ORIGINAL ARTICLES

Study on a Removal Mechanism for Residual Chlorine by Copper Fiber

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Abstract

We examined a removal effect and a removal mechanism of residual chlorine by copper fiber made from copper sticks. A copper fiber of 1.0 g could remove residual chlorine of about 1.0 mg/L (100 mL) for 60 min. However, the removal effects by copper board, copper line, copper eluate, copper sulfate solution and copper nitrate solution were low. Furthermore, because the removal effects were depressed by addition of bathocuproine which is a chelating agent of copper (I) ion or DMPO (5,5-dimethyl-1-pyrroline-N-oxide) which is a spin trapping agent of radical species, it was presumed that an active substance, such as radical species which might be formed from dissolved oxygen in case of changing from copper (I) ion to copper (II) ion, decomposed residual chlorine. Practically, when chemiluminescence by luminol was measured, the chemiluminescence from a test of copper fiber was detected more than from the test of copper sulfate solution. Furthermore, when the removal effect in sodium hypochlorite solution prepared with degassed purified water was tested, the removal effect was depressed. Therefore, it was presumed that radical species were formed from copper and dissolved oxygen in the water. With regard to the mechanism of the removal effect by copper fiber, it was shown that active radical species, which formed from copper and dissolved oxygen in for copper (I) ion changing to copper (II) ion, partially decomposed residual chlorine.

Key words: copper fiber, copper, residual chlorine, radical species, water treatment

INTRODUCTION

Pasteurization by chlorine of tap water is a bactericidal method well used at present because of reliability and economy. Although the guideline value of residual chlorine concentration in tap water is set under approximately 1 mg/L by the Waterworks Law in Japan, the tap water is unsuitable in some regions because of the strong odor from residual chlorine. Recently, this problem has caused many peoples to install a filtering system or to buy mineral water. Most filtering systems remove residual chlorine by catalysis such as activated carbon and charcoal or decompose residual chlorine by an oxidation-reduction reaction with calcium sulfite or ascorbic acid. Further, it is reported that residual chlorine is removed by the metal, such as copper, zinc, lead and iron [1,2].

In this study, we examined the removal effect for residual chlorine by a copper fiber, which is known to have bactericidal action since ancient. When the copper fiber produced from copper, which has bactericidal action, is used for removal residual chlorine in the tap water, it can be use for a potable purification device and bath water. Specially, the potable purification device may be useful for getting the drinking water on a disaster because

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of the bactericidal effect and the removal effect of residual chlorine, and the use in the bath water may be useful for protection from rough skin and maintenance of bath water. Further, a mechanism of the removal effect by copper was also examined in this study.

MATERIALS AND METHODS
Copper Fiber

Copper fiber (ϕ 30 - 100 μ m) was produced by drawing out copper sticks(ϕ 15 mm) of a purity of not less than 99.99%.

Reagents

Sodium hypochlorite solution (Wako Pure Chemical Industries, Ltd., Japan) was used for preparation of residual chlorine. Purified water for the preparation was obtained from the Milli-Q purification systems (Millipore Co., U.S.A.). Furthermore, degassed purified water was prepared from the purified water by reducing the pressure using an aspirator and stirring using a magnetic stirrer for 30 min and over. All other reagents were of analytical grade.

Determination of Residual Chlorine

Concentration of residual chlorine was determined by the Pocket Chlorimeter 46700-00 (Hach Company, U.S.A.), which used the principle of a colorimetric method by oxidation of DPD (N,N-diethyl-p-phenylenediamine). Residual chlorine was estimated from the concentration of total residual chlorine in all experiments.

Determination of Copper Concentration

Copper ion in water was determined by ion chromatography. The ion chromatography was performed with a MIC (Metrohm, Ltd., Switzerland) using the nonesuppressor system equipped with the 732 IC Detector (Metrohm). The eluent, 4 mM tartaric acid/1 mM ethylenediamine, was flowed into an analytical column, Shodex IC Y521 (Shoko Co., Ltd., Japan), at the flow rate of 1.0 mL/min. A 250 μ L sample loop was used for all injection.

SEM (scanning electron microscope) Image and Elemental Analysis on Surface of Copper Fiber

SEM images on the surface of copper fiber were obtained by a scanning electron microscope S-4100 (Hitachi High-Technologies Co., Japan), and elemental analysis on the surface of copper fiber was analyzed by a X-ray micro analyzer EMAX-5770 (HORIBA, Ltd.,

Japan). Analytical conditions for the X-ray micro analyzer were as follows; an accelerating voltage of 10 kV and a measuring time of 100 sec. Samples were affixed to a sampling stand of SEM made from aluminum by carbon tape.

Measure of Chemiluminescence

It was known that luminol-based chemiluminescent methods can be used to detect many radical species which oxidize luminol to 3-aminophthalate [3,4]. In this study, luminol-based chemiluminescent methods were used for detection of the radical species. A luminol solution of 2 mmol/L was prepared with sodium hydroxide solution of 10 mmol/L, as described by Battino et al [4]. After 200 μ L of the prepared luminol solution was put in a test tube, a sample of 200 μ L was added in the test tube and then the chemiluminescence was instantly measured for 10 sec by the compact lumi VS-5500 (Yamato Scientific Co., Ltd., Japan). The chemiluminescence was estimated by a value of RLU (relative light unit), which was the specific value in this compact lumi VS-5500.

Statistical Analysis

Statistical analyses were performed using Excel Toukei 2002 (SSRI Co. Ltd.). Significance v. s. control on the effect of bathocuproine, DMPO, and degas water was tested by t-test. Further, we used multiple comparison of LSD test to compare chemiluminescence. Statistical significances were set at $p < 0.05$.

RESULTS   AND   DISCUSSION
Comparison of Removal Effect for Residual Chlorine by Various Forms of Copper

When a copper board, a copper line or copper fiber of about 2.0 g was put in sodium hypochlorite solution of 100 mL prepared at a residual chlorine concentration of about 1.0 mg/L, the time course of the residual chlorine concentration was examined under dark and at 20 ℃. The results are shown in Fig.1. Although the copper board and the copper line could hardly remove any residual chlorine, the copper fiber could remove residual chlorine to a concentration of about 0 mg/L for 20 min.

Effect of the Weight of Copper Fiber on the Removal Effect for Residual Chlorine

When copper fiber of 0.1, 0.5, 1.0 and 2.0 g was put in 100 mL of sodium hypochlorite solution which contains a residual concentration of about 1.0 mg/L, the time course of the residual chlorine concentration was examined under dark and at 20 ℃. The results are shown in
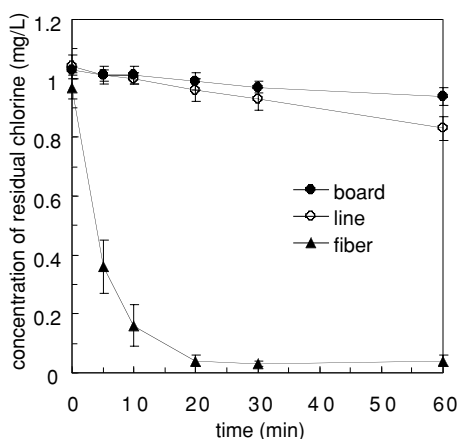
Fig. 1 Time course of the mean and standard deviation (n=5) of the residual chlorine concentration when copper (board, line, fiber) was put in sodium hypochlorite solution
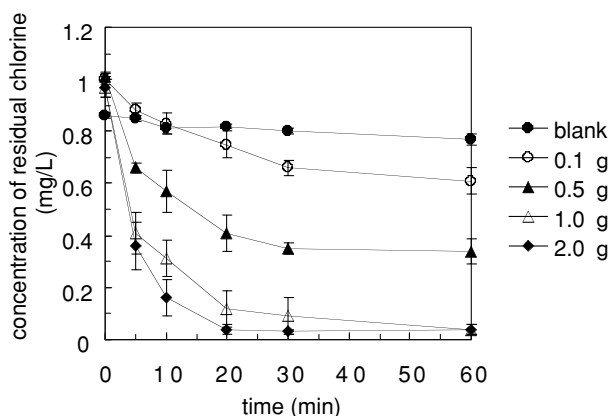

Fig. 2 Effect of copper fiber weight for removal effect of residual chlorine (the mean and standard deviation obtained from five replicate results)

Fig.2. Removal effects tended to increase as the weight of copper fiber increased; the copper fiber of 0.5 g could reduce the residual chlorine concentration to about half of the initial concentration.

Elemental Analysis of the Surface of Copper Fiber after the Removal Test of Residual Chlorine

SEM (scanning electron microscope) images on the surface of the copper fiber were obtained, and elemental analysises on the surface of the copper fiber were analyzed, because the color of the copper fiber changed to black during a removal test of residual chlorine. A slight-
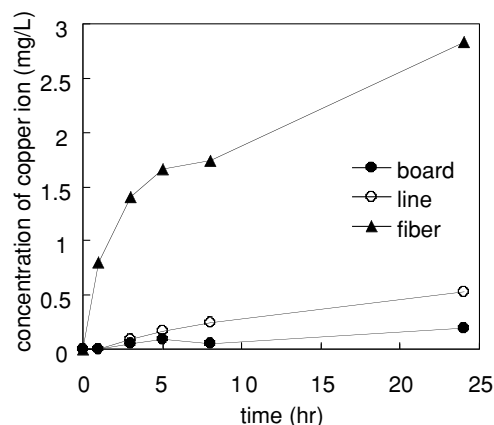

Fig. 3 Copper ion concentration eluating from copper board, line and fiber (the mean obtained from three replicate results)

ly rough surface was observed from the SEM images. From the results of the elemental analysis, the energy value counts of K α X-ray of oxygen against copper, were about 1/10 of the discolored places, and were about 1/20 of the initial places. Although the counts of O(oxygen) on some places tended to increase, existence of oxygen couldn't be concluded because of very few counts of O. Therefore, production of copper oxide or cuprous oxide, which is expected to be a product by an oxidation-reduction reaction between sodium hypochlorite and copper, couldn't be confirmed.

Determination of Eluting Copper Ion in Water

Fig. 3 shows the time course of copper concentration on each copper (board, line and fiber) of about 3.5 g being put in purified water of 100 mL. Copper hardly eluted into the purified water for 24 hr from the copper board, copper at about 3 mg/L eluted into the purified water for 24 hr from the copper fiber. Although 3.5 g of the copper fiber sufficiently removes residual chlorine, eluting copper concentration was larger than 1.0 mg/L of the establish value by The Waterworks Law in Japan. Since copper of 1 mg/L and over may be influence to human health on account of 1 mg/L by the Waterworks Law, considerations of the copper fiber weights and immersing time need for the use as the drinking water.

Removal Effect of Residual Chlorine by Copper Eluate

The removal effect of residual chlorine in copper eluate, to which sodium hypochlorite was added, was examined as to whether eluting copper into purified water remove residual chlorine. Residual chlorine concentration
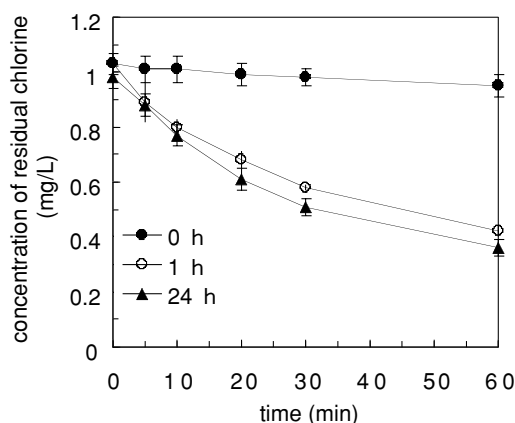
Fig. 4 Removal effect of residual chlorine on copper eluate (the mean and standard deviation obtained from five replicate results)
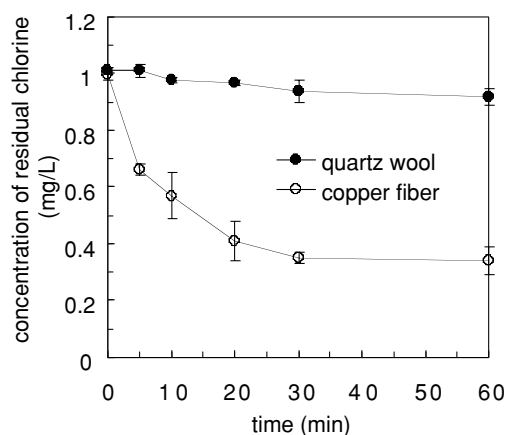

Fig. 5 Comparison of removal effect for residual chlorine between quarts wool and copper fiber (the mean and standard deviation obtained from five replicate results)

at 0 time was determined from residual chlorine concentration in 100 mL purified water, to which equal volume of sodium hypochlorite was added. The copper eluate was prepared as follows: copper fiber of about 5.0 g was put in purified water of 1000 mL, and then was left alone for 1 and 24 hours at 20 ℃. After 1 and 24 hours, the copper fiber was removed and copper eluate was filtered. The filtrate was the copper eluate used for the removal test. The results of removal tests in copper eluate under dark and 20 ℃ are shown in Fig. 4. The removal effect tended to increase as elution times became longer. Therefore, it was showed that the removal effect increased as copper concentration increased, but that the removal effect of copper eluate wasn't as high as the removal effect of copper fiber. Furthermore, the decreasing rate of residual chlorine concentration was very slow, and the decrease of residual chlorine concentration continued after 60 min. Therefore, it is presumed that two mechanisms exist for the removal effect for residual chlorine. Firstly, removal of residual chlorine by the specific effect of copper fiber was caused for 5 min after adding copper fiber, because the removal effect by copper eluate for 5 min was lower than that by copper fiber. Secondly, the removal effect after 5 min wasn't due only to the copper fiber but also was due to the effect by the copper eluate, because the removal effect by copper eluate was similar to the effect by copper fiber after 5 min.

Removal Effect of Residual Chlorine by Quartz Wool

Because the specific surface area of copper fiber was very large as compared with copper board and copper

line, it was also suspected that the mechanism of the removal effect was physical adsorption or retentiveness. Therefore, the removal effect by a fiber other than the copper fiber was examined. The sample was quartz wool, which does not react with sodium hypochlorite because of it's inactive property. The quartz wool or the copper fiber of about 0.5 g was put in sodium hypochlorite solution of 100 mL prepared at residual chlorine concentration of about 1.0 mg/L and the time course of residual chlorine concentration was examined under dark and 20 ℃. The results are shown in Fig. 5. Residual chlorine concentration hardly decreased, when the quartz wool was used. From this result, it was confirmed that the removal effect was not physical adsorption or retentiveness due to the large surface area of the fiber but a chemical effect by the copper fiber.

Removal Effect of Residual Chlorine by Copper(II) Sulfate Solution

The removal effect was examined as to whether copper (II) ion influences a removal effect by using a copper(II) solution, such as copper (II) sulfate solution or copper(II) nitrate solution. Copper (II) sulfate solution or copper (II) nitrate solution of 1 mL (1000 mg/L) was added to a sodium hypochlorite solution (100 mL) at the residual chlorine concentration of about 1.0 mg/L, and time course was examined under dark and 20 ℃. Purified water of 1 mL was added to sodium hypochlorite solution (100 mL) for a control test. The results of removal effect by copper (II) solution are shown in Fig. 6. The removal effect of copper (II) solution was lower than that
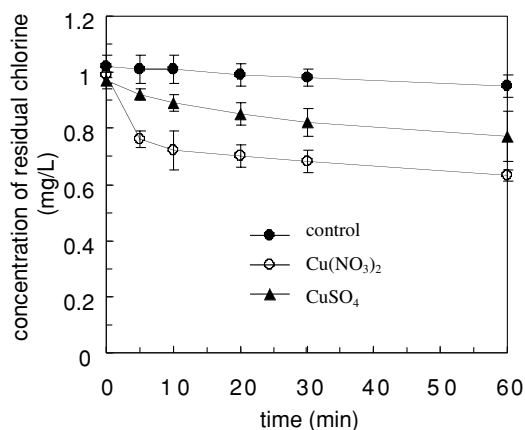
Fig. 6 Removal effect of residual chlorine by $Cu(NO_3)_2$ and $CuSO_4$ (the mean and standard deviation obtained from five replicate results)

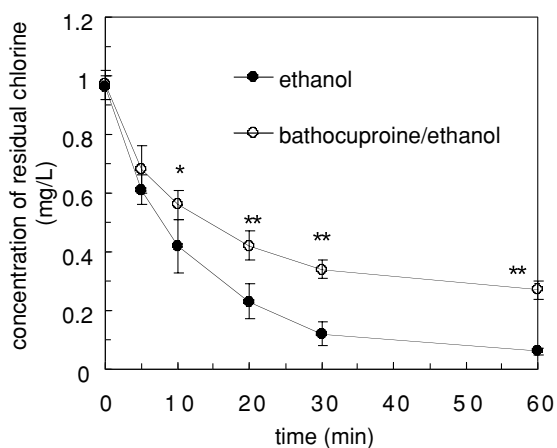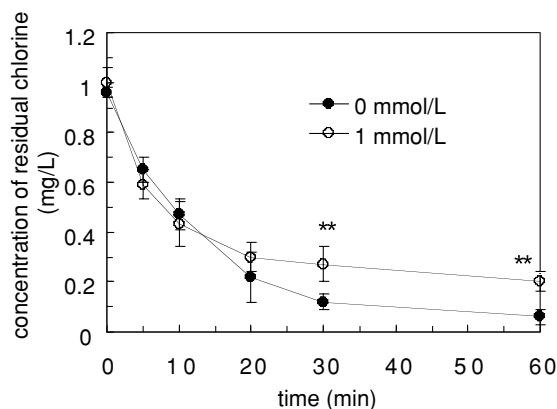Fig. 8 Effect of DMPO for removal effect of residual chlorine (the mean and standard deviation obtained from five replicate results; **Significance at $p<0.01$ v. s. control)

Fig. 7 Effect of bathocuproine for removal effect of residual chlorine (the mean and standard deviation obtained from five replicate results; *Significance at $p<0.05$ v. s. control, **Significance at $p<0.01$ v. s. control)

added, and the removal effect for residual chlorine was examined under dark and 20 ℃ . The effect of bathocuproine is shown in Fig. 7. When bathocuproine was added, the removal effect was similar to the effect without bathocuproine for about 5 min. However, the removal effect was different after 5 min. Although residual chlorine concentration continued to decrease in the removal test without bathocuproine, the removal effect was depressed by addition of bathocuproine. As a result, a mechanism was presumed as follows: the removal effect after 5 min may be caused by copper (I) ion, because the effect was depressed by bathocuproine, a chelating agent for copper (I) ion. At the same time, it was confirmed that the removal effect after 5 min was hardly caused by copper which don't have positive charge, too.

Effect of DMPO (5,5-Dimethyl-1-pyrroline-N-oxide) on the Removal Effect for Residual Chlorine

Although it was confirmed after the first 5 min of a time course test that copper (I) ion influenced the removal effect for residual chlorine, a long time was necessary to decrease residual chlorine concentration in the test using copper eluate. Accordingly, we supposed that a radical species is secondarily formed from water or dissolved oxygen in producing copper (II) ion from copper (I) ion. Depression test by addition of DMPO, which is a radical trapping agent, was examined to determine whether the radical species relate to the removal effect of residual chlorine. DMPO was added to become concentration of 1.0 mmol/L in about 1.0 mg/L sodium hypochlorite solution (50 mL), and then copper fiber of 0.5 g was put in the prepared solution. Fig. 8 shows the time

of copper eluate, although much copper ought to exist in copper(II) solution compared with copper eluate. Therefore, it was presumed that there is not much possibility of the removal of residual chlorine by copper (II) ion.

Effect of Bathocuproine on the Removal Effect of Residual Chlorine

The effect of bathocuproine, which selectively forms a chelate with copper (I) ion, was tested to examine whether copper (I) ion influences on the removal effect. Bathocuproine was dissolved in ethanol solution (0.1 g/100 mL), because it was insoluble in water. A copper fiber of 1.0 g was put in sodium hypochlorite solution of 100 mL (residual chlorine concentration of about 1.0 mg/L) to which a bathocuproine solution of 1 mL was
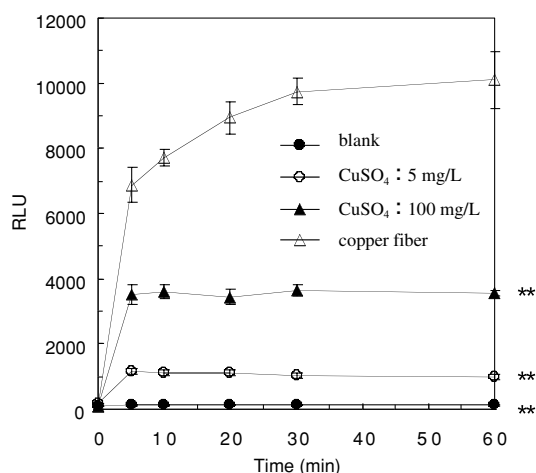
Fig. 9 Comparison of chemical luminescence between copper fiber and copper sulfate solution (the mean and standard deviation obtained from five replicate results; **Significance at p<0.01 v. s. copper fiber)
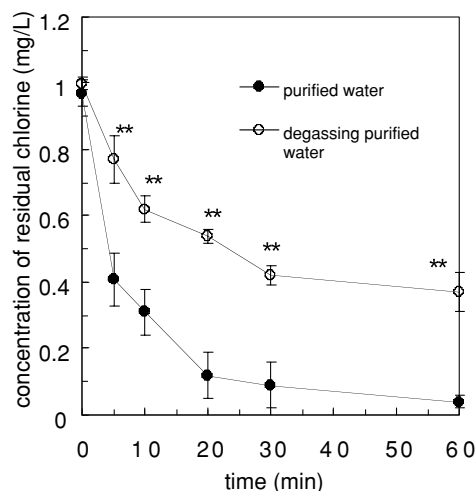

Fig. 10 Effect of degassing purified water for removal effect of residual chlorine (the mean and standard deviation obtained from five replicate results; **Significance at p<0.01 v. s. control)

course of the residual chlorine concentration under dark and 20 ℃. In the removal test with added DMPO, the removal effect was depressed after 30 min. Therefore, it was thought that residual chlorine concentration decreased because of radical species, which can be trapped by DMPO after 30 min.

Confirmation of Radical Species Formation

The test using a chemiluminescent method by luminol solution was experimented to confirm that eluting copper ion from copper fiber forms radical species. Copper fiber of about 2.0 g, was put in 100 mL of purified water, and then the time course of chemiluminesence by luminol was measured under dark and 20 ℃. Furthermore, a copper （Ⅱ） sulfate solution was used for comparison, because it is well known that the chemiluminescence by luminol can be catalyzed by Cu(Ⅱ) ion [5,6]. The results are shown in Fig. 9. Although absolute values of the chemiluminescence cannot be discussed because of the relative values in this study, it was confirmed that reactive substances, which cause the luminescence, were detected in the sample of copper fiber in purified water. The chemiluminescence by the copper fiber was about 2 - 10 times that of copper （Ⅱ） sulfate solution (5 and 100 mg/L). Therefore, it was presumed that reactive substances, such as radical species, were secondarily formed from the copper fiber and that part of residual chlorine was decomposed by those species.

Effect of Degases

The removal effect of residual chlorine in sodium hypochlorite solution prepared with degassed purified water was tested to confirm that radical species were formed from copper ion and dissolved oxygen. As regards to iron, it is reported that dissolved oxygen decreases during contact with iron, when residual chlorine disappears during contact with iron [7]. Therefore, it is presumed that dissolved oxygen influences on the removal effect of residual chlorine. The results of depression test are shown in Fig. 10. The removal effect of residual chlorine in sodium hypochlorite solution prepared with the degassed purified water was depressed in comparison with the removal effect in sodium hypochlorite solution prepared with non degassed purified water. Therefore, it was confirmed that both copper ion and dissolved oxygen were partially responsible for the removal effect of chlorine, and it was presumed that radical species were secondarily formed from copper ion and dissolved oxygen.

CONCLUSION

Removal capability of residual chlorine by the copper fiber was very high; a copper fiber of about 1.0 g in 100 mL sodium hypochlorite solution could remove residual chlorine sufficiently. As regard to the mechanism of the removal effect of residual chlorine by copper fiber, it was presumed that very reactive substances, such as radical species, which were secondarily formed from dissolved oxygen in case of changing from copper(Ⅰ) ion to copper(Ⅱ) ion, partially decompose residual chlorine after

5 min. Although it was a main mechanism that residual chlorine was decomposed by an oxidation-reduction reaction between copper and sodium hypochlorite soon after putting in the copper fiber, it was presumed that radical species partially concern with removal of residual chlorine after about 5 min. Although it was known well that hydroxyl radical is formed from copper and hydrogen peroxide such as in the Fenton reaction [8], it has not been reported that radical species are formed from copper and water. For the mechanism of bactericidal effect by metal such as copper or silver, it is reported that the bactericidal effect by metallic ion is concerned with a very small amount of radical species, which is produced by catalysis of metal [9,10]. In this study, it is presumed that radical species were effectively formed by use of the copper fiber. It was expected that the copper fiber was used for the removal of residual chlorine in tap water as a highly efficient material also having bactericidal effects.

ACKNOWLEDGEMENTS

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