Decomposition of Monochloramine from Water with Rice Bran

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

Department of Hygienic Sciences, Kobe Pharmaceutical University, Motoyamakita-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 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) Zillich8) 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 carbon9,10) or photochemical decomposition11) 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 O3 or H2O2 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.

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.
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 Erlenmeyer 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. 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.

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

\begin{align}
\text{NH}_2\text{Cl} + \text{H}_2\text{O} + \text{C}^* & \rightarrow \text{NH}_3 + \text{H}^+ + \text{Cl}^- + \text{CO}^* \\
2\text{NH}_2\text{Cl} + \text{CO}^* & \rightarrow \text{N}_2 + 2\text{H}^+ + 2\text{Cl}^- + \text{H}_2\text{O} + \text{C}^* 
\end{align}

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\textsubscript{2}Cl–N is converted to NH\textsubscript{3} and a portion to N\textsubscript{2}. Activated carbon is a well-known dechlorinating agent for water. It reacts with chlorine as shown in Eq. (3):

\[ \text{HOCl} + \text{C}^* \rightarrow \text{H}^+ + \text{Cl}^- + \text{CO}^* \]

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,\textsuperscript{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\textsubscript{2}Cl to an end product other than NH\textsubscript{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\textsubscript{2} necessary in terms of stoichiometry.

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


