Decomposition of Monochloramine from Water with Rice Bran

Atsuko Adachi,* Shiho Kimata, Mika Noguchi, and Toshio Okano

Department of Hygienic Sciences, Kobe Pharmaceutical University, Motoyamakitamachi 4-chome, Higashinada-ku, Kobe 658–8558, Japan

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Removal efficiency of monochloramine by rice bran was investigated over the range of pH 3–12. The removal rate of residual chlorine by rice bran was similar to activated carbon. Monochloramine was successfully removed with an average removal efficiency of 95% after 90 min when rice bran was applied to chlorinated sewage effluents that contained 0.22–0.46 mg/l monochloramine. The removal of monochloramine by rice bran was attributed to its decomposition by direct reaction with rice bran. Here, we report the findings of the efficiency of rice bran removal of monochloramine using the batch system in laboratory tests, and describe elucidation of the mechanism of its removal.

Key words —— rice bran, monochloramine, sewage effluent, activated carbon

INTRODUCTION

Free chlorine has been widely used as a disinfectant for urban wastewater treatment and biofouling in condensers at power plants. If the water contains ammonia, the solution will probably also contain two forms of combined chlorine: monochloramine and dichloramine.[1,2] Snoeyink *et al.*[3] investigated chlorinated effluents from 20 wastewater treatment plants and showed total chlorine residuals ranging from 1 to 1.5 mg/l. They also found that the predominant species in chlorine residuals was monochloramine. Monochloramine was been found to cause the formation of methemoglobin, depression of the hexose monophosphate pathway, shortened erythrocyte survival, and hemolysis in hemodialyzed uremic patients.[4] Shih *et al.*[5] reported monochloramine to be a weak mutagen when reversion of trp C to trp^+ in strain No. 168 of *Bacillus subtilis* was used as an indicator. This strain is biochemically deficient, requiring L-tryptophan to be converted to trp^+ for nutritional independence. The trp C marker of the strain is a stable locus with a low spontaneous-reversion frequency. Small increases in absolute numbers of trp^+ revertants provided evidence of mutagenesis by chloramine, as judged by the increase in survivors. Numerous toxic effects of chloramine on aquatic species, as evidenced by fish deaths in rivers with chlorinated effluents, have been reported.[6,7] Zillich[8] reported that chloramines at a concentration of 0.085 mg/l nearly eliminated spawning, and that at 0.043 mg/l significantly reduced the number of spawnings and the number of eggs produced per spawning in freshwater fish. To remove monochloramine, adsorption on activated carbon[9,10] or photochemical decomposition[11] have usually been used. One problem with the use of activated carbon is its cost. The photochemical reaction with ultraviolet irradiation hardly occurs without a combination of oxidants, and oxidants such as O_3 or H_2O_2 have been used predominantly. Based on this information, we studied several scavengers to find an effective one. In the process of these examinations, it was found that rice bran had a removal effect on monochloramine.

*To whom correspondence should be addressed: Department of Hygienic Sciences, Kobe Pharmaceutical University, Motoyamakitamachi 4-chome, Higashinada-ku, Kobe 658–8558, Japan. Tel.: +81-78-441-7564; Fax: +81-78-441-7565; E-mail: a-adachi@kobepharma-u.ac.jp

MATERIALS AND METHODS

Materials —— Rice bran was purchased at a local market. Monochloramine solution was synthesized by the addition of chlorine and ammonium hydroxide to a bicarbonate buffer of pH 9.0, as described by Rahman *et al.*[12] Activated carbon (powder and granular, coal based carbon) were purchased of practical grade from Wako Pure Chemical Industries Ltd.

(Amagasaki, Japan).

Procedure —— For the study of the removal reaction, batch tests were carried out. Sample 100 ml monochloramine solutions were placed into 100 ml glass-stoppered Erlenmyer flasks, to which 0.1–1 g of rice bran was then added. The samples were mixed with a stirrer. The reaction mixture was filtered through filter paper (quantitative ashless no. 5A Toyo Roshi, Ltd., Japan) to remove the rice bran. The initial 10 ml of filtrate was discarded because of the adsorption of monochloramine by the filter paper. Ten ml of this filtrate was placed in a test tube and the concentration of monochloramine was then determined by the DPD method of Palin.[13] A blank containing only monochloramine solution was used to monitor the stability of the monochloramine solution with respect to time. In most cases, no loss was detected. The removal efficiency of rice bran was calculated by eliminating the contribution. Activated carbon (powder and granular) was tested by the same procedure as rice bran for removal of monochloramine. Chloride ion was analyzed using the Mohr method. Ammonia was measured by the indophenol method.

Statistical Analysis —— Values are shown as means ± S.D. Data were analyzed using one-way ANOVA and, when appropriate, by the Student-Newman-Keul test. Results were considered significant at $p < 0.05$.

RESULTS AND DISCUSSION

Figure 1 shows monochloramine removal efficiencies as a function of time for rice bran and activated carbon (powder and granular). The removal by rice bran was similar to that by activated carbon (granular). Monochloramine was successfully removed from water samples with an average removal efficiency of 95% after 90 min when rice bran was added to water samples containing from 0.2 to 50 mg/l monochloramine. During the first 2 hr of the reaction, no decrease in monochloramine in the blank was observed. After 2 hr of reaction time, 0.092 mmol of monochloramine had reacted with each gram of rice bran. Reaction time is an important parameter. The reduction is initially very fast, but after a short time the rate is reduced and the removal appears to plateau. Figure 2 shows the effect of amount of rice bran on the decomposition of monochloramine. The residual monochloramine decreases in response to the amount of rice bran. In this experiment, 10 g/l of rice bran showed the highest efficiency in the decomposition reaction; that is, more than 95% of monochloramine was decomposed after a 90 min treatment.

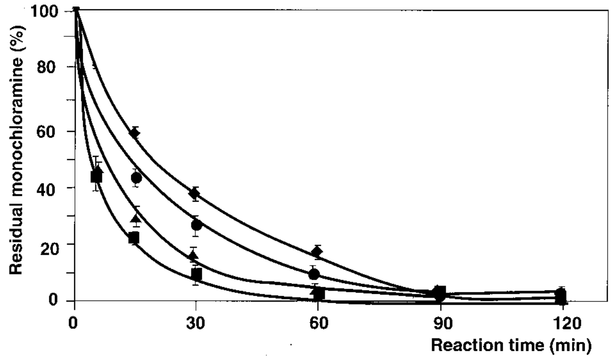

Fig. 1. Removal Efficiency of Monochloramine

Data represent the means ± S.D. of three separate samples. ●: Rice bran 10 g/l, NH_2Cl 50 mg/l, ▲: Rice bran 10 g/l, NH_2Cl 0.2 mg/l, ◆: Activated carbon (granular) 10 g/l, NH_2Cl 50 mg/l, ■: Activated carbon (powder) 10 g/l, NH_2Cl 50 mg/l, pH, 7.0.

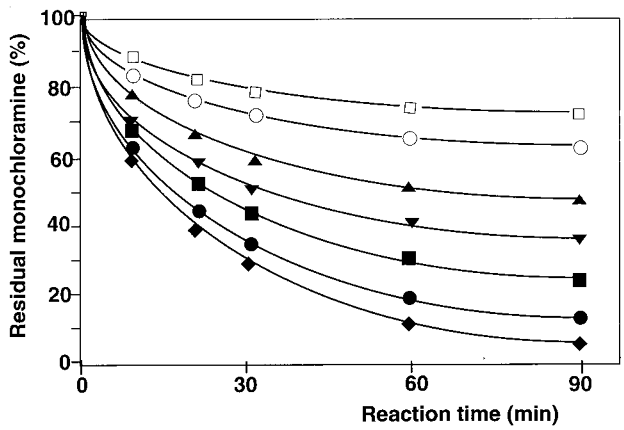

Fig. 2. Effect of Amount of Rice Bran on the Decomposition of Monochloramine

NH_2Cl: 50 mg/l, Reaction time: 1.5 hr, pH 7.0, Rice bran: □ 1 g/l, ○ 2 g/l, ▲ 3 g/l, ▼ 4 g/l, ■ 5 g/l, ● 7 g/l, ◆ 10 g/l.

Figure 3 shows the effect of pH on the reaction of monochloramine by rice bran using buffer solutions at a reaction time of 90 min. Removal was observed over the range of pH 3–12, and it was a fixed value up to pH 10. Therefore, it can be used to treat water samples over a wide range of pH.

When rice bran was applied to sewage effluents containing 0.22–0.46 mg/l monochloramine (Fig. 4), the removal efficiency was almost equivalent to that in pure water. Monochloramine was successfully removed from sewage effluents with average removal efficiency of 95% after 90 min. These observations indicate that rice bran can be used for treatment of environmental water containing monochloramine.

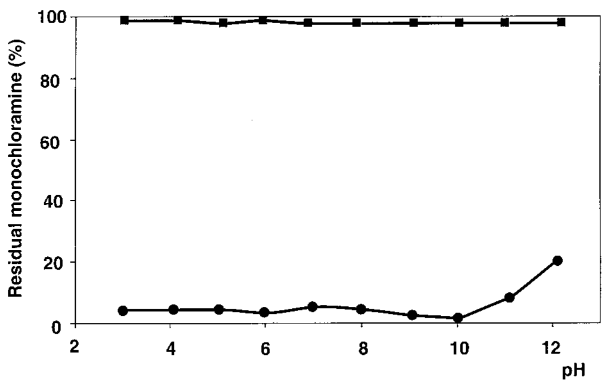

Fig. 3. Effect of pH on the Decomposition of Monochloramine by Rice Bran

NH_2Cl: 50 mg/l, Reaction time: 1.5 hr, pH 7.0, Rice bran: ● 10 g/l, ■ 0 g/l, Citric acid-phosphate buffer, carbonate buffer and sodium hydroxide solution were used for preparation of pH 3–7 and pH 8–12 solutions, respectrvely.

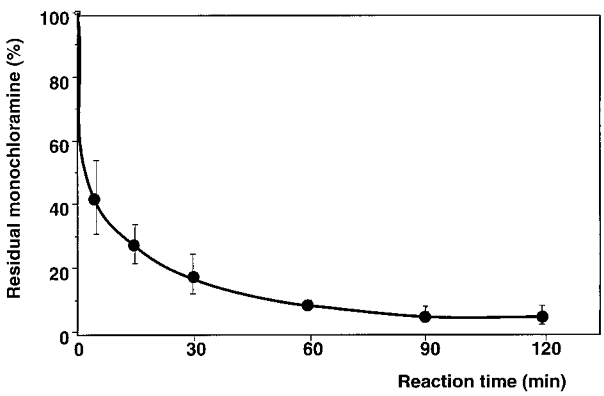

Fig. 4. Removal Efficiency of Monochloramine in Chlorinated Sewage Effluents by Rice Bran

NH_2Cl: 0.22 mg/l (1999, 10/25), 0.37 mg/l (1999, 10/28), 0.46 mg/l (1999, 11/10), Rice bran: 1 g/l, pH: 7.1–7.6

Next, we investigated the mechanism of removal. Kim *et al.*[9] reported that monochloramine reacts with granular activated carbon as shown in Eqs. (1) and (2):

$$NH_2Cl + H_2O + C^* \rightarrow NH_3 + H^+ + Cl^- + CO^* \quad (1)$$

$$2NH_2Cl + CO^* \rightarrow N_2 + 2H^+ + 2Cl^- + H_2O + C^* \quad (2)$$

Two different reactions apparently take place: where C^* and CO^* represent the granular activated carbon surface and a surface oxide, respectively. Thus a portion of the NH_2Cl–N is converted to NH_3 and a portion to N_2. Activated carbon is a well-known dechlorinating agent for water. It reacts with chlorine as shown in Eq. (3):

$$HOCl + C^* \rightarrow H^+ + Cl^- + CO^* \quad (3)$$

They examined the effect of the presence of surface oxides on the reaction with monochloramine; activated carbon samples were reacted with 0.003, 0.007, and 0.010 mol of HOCl/g. As shown by Johnson,[14] this reaction results in an accumulation of acidic surface oxides, the concentration of which increased with the amount of HOCl reacted for these levels of treatment. During the first 1 hr of the reaction, no increase in concentration of other chlorine-containing species was noted as monochloramine was destroyed. The chloride ion concentration began to increase (Fig. 5), put at this point, the total N concentration began to decrease, indicating conversion of NH_2Cl to an end product other than NH_3. The pH was essentially constant throughout the duration of the test. Taking the findings into account, we concluded that the reaction was equivalent to activated carbon. The monochloramine reaction with carbon appears complex. All reaction products except the surface oxides were measured in this study, thus making the production of surface oxides, CO or CO_2 necessary in terms of stoichiometry.

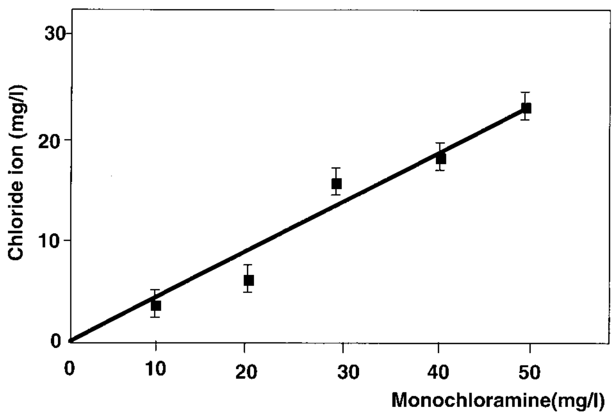

Fig. 5. Formation of Chloride Ion by the Reaction of Monochloramine with Rice Bran

Rice bran: 10 g/l, Reaction time: 1.5 hr, pH: 7.0.

Further studies are needed to determine whether the surface oxides are present on the surface after this reaction.

Rice bran is a waste product from the process of making polished rice from brown rice. Therefore, rice bran is very inexpensive, with a cost of 1/40–1/50 that of activated carbon, and thus its use would significantly lower the cost of wastewater treatment. Additionally, the use of rice bran would represent effective re-use of waste matter. Taken together, the findings of this study suggest that the use of rice bran is an efficient and cost effective method for removing monochloramine from environmental water.

REFERENCES

1) Hopkins, E. S. and Bean, E. L. (1966) *In water purification control, 4th Edn*, p. 108, Williams and Wilkins, Baltimore.
2) Bousher, A., Brimblecomer, P. and Midgley, D. (1989) Kinetics of reactions in solutions containing monochloramine and bromide. *Water Res.*, **23**, 1049–1058.
3) Snoeyink, V. L. and Markus, F. I. (1973) Chlorine residuals in treated effluents. Report prepared in department of civil engineering, university of Illinois at urbana-champaign, for the Illinois institute for environmental quality.
4) Eaton, J. W., Dolpin, C. F., Kjellstrand, C. M. and Jacob, H. S. (1973) Chlorinated urban water: a cause of dialysis-induced hemolytic anemia. *Science*, **181**, 463–464.
5) Shih, K. and Lederberg, J. (1976) Chloramine mutagenesis in Bacillus subtillis. *Science*, **192**, 1141–1143.
6) Grothe, D. R. and Eaton, J. W. (1975) Chlorine-induced mortality in fish. *Trans. Am. Fish Soc.*, **104**, 800–802.
7) Moore, G. S. and Calabrese, E. J. (1980) The health effects of chloramines in potable water supplies. *J. Environ. Pathol. Toxicol.*, **4**, 257–263.
8) Zillich, J. A. (1972) Toxicity of combined chlorine residuals to freshwater fish. *J. Water Pollut. Control Fed.*, **44**, 212–220.
9) Kim, B. R. and Snoeyink, V. L. (1980) The monochloramine-granular activated carbon reaction in adsorption systems. *J. AWWA.*, **72**, 488–491.
10) 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. Tchnol.*, **11**, 785–789.
11) Beltran, F. J., Araya, J. F. and Acedo, B. (1994) Advanced oxidation of atrazine in water-ll. Ozonation combined with ultraviolet radiation. *Water Res.*, **28**, 2165–2174.
12) Rahman, M. S., Berardi, M. R. and Bull, R. J. (1980) The monochloramine-granular activated carbon reaction in adsorption systems. *J. AWWA.*, **72**, 488–491.
13) Palin, A. T. (1967) Methods for the determination in water, of free and combined available chlorine dioxide and chlorine, bromine, iodine and ozone using diethyl-p-phenylene diamine (DPD). *J. Inst. Water Eng.*, **21**, 537–547.
14) Johnson, J. H. (1970) *The effect of dechlorination on the adsorptive capacity of active carbon*. Special problem, Univ. of Illinois, Urbana.