. The performance by BC1000 was greater than that by BC700. It has been described that chloramine, such as monochloramine and dichloramine, react with carbon on the surface of activated carbon by oxidation-reduction reactions.⁷⁾ Consequently, although it is thought that a porous carbon having large surface area is effective for the removal of combined chlorine, the removal performance by BC400 with the smallest surface area was greater

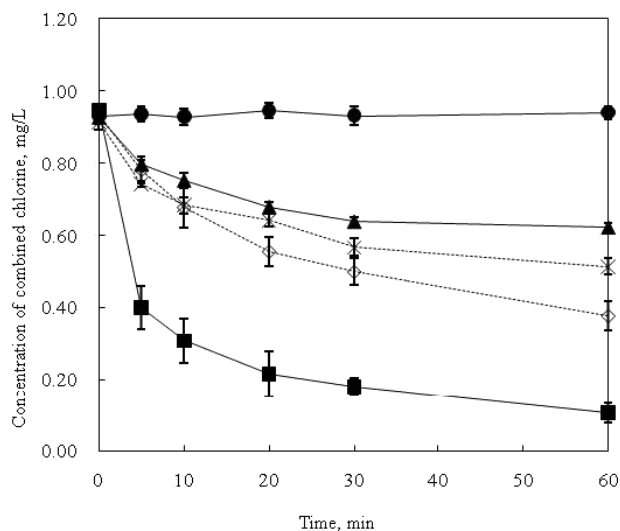


Fig. 3. The Change in Residue Concentration of Combined Chlorine with Contact Time. The Mean and Standard Deviation Obtained from Five Replicate Results are Shown

●, blank; ◇, BC400; ▲, BC700; ×, BC1000; ■, AC.

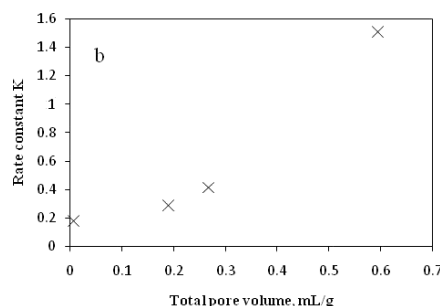


Fig. 2. Relation between the BET Surface Area or Total Pore Volume of Each Porous Carbon and the Rate Constants of Free Chlorine Removal

(a) □, BET surface area; (b) ×, Total pore volume.

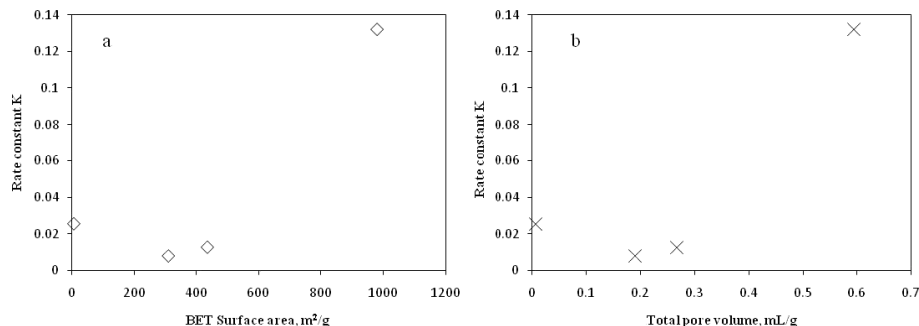


Fig. 4. Relation between the BET Surface Area or Total Pore Volume of Each Porous Carbon and the Rate Constants of Combined Chlorine Removal (a) □, BET surface area; (b) ×, Total pore volume.

Table 3. Rate Constant and Correlation Constant Which was Calculated by Regarding the Removal Rate of the Combined Chlorine as Second-order Reaction

	Rate constant (l/mg/min)	Correlation constant
BC400	0.026	0.990
BC700	0.008	0.870
BC1000	0.013	0.937
AC	0.132	0.993

than that by BC700 and BC1000 in this study.

The relationship between the rate constants, which was calculated by regarding the removal rate of the combined chlorine as a second-order reaction, and the removal performance of the combined chlorine, and the correlation constants is shown in Table 3. The correlation constants of all the porous carbons had a linearity over 0.870. The relationship between the BET surface area or the total pore volume of each porous carbon and the rate constants is shown in Fig. 4. The relationship between the solution pH after 60 min and the rate constants is shown in Fig. 5.

The solution pH rather than the BET surface area and the total pore volume influenced the removal performance of the combined chlorine. The lower the solution pH, the higher the rate constants. Therefore, it was found that the removal performance of the combined chlorine increased with a decrease in the solution pH.

Influence of pH on Free Chlorine Removal by Porous Carbon

The removal performance of the free chlorine under conditions of acid, neutral, and basic and the pH change of the solution are shown in Fig. 6.

The time course of the free chlorine concentra-

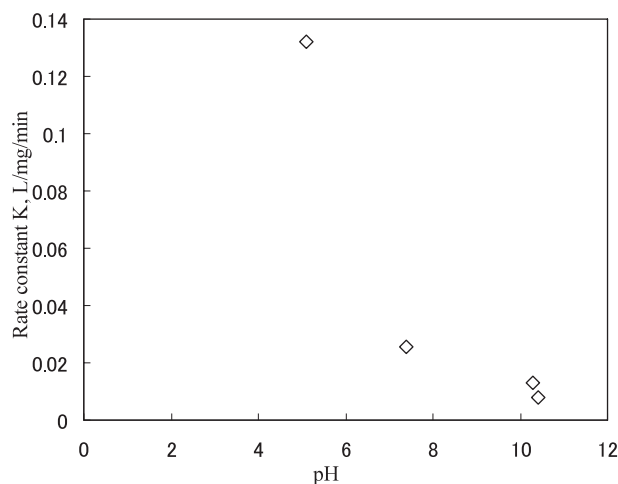


Fig. 5. Relation between Solution pH after 60 Minutes and the Rate Constants of Combined Chlorine Removal by Each Porous Carbon

tion in the blank test was the similar under all conditions. However, the removal performance of the free chlorine under the three conditions was different in all the porous carbons. The influence of pH on the free chlorine removal by BC400 is shown in Fig. 6(b). The removal performance of the free chlorine under the conditions of neutral and acid was higher than that under a basic condition. The removal performance under the neutral condition was equal to that under the acid condition. The influence of pH for the free chlorine removal by BC700 and BC1000 are shown in Fig. 6(c) and Fig. 6(d), respectively. The solution pH after 5 min in BC700 and BC1000 sharply increased. When these porous carbons were added in a free chlorine solution, minerals were found to elute from these porous carbons. Generally, the minerals eluting from the porous carbons increase the solution pH, when the porous carbons are add in the solution. It has been described

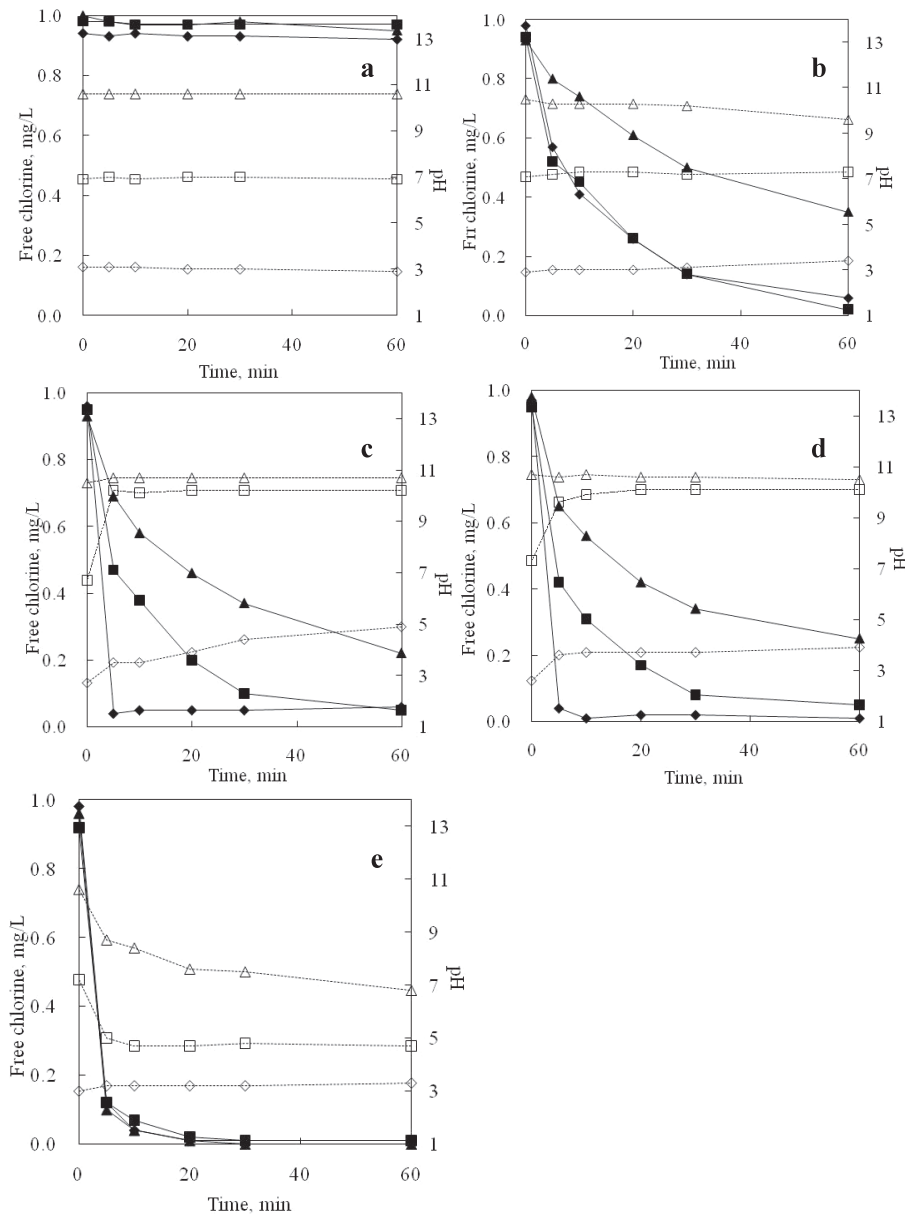


Fig. 6. The Change in Residue Concentration of Free Chlorine and pH of the Solution in (a) Blank Test (b) Removal Test by BC400 (c) Removal Test by BC700 (d) Removal Test by BC1000 and (e) Removal Test by AC under Conditions of Acid, Neutral, and Basic

Free chlorine concentration: ■, neutral condition; ◆, acid condition; ▲, basic condition. pH: □, neutral condition; ◇, acid condition; ◻, basic condition.

that the solution pH increases with the increase of carbonization temperature.¹⁴⁾ In both BC700 and BC1000, a similar tendency was observed, and the removal performance of the free chlorine tended to increase with a decrease of the solution pH. The influence of the pH on the free chlorine removal by AC is shown in Fig. 6 (e). The solution pH in AC only slightly influenced the free chlorine removal.

Overall, the removal performance of free chlorine by porous carbon was influenced by the pH of the solutions, and the removal performance tended to increase with a decrease in the solution pH. Fur-

thermore, when the solution pH was below 8, the removal performance of the free chlorine tended to significantly increase. For instance, the removal performance of the free chlorine under the acid condition by BC400 was equal to that under the neutral condition below pH 8. When the solution pH after 60 min was below pH 8, the removal performance by BC700 and BC1000 was especially high. The solution pH after 60 min under all conditions by AC was below pH 8, and the removal performance by AC was the similar under all the conditions. This occurred from the different forms of free chlorine

such as HClO and ClO^- by the effect of pH. It is widely known that the pH of the solution influences the free chlorine form such as HClO and ClO^- .¹⁵⁾ Although the form of the free chlorine is almost the ion of ClO^- under the basic condition, the ratios of the molecule form as HClO increase with a decrease in pH. Especially, the ratios of the molecule's form sharply increases in the pH range of 7 to 8, and the ratios of the molecule's form is 28.0% at pH = 8 (15°C), 79.7% at pH = 7 (15°C), and 97.5% at pH = 6 (15°C).¹⁵⁾ Since the change in free chlorine form in the pH range of 7 to 8 coincides with the increase in the removal performance of the free

chlorine below pH 8, the free chlorine molecule such as HClO was considered to be removed by the porous carbon.

The removal performance of the free chlorine by AC did not make a difference, although the solution pH was different as pHs 3.3 and 6.8. This reason is probably explained by the similar ratio of the molecule form below pH = 6. This was the similar to the results reported by Suidan *et al.*⁵⁾ that the OCl^- species reacts more slowly than HClO . Therefore, the removal performance study of the free chlorine by porous carbon concluded that the performance is especially effective below pH 8, and

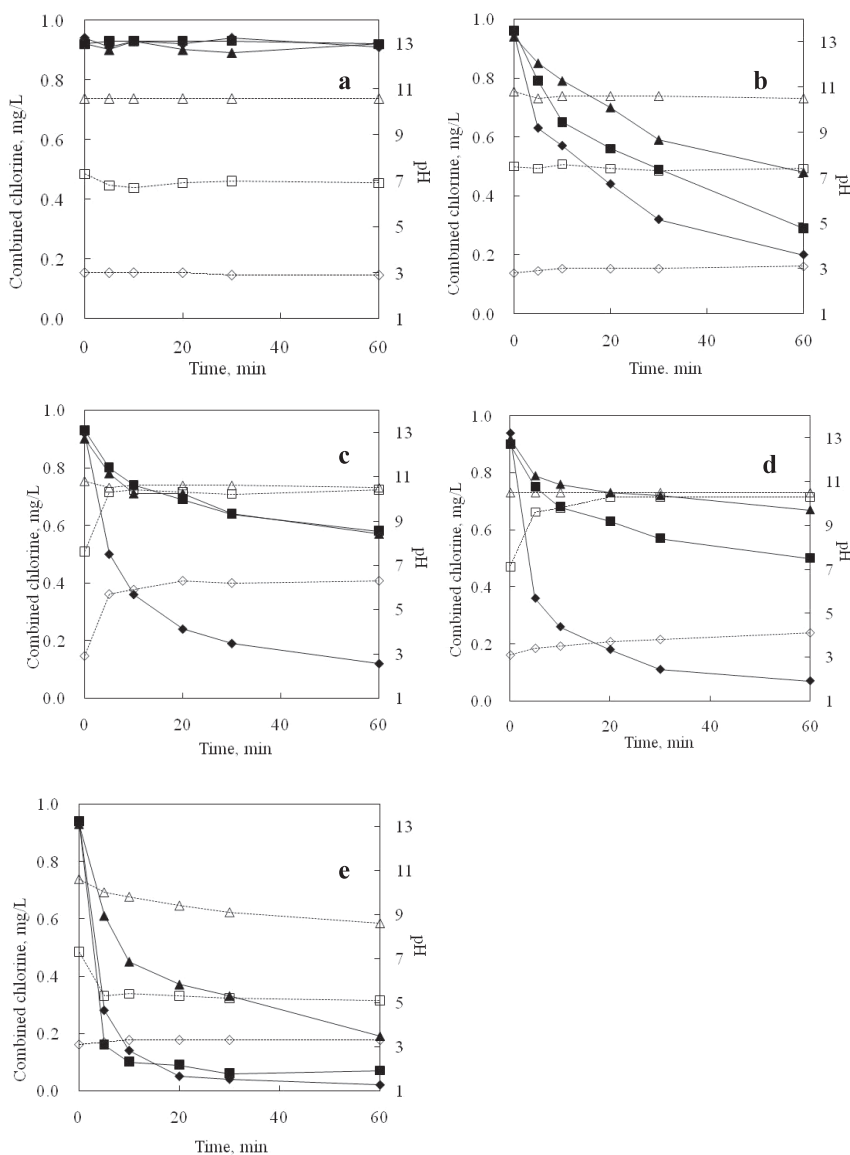


Fig. 7. The Change in Residue Concentration of Combined Chlorine and pH of the Solution in (a) Blank Test (b) Removal Test by BC400 (c) Removal Test by BC700 (d) Removal Test by BC1000 and (e) Removal Test by AC under Conditions of Acid, Neutral, and Basic

Combined chlorine concentration: ■, neutral condition; ◆, acid condition; ▲, basic condition. pH: □, neutral condition; ◇, acid condition; ◻, basic condition.

effectively the molecule form of HClO tended to be removed. In this study, the removal performance of the free chlorine by AC was especially high, because the activated carbon was produced by the ZnCl₂ activation. In the activation method, the activated carbon is washed with an acid due to the removal of zinc. Therefore, the pH of the activated carbon surface is low. Generally, the pH of the activated carbon surface varies with an activation process and following treatments. Even if pore structures of the activated carbons were similar, the removal performance for the free chlorine will be not similar. The removal performance was found to increase with decrease in solution pH caused by the activated carbon.

Influence of pH on Combined Chlorine Removal by Porous Carbon

The removal performance of the combined chlorine under the conditions of acid, neutral, and basic and the pH change of the solution are shown in Fig. 7. The time course of the combined chlorine concentration in the blank test was similar under all conditions. However, the removal performance of the combined chlorine under the three conditions was different in all the porous carbons like that of the free chlorine. The influence of the pH on the combined chlorine removal by BC400 is shown in Fig. 7(b). The removal performance of the combined chlorine tended to increase with a decrease in the solution pH. However, the removal performance for free chlorine was equal below pH = 8, while that for combined chlorine at pH = 7 was difference from that at pH = 3. The influence of pH on the combined chlorine removal by BC700 is shown in Fig. 7(c). The removal performance under the acid condition was especially high. The removal performance for the combined chlorine under the neutral condition was equal to that under the basic condition, although that for the free chlorine under the neutral condition was different from that under the basic condition. The reason for this is that the time course of the pH change is almost equivalent.

The removal performance of combined chlorine by BC1000 is shown in Fig. 7(d). The performance under the acid condition was especially high, similar to BC700. The performance tended to increase with a decrease in the pH of the solution. The removal performance of the combined chlorine by AC is shown in Fig. 7(e). The performance was high under both the neutral and acid conditions, while the performance is almost equivalent below pH 5.

Overall, the removal performance of the combined chlorine by porous carbon was influenced by the pH of the solutions, and the removal performance tended to increase with a decrease in the solution pH. The form of combined chlorine is also different and influenced by the pH. Normally monochloramines will be formed at pH greater than 8.5, dichloramines between pH 4.8 and 8.5, and trichloramines below pH 4.8.¹⁶⁾ In Fig. 4, the correlation between the BET surface area and the total pore volume wasn't found. This will be due to a change in the form of combined chlorine with the change in solution pH by the porous carbons. The solution pH of BC400 with the smallest surface area and total pore volume was about 7, and that of BC700 was about 10. Therefore, dichloramine will be mainly formed in BC400, and monochloramine will be mainly formed in BC700 and BC1000.

It is expected that the removal performance of the dichloramine and trichloramine is higher than that for the monochloramine. Further, the removal performance of the combined chlorine by AC was especially high. It is considered to be based on the same reason as that of the free chlorine. The removal performance study of the combined chlorine by porous carbon concluded that the performance is especially effective below pH 5.

REFERENCES

- 1) Manahan, A. E. (1991) *Environmental Chemistry*, 5th Ed., Lewis Publishers, Michigan, pp. 209–210.
- 2) Asada, T., Omichi, M., Yamada, A., Yamada, M. and Oikawa, K. (2004) Study on a Removal Mechanism for Residual Chlorine by Copper Fiber. *Biomed. Res. Trace Elem.*, **15**, 42–48.
- 3) Ozdemir, M. and Tufekci, M. (1997) Removal of Chlorine Residues in Aqueous Media by Metallic Iron. *Water Res.*, **31**, 343–345.
- 4) Onodera, S., Tabata, M., Nakajima, Y., Shimizu, A., Shimada, T., Ishikura, S. and Suzuki, S. (1981) Hygienic Chemical Study of Water Supply. *EISEI KAGAKU*, **27**, 317–322 (in Japanese).
- 5) Suidan, M. T., Snoeyink, V. L. and Schmitz, R. A. (1977) Reduction of Aqueous Free Chlorine with Granular Activated Carbon—pH and Temperature Effects—. *Environ. Sci. Technol.*, **11**, 785–789.
- 6) Kim, B. R. and Snoeyink, V. L. (1980) The Monochloramine-GAC Reduction in Adsorption Systems. *J. Am. Water Works Assoc.*, 488–490.
- 7) Jaguaribe, E. F., Medeiros, L. L., Barreto, M. C. S.

- and Araujo, L. P. (2005) The performance of activated carbon bagasse, babassu, and coconut shells in removing residual chlorine. *Brazilian Journal of Chemical Engineering*, **22**, 41–47.
- 8) Fukuhara, T., Iwasaki, S., Baba, M., Kawasaki, N., Nakamura, T., Tanada, S. and Abe, I. (2008) Removal of Chlorine Residues in Water by Porous Carbonaceous Materials., *Kagaku to Kougyou*, **82**, 120–126 (in Japanese).
- 9) Franson, M. A. (1975) *Standard Methods for the Examination of Water and Wastewater*, 14th Ed., American Publish Health Association, Washington DC., pp. 332–334.
- 10) Asada, T., Ishihara, S., Yamane, T., Toba, A., Yamada, A. and Oikawa, K. (2002) Science of Bamboo Charcoal—Study on Carbonizing Temperature of Bamboo Charcoal and Removal Capability of Harmful Gases. *J. Health Sci.*, **48**, 473–479.
- 11) Asada, T., Oikawa, K., Kawata, K., Iyobe, T. and Yamada, A. (2004) Ion Chromatographic Determination of Ammonia in Air Using Sampling Tube of Porous Carbon. *Anal. Sci.*, **40**, 125–128.
- 12) Asada, T., Oikawa, K., Kawata, K., Ishihara, S., Iyobe, T. and Yamada, A. (2004) Study of Removal Effect of Bisphenol A and β -Estradiol by Porous Carbon. *J. Health Sci.*, **50**, 588–593.
- 13) Asada, T., Ohokubo, T., Kawata, K. and Oikawa, K. (2006) Ammonia Adsorption on Bamboo Charcoal with Acid Treatment. *J. Health Sci.*, **52**, 585–589.
- 14) Matsui, T., Matsushita, Y., Sugamoto, K., Tokuda, Y., Kodama, K., Nakata, K., Oda, M. and Yamauchi, H (2000) Preparation and Analysis of Carbonization Products from Sugi Wood. *Nippon Kagakukai-shi*, 53–61 (in Japanese).
- 15) Jolley, R. L. (1978) *Water Chlorination Environmental Impact and Health effects*, Vol. 1, p. 23, Ann Arbor Science, Michigan.
- 16) Roberts, A. E. (2006) *Water Quality Control Handbook*, 2ed Ed., p. 9.34, McGraw-Hill, New York.