The influence of Cu(II) on the decay of monochloramine

Jun Fu^{a,b}, Jiuhui Qu^{a,*}, Ruiping Liu^a, Xu Zhao^a, Zhimin Qiang^a

^aState Key Laboratory of Environmental Aquatic Chemistry, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China

^bGraduate School of Chinese Academy of Sciences, Beijing 100039, China

ARTICLE INFO

Article history:

Received 4 July 2008

Received in revised form 30 September 2008

Accepted 30 September 2008

Keywords:

Monochloramine decay

Cu(II)

pH

Complexation

ABSTRACT

Maintenance of monochloramine concentration during water disinfection is important to ensure the microbial safety of drinking water. The decay of monochloramine always occurs and some substances present in the water can accelerate this process. Copper often exists in ionic form in water, but the effect of Cu(II) on the decomposition of monochloramine is largely unknown. In this paper, a series of experiments were carried out under varying conditions of pH, Cu(II) and initial monochloramine concentrations. Results showed that the decomposition rate of monochloramine was greatly enhanced by Cu(II), and this enhancement decreased with the increase of solution pH and the decrease of Cu(II) concentration. It was proposed that the monochloramine decomposition in the presence of Cu(II) was catalyzed via complexation between Cu(II) and monochloramine. The X-ray absorption fine structure experiments gave further evidence to this conclusion. The results will provide useful information for selecting proper disinfection method in water disinfection where Cu(II) exists and reasonable monochloramine dosage during chloramination.

© 2008 Elsevier Ltd. All rights reserved.

1. Introduction

As a secondary disinfectant, monochloramine has been used for drinking water more and more prevalently. It produces much less disinfectant byproducts, such as trihalomethanes and haloacetic acids than chlorine. Especially, when maintaining a free chlorine residual is difficult or natural organic matter (NOM) level is high, monochloramine is usually applied (Jafvert and Valentine, 1992; Than et al., 2001). Monochloramine is less reactive than free chlorine, thus maintaining a higher level of monochloramine residual than free chlorine during water disinfection is necessary for effective inactivation of pathogenic microorganisms.

In order to ensure the disinfection efficiency and minimize the formation of disinfection byproducts, the monochloramine residual in the water should be as stable as possible. It is therefore important to make clear the factors that affect the decomposition of monochloramine during water disinfection. The decay of monochloramine in drinking water can be attributed to both auto-decomposition and reactions with organic or inorganic constituents. The auto-decomposition processes of monochloramine were studied in details (Jafvert and Valentine, 1987; Valentine and Jafvert, 1988). It was found that the auto-decomposition of monochloramine is acid-catalyzed and the reaction rate is highly pH dependent. NOM, ubiquitous in drinking water, can react with monochloramine via redox processes and accelerate the decay of monochloramine (Kawamura, 1983; Ozekin et al., 1996; Vikesland et al., 1998). Inor-

ganic species such as NO_3^- and Fe^{2+} are often present in drinking water. Several studies have noted that the accelerated chloramine decay is related to high levels of nitrification (Wolfe et al., 1990). Fe^{2+} released from corroded iron pipe is one type of oxidizable species that can exert a monochloramine demand, and this process of oxidation was catalyzed by iron oxide on surface (Vikesland and Valentine, 2002a,b). Lead scales on pipes were dissolved into drinking water in the presence of chloramines (Switzer et al., 2006).

However, the stability of monochloramine in the presence of copper, especially dissolved copper, is largely unknown. Dissolved copper mainly including Cu(II) is very persistent and frequently detected in the drinking water (Boulay and Edwards, 2001; Zhang et al., 2002). Copper is widely used as pipe material in household plumbing systems of drinking water throughout the world (Feng et al., 1996). Concentrations greater than 1.0 mg L^{-1} have been reported due to corrosion of copper pipes and brass faucets (Wang et al., 2003). Elemental copper can react with monochloramine through the following reactions at 25°C (Zhang et al., 2002):

The large equilibrium constants of the above reactions show the strong oxidizing capability of monochloramine toward elemental copper. Copper oxide solids are formed according to these reactions. Ammonia, chloride and many organic materials, which are strong

* Corresponding author. Tel.: +86 10 62849151; fax: +86 10 62923558.

E-mail addresses: jhqu@rcees.ac.cn, hjliu@rcees.ac.cn (J. Qu).

ligands for copper ions, can weaken the deposit formation by forming dissolved complexes. The formation of these dissolved complexes caused the dissolution of copper ions into the bulk aqueous solution (Zhang et al., 2002; Christl et al., 2005). Additionally, copper is used as an algicide in the raw water of reservoirs. Long known that copper can act as a heterogeneous or homogeneous catalyst in many reactions (Wang et al., 2003; Lin et al., 2004).

Due to its catalysis, Cu(II) in drinking water supplies may play an important role in the decomposition of monochloramine upon chloramination. But to our best knowledge, the effect of Cu(II) on monochloramine decomposition has not been reported. In this paper, it was for the first time observed that Cu(II) could obviously promote the monochloramine decay in the simulated and real drinking waters, and a complexation mechanism between Cu(II) and monochloramine was proposed.

2. Materials and methods

2.1. Reagents

Experiments were conducted using phosphate-buffered simulated water as well as two types of real drinking water collected from waterworks. The deionized water used for preparing the simulated solutions was obtained from a Barnstead ULTRO pure water system (chemical resistivity > 18 MΩ cm). The two types of real drinking water were respectively collected from Beijing and Shanghai where their source water qualities and treatment processes were largely different. Chemicals used in experiments were all of analytical grade. For glassware cleaning, they were soaked in a concentrated chlorine bath ($\approx 5000 \text{ mg L}^{-1} \text{ Cl}_2$) for at least 24 h, rinsed with deionized water, and dried at 105 °C. Copper and zinc were added into the reaction solution in the form of their sulfate salts (i.e., $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and ZnSO_4).

2.2. Apparatus and procedures

The pH of all solutions was measured with a Fisher 420 meter. Experiments were conducted using phosphate-buffered aqueous solution (7 mM KH_2PO_4). The pH of the solutions was adjusted from 5.0 to 8.0 by the addition of NaOH. Monochloramine stock solutions were prepared by the addition of free chlorine to a well-stirred solution of ammonium chloride. The Cl_2/N molar ratio was about 0.7 and solution pH was adjusted to 8. Under these conditions, over 99% of all active chlorine is monochloramine, which is generally acknowledged (Jafvert and Valentine, 1987; Valentine and Jafvert, 1988). After a designated amount of monochloramine was added to the solution, it was mixed for 20 min before use. The concentration of monochloramine in the stock solution was measured using the N,N-diethyl-p-phenylenediamine-ferrous ammonium sulfate titrimetry method.

Monochloramine decay experiments were conducted by spiking aliquots of monochloramine stock into the aqueous systems. The exact volume of the aliquot was determined according to a targeted initial monochloramine concentration and the sample volume. Experiments were all carried out in a series of 250-mL glass

containers, which were covered with aluminum foil to prevent lights from affecting the reaction solutions. All containers were placed in a temperature controlled ($25 \pm 1 \text{ }^\circ\text{C}$) vibrator. The reactants were added in the following order: buffer, monochloramine precursor, copper (if applicable).

2.3. X-ray absorption fine structure (XAFS) experiments

2.3.1. Sample preparation

The complex $[\text{Cu(II)}-\text{NH}_2\text{Cl}]$ sample was prepared by adding 10 μL of 5 mM CuSO_4 to 30 μL of 10 mM NH_2Cl . The model material was 1.25 mM CuCl_2 solution. The pH values of these solutions were all controlled at 6.5 by phosphate-buffer.

2.3.2. Collection of XAFS data

XAFS experiments were conducted with Beijing Synchrotron Radiation Facility in the Institute of High Energy Physics, Chinese Academy of Sciences. XAFS data acquisition of Cu K-edge (8979 eV) was conducted on 4W1B beamline. The electron beam energy was 1.5–2.2 GeV, and the average beam current was 80 mA. The monochromator consisted of two parallel Si(111) crystals with an entrance slit of 2 mm (Valli et al., 1996). The XAFS spectra were collected in fluorescence mode using an argon-filled ionization chambers detector at room temperature ($\sim 25 \text{ }^\circ\text{C}$).

3. Results and discussion

3.1. Effect of Cu(II) on monochloramine decay in two real drinking waters

The water samples were collected from two cities at the end of each plant's treatment scheme. The water quality characteristics of both drinking waters are presented in Table 1. The contribution of Cu(II) to monochloramine decomposition was calculated using the following equation:

$$f = \frac{\Delta\text{NH}_2\text{Cl}^b - \Delta\text{NH}_2\text{Cl}^a}{[\text{NH}_2\text{Cl}]_0} \times 100\% \quad (4)$$

$\Delta\text{NH}_2\text{Cl}^a$ and $\Delta\text{NH}_2\text{Cl}^b$ expressed amounts of monochloramine decay without and with Cu(II), and $[\text{NH}_2\text{Cl}]_0$ was the initial concentration of monochloramine. As shown in Table 1, the f values for the samples from Shanghai and Beijing were 12–13% and 10–11%, respectively. It was seen clearly that Cu(II) notably promoted the decay of monochloramine in real drinking waters.

3.2. Effect of Cu(II) and monochloramine concentration on monochloramine decomposition

The effect of Cu(II) concentration on the degradation of monochloramine was evaluated at a specific monochloramine dose of 0.042 mM. As shown in Fig. 1a, a slight acceleration of monochloramine decay was found when 0.01 mg L^{-1} Cu(II) was present. However, as the concentration of Cu(II) was increased to 0.1 mg L^{-1} , the decomposition rate of monochloramine was significantly enhanced, and this enhancement could be detected within

Table 1
Monochloramine decay in two real drinking waters

Water	pH	TOC (mg L^{-1})	Ammonia (mg L^{-1})	Alkalinity (as CaCO_3) (mg L^{-1})	$[\text{NH}_2\text{Cl}]_0$ (mM)	Time (d)	$\Delta\text{NH}_2\text{Cl}^a$ (no Cu^{2+}) (mM)	$\Delta\text{NH}_2\text{Cl}^b$ (1.0 mg L^{-1} Cu^{2+}) (mM)	$\frac{\Delta\text{NH}_2\text{Cl}^b - \Delta\text{NH}_2\text{Cl}^a}{[\text{NH}_2\text{Cl}]_0} \times 100$ (%)
Shanghai	6.85	4.51	1.22	107	0.0239	1	0.0041	0.0070	12
						3	0.012	0.015	13
Beijing	7.03	1.83	0.20	175	0.0132	1	0.0034	0.0046	10
						3	0.0063	0.0077	11

Fig. 1. Monochloramine decomposition at (a) different concentrations of $\text{Cu}(\text{II})$ and (b) different initial monochloramine concentrations with and without $\text{Cu}(\text{II})$ (open symbol – without $\text{Cu}(\text{II})$; solid symbol – with 1.0 mg L^{-1} $\text{Cu}(\text{II})$). Experimental conditions: pH = 6.5, temperature = 25 °C, $\text{Cl}_2/\text{N} = 0.62$ (molar ratio).

1–3 h evidently. Thus, the half-life of monochloramine was roughly 130 h when no $\text{Cu}(\text{II})$ existed, which decreased to 78 h and 48 h when 0.1 and 1.0 mg L^{-1} $\text{Cu}(\text{II})$ was present, respectively. However,

the decomposition rate of monochloramine was not enhanced when the $\text{Cu}(\text{II})$ concentration increased from 1.0 to 5.0 mg L^{-1} . It suggested that $\text{Cu}(\text{II})$, at low concentrations, yielded a homogeneous catalytic effect on monochloramine decomposition in aqueous solution.

Monochloramine decay in the presence and absence of 1.0 mg L^{-1} $\text{Cu}(\text{II})$ was investigated over its initial concentration range of 0.01–0.05 mM (i.e., 0.71–3.55 mg L^{-1} as Cl_2). These concentrations are similar to those used in drinking water treatment. As shown in Fig. 1b, the rate of monochloramine loss became faster as the initial monochloramine concentration increased, and obviously $\text{Cu}(\text{II})$ promoted the monochloramine decay more significantly when the initial concentration of monochloramine was higher.

3.3. Effect of pH on monochloramine decomposition in the presence of $\text{Cu}(\text{II})$

The influence of pH on monochloramine decomposition in the presence of 1.0 mg L^{-1} $\text{Cu}(\text{II})$ was studied in the pH range from 6.1 to 8.0. The initial monochloramine concentrations were controlled at 0.042–0.050 mM and the concentration of $\text{Cu}(\text{II})$ was maintained at 1.0 mg L^{-1} . As observed in Fig. 2, the decomposition rate of monochloramine was greatly enhanced by $\text{Cu}(\text{II})$ and this enhancement obviously declined when the solution pH increased. Also an increase of pH resulted in a lower rate of monochloramine decay. When pH was raised to 8.0, the catalytic effect of $\text{Cu}(\text{II})$ on the monochloramine decomposition disappeared.

It is reported that monochloramine decay follows the second-order dynamic reaction (Valentine and Jafvert, 1988; Vikesland et al., 2001). The k_d value was described as the second-order dynamic index. To compare monochloramine decay in the absence or presence of $\text{Cu}(\text{II})$, the experimental data were fitted with this model and high correlation coefficients were obtained ($R^2 > 0.98$). The k_d values of monochloramine decay are shown in Fig. 3. The results indicated that the k_d value increased when pH decreased with or without $\text{Cu}(\text{II})$, and the lower the pH, the greater the catalytic effect. At pH 8.0, the k_d value was equal to $0.07 \times 10^3 \text{ M}^{-1} \text{ h}^{-1}$ and the presence of 1.0 mg L^{-1} $\text{Cu}(\text{II})$ had little effect on monochloramine decomposition. But at pH 6.1, the k_d value was obviously enhanced from 0.15×10^3 (without $\text{Cu}(\text{II})$) to $0.33 \times 10^3 \text{ M}^{-1} \text{ h}^{-1}$ (with $\text{Cu}(\text{II})$). It was clear that the effect of $\text{Cu}(\text{II})$ became more significant as the pH decreased. When the pH further decreased to below 6.1, certain amount of dichloramine (NHCl_2) would be formed (Valentine and Jafvert, 1988). However, such low pH value did not

Fig. 2. Effect of pH on monochloramine decomposition with and without $\text{Cu}(\text{II})$. Experimental conditions: $[\text{Cu}^{2+}] = 1.0 \text{ mg L}^{-1}$, temperature = 25 °C, $\text{Cl}_2/\text{N} = 0.62$ (molar ratio).

Fig. 3. Comparison of the decomposition rate constants of monochloramine (k_d) with and without Cu(II) in the pH range from 6.1 to 8.0. Experimental conditions: $[\text{NH}_2\text{Cl}]_0 = 0.045 \text{ mM}$, $[\text{Cu}^{2+}] = 1.0 \text{ mg L}^{-1}$, temperature = 25°C , $\text{Cl}_2/\text{N} = 0.62$ (molar ratio).

exist in practice. So pH values below 6.1 were not discussed in this paper. Besides, several studies have investigated the effects of phosphate-buffer and ionic strength on monochloramine decay (Valentine and Jafvert, 1988; Ozekin et al., 1996). According to their results, a low concentration of phosphate (e.g., 7 mM used in our experiments) would not have any notable effect on the chloramine species.

The speciation of Cu(II) was largely dependent on the solution pH. Taking both the cumulative formation constants (Dean, 1999) of Cu(II) complexes with hydroxyl and our experimental conditions into consideration, the dominant Cu(II) species will be Cu^{2+} at $\text{pH} < 5.5$, Cu^{2+} and CuOH^+ at $5.5 < \text{pH} < 7.2$, and $\text{Cu}(\text{OH})_2^0$ at $\text{pH} > 7.4$. As the pH decreased, the concentration of Cu^{2+} ions increased, and also the catalytic effect of Cu(II) on monochloramine decay was enhanced. Therefore, it may be reasonable to suggest that the decomposition of monochloramine was mainly enhanced by Cu^{2+} rather than other copper species.

3.4. Comparison of monochloramine and chlorine decay in the presence of Cu(II)

It is well known that monochloramine hydrolysis can produce chlorine and ammonia (Valentine and Jafvert, 1988) and this process can be incorporated into the overall kinetics by considering an equilibrium between chlorine and monochloramine. So the change of chlorine decay rate may influence the monochloramine decomposition. The effect of Cu(II) on chlorine decomposition was examined, as shown in Fig. 4a. The results showed that Cu(II) had little effect on chlorine decay. In contrast, Cu(II) could significantly enhance monochloramine decay. This indicated that the promotion effect of Cu(II) on monochloramine decay may be induced by catalyzing other reactions of monochloramine decomposition. It also implied that monochloramine was less stable than chlorine in the presence of Cu(II).

3.5. Contribution of Cu(II)– NH_3 complexation to monochloramine decay

Since Cu(II) can complex with ammonia, the monochloramine hydrolysis might be affected by this complexation. Because Zn^{2+} can also complex with NH_3 and each stability constant of $\text{Cu}(\text{NH}_3)_n$ is nearly 100 times that of $\text{Zn}(\text{NH}_3)_n$ correspondingly (the stability constants of Zn^{2+} – NH_3 complexes are: $\beta_1 = 1.86 \times 10^2$, $\beta_2 = 4.1 \times$

Fig. 4. (a) Effect of Cu(II) on monochloramine and chlorine decays, $[\text{Cl}_2]_0 = 0.052 \text{ mM}$, $[\text{NH}_2\text{Cl}]_0 = 0.052 \text{ mM}$, $[\text{Cu}^{2+}] = 1.0 \text{ mg L}^{-1}$, $\text{pH} = 6.2$, temperature = 25°C , $\text{Cl}_2/\text{N} = 0.62$ (molar ratio); and (b) monochloramine decomposition in the presence of Cu(II) and Zn(II), experimental conditions: $[\text{NH}_2\text{Cl}]_0 = 0.035 \text{ mM}$, $\text{pH} = 6.3$, temperature = 25°C , $\text{Cl}_2/\text{N} = 0.62$ (molar ratio).

10^4 , $\beta_3 = 1.0 \times 10^7$, $\beta_4 = 1.1 \times 10^9$; the stability constants of Cu^{2+} – NH_3 complex are: $\beta_1 = 1.4 \times 10^4$, $\beta_2 = 4.2 \times 10^7$, $\beta_3 = 3.0 \times 10^{10}$, $\beta_4 = 3.9 \times 10^{12}$, the effect of Zn^{2+} – NH_3 complexation was also investigated for comparison purpose. The initial concentrations of 0.1 mg L^{-1} Cu^{2+} and 10 mg L^{-1} Zn^{2+} approximately consume an equal amount of NH_3 . Fig. 4b shows that Zn^{2+} had no effect on the decomposition of monochloramine, while Cu^{2+} significantly promoted the decomposition reaction. This indicated that the Cu^{2+} – NH_3 complexation had no contribution to the monochloramine decay. It must be specially mentioned that previous studies (Jafvert and Valentine, 1992; Vikesland et al., 2001) had shown that Cl_2/N molar ratio could affect monochloramine decay rate. Therefore, the contribution of Cu(II)– NH_3 complexation to monochloramine decay could not be examined by regulating the NH_3 concentrations.

3.6. Proposed catalysis mechanism

Monochloramine disproportionation, which results in the formation of dichloramine, is a general acid-catalyzed process. Once dichloramine forms, it decomposes via a series of rapid redox reactions. Chloramine loss by auto-decomposition is a relatively complex process. The overall rate of chloramine loss is primarily

limited by the rate of dichloramine formation. The formation of dichloramine is highly dependent on reaction conditions such as pH, temperature and alkalinity. The subsequent decomposition of dichloramine is primarily responsible for actual oxidant loss, which may be governed by monochloramine disproportionation. These processes are described in the following reactions (Jafvert and Valentine, 1987; Valentine and Jafvert, 1988):

In acidic solutions, both proton transfer and Cl^+ transfer are known to occur (Snyder and Margerum, 1982; Ricci and Rosi, 1998). The reaction proceeds by nucleophilic attack of the unprotonated amine nitrogen on the chlorine of the protonated monochloramine and shifts to a rate-limiting step of electrophilic bond breaking in NH_3Cl^+ as the amine nitrogen becomes more basic than ammonia.

Monochloramine decomposition is greatly enhanced in the presence of Cu(II) when the pH of solution is below 7.0. According to the previous discussion, the catalysis is ascribed to the effect of Cu(II) on Reaction (6). Cu(II) in solution behaves as Lewis acid and is often dubbed as super acid. Cu(II) has a small atomic radius as well as a vacant electron path, whereas it is strongly complexible with several inorganic and organic ligands to form square planar or octahedral complexes. As reported, humic and fulvic acids in water can bind Cu(II) with a high concentration by chelation (Christl et al., 2005; Saito et al., 2005).

The XAFS spectra of Cu(II) solution with and without monochloramine addition are compared in Fig. 5. In the presence of monochloramine, there was a marked change of the scanning curve in the range of 9114–9554 eV, which indicated that a complex of Cu(II) and nitrogen was formed. The complex might be formed between Cu(II) and monochloramine or free ammonia that was generated from monochloramine decay. The concentration of free ammonia in this reaction system was theoretically calculated to be 10^{-8} M (Vikesland et al., 2001). At such a low concentration, the Cu^{2+} – NH_3 complex even could not induce a response from this apparatus. So it suggested that the complexation occurred between Cu(II) and monochloramine nitrogen.

Since Cu(II) can complex with the central nitrogen of monochloramine molecule, both proton transfer and Cl^+ transfer in

monochloramine disproportionation are promoted. In acidic solution, the complex of Cu(II)–monochloramine is easily formed. Subsequently the complex is attacked by the transferred Cl^+ to form NHCl_2 , which is further oxidized quickly. Thus the overall rate of monochloramine decomposition was increased.

4. Conclusions

Monochloramine decomposition can be catalyzed by Cu(II) in simulated and real drinking waters. The catalytic effectiveness was obviously affected by Cu(II) concentration. The decomposition of monochloramine was more enhanced when the initial Cu(II) concentration increased during 0–1.0 mg L⁻¹. The pH also played an important role in the decomposition of monochloramine. The catalysis became more significant when the pH decreased from 8.0 to 6.1. It was the dissolved Cu^{2+} that catalyzed the monochloramine decay. It was also observed that monochloramine was less stable than chlorine when Cu(II) was present in moderately acidic solutions.

Furthermore, the XAFS spectra indicated that Cu(II) could form complex with nitrogen in monochloramine. The complexation promoted the formation of dichloramine, which is a controlling step for monochloramine decay. Thus, the decomposition of monochloramine was catalytically enhanced by Cu(II).

This work provides useful information for selection of proper disinfection method where copper ion exists in water disinfection process, determination of initial monochloramine dosage, and maintenance of effective monochloramine residual.

Acknowledgements

The authors greatly appreciate the financial support for this work from the National Natural Science Foundation of China (Grant No. 50538090) and the International Copper Association Ltd (H-AS-04-03).

References

- Boulay, N., Edwards, M., 2001. Role of temperature, chlorine, and organic matter in copper corrosion by-product release in soft water. *Water Res.* 35, 683–690.
- Christl, I., Metzger, A., Heidmann, I., Kretzschmar, R., 2005. Effect of humic and fulvic acid concentrations and ionic strength on copper and lead binding. *Environ. Sci. Technol.* 39, 5319–5326.
- Dean, J.A., 1999. *Lange's Handbook of Chemistry*, 15th ed. McGraw-Hill, New York.
- Feng, Y., Teo, W.K., Siow, K.S., Tan, K.L., Hsieh, A.K., 1996. The corrosion behaviour of copper in neutral tap water. Part I: corrosion mechanisms. *Corros. Sci.* 38, 369–385.
- Jafvert, C.T., Valentine, R.L., 1987. Dichloramine decomposition in the presence of excess ammonia. *Water Res.* 21, 967–973.
- Jafvert, C.T., Valentine, R.L., 1992. Reaction scheme for the chlorination of ammoniacal water. *Environ. Sci. Technol.* 26, 577–586.
- Kawamura, K., 1983. Organic compounds in the rainwater of Los Angeles. *Environ. Sci. Technol.* 17, 497–501.
- Lin, X., Pan, Q., Rempel, G.L., 2004. Cupric ion catalyzed diimide production from the reaction between hydrazine and hydrogen peroxide. *Appl. Catal. A-Gen.* 263, 27–32.
- Ozekin, K., Valentine, R.L., Vikesland, P.J., 1996. Modeling the decomposition of disinfecting residuals of chloramine. *ACS Sym. Ser.* 649, 115–125.
- Ricci, A., Rosi, M., 1998. Gas-phase chemistry of NH_2Cl^+ . 1. Structure, stability, and reactivity of protonated monochloramine. *J. Phys. Chem. A* 102, 10189–10194.
- Saito, T., Koopal, L.K., Nagasaki, S., Tanaka, S., 2005. Analysis of copper binding in the ternary system Cu^{2+} /humic acid/goethite at neutral to acidic pH. *Environ. Sci. Technol.* 39, 4886–4893.
- Snyder, M.P., Margerum, D.W., 1982. Kinetics of chlorine transfer from chloramine to amines, amino acids, and peptides. *Inorg. Chem.* 21, 2545–2550.
- Switzer, J.A., Rajasekharan, V.V., Boonsalee, S., Kulp, E.A., Bohannon, E.W., 2006. Evidence that monochloramine disinfectant could lead to elevated Pb levels in drinking water. *Environ. Sci. Technol.* 40, 3384–3387.
- Than, T.A., Ogino, T., Omori, M., Okada, S., 2001. Monochloramine inhibits etoposide-induced apoptosis with an increase in DNA aberration. *Free Radical Biol. Med.* 30, 932–940.

Fig. 5. Cu K-edge XAFS spectra for Cu^{2+} and Cu^{2+} – NH_2Cl solutions. Cu^{2+} was added in the form of CuCl_2 .

- Valentine, R.L., Jafvert, C.T., 1988. General acid catalysis of monochloramine disproportionation. *Environ. Sci. Technol.* 22, 691–696.
- Valli, M., Matsuo, S., Wakita, H., Yamaguchi, T., Nomura, M., 1996. Solvation of copper(II) ions in liquid ammonia. *Inorg. Chem.* 35, 5642–5645.
- Vikesland, P.J., Ozekin, K., Valentine, R.L., 1998. Effect of natural organic matter on monochloramine decomposition: pathway elucidation through the use of mass and redox balances. *Environ. Sci. Technol.* 32, 1409–1416.
- Vikesland, P.J., Ozekin, K., Valentine, R.L., 2001. Monochloramine decay in model and distribution system waters. *Water Res.* 35, 1766–1776.
- Vikesland, P.J., Valentine, R.L., 2002a. Modeling the kinetics of ferrous iron oxidation by monochloramine. *Environ. Sci. Technol.* 36, 662–668.
- Vikesland, P.J., Valentine, R.L., 2002b. Iron oxide surface-catalyzed oxidation of ferrous iron by monochloramine: implications of oxide type and carbonate on reactivity. *Environ. Sci. Technol.* 36, 512–519.
- Wang, Z., Liu, Q., Yu, J., Wu, T., Wang, G., 2003. Surface structure and catalytic behavior of silica-supported copper catalysts prepared by impregnation and sol-gel methods. *Appl. Catal. A-Gen.* 239, 87–94.
- Wolfe, R., Lieu, N., Izaguirre, G., Means, E., 1990. Ammonia-oxidizing bacteria in a chloraminated distribution system: seasonal occurrence, distribution, and disinfection resistance. *Appl. Environ. Microb.* 56, 451–462.
- Zhang, X., Pehkonen, S.O., Kocherginsky, N., Andrew Ellis, G., 2002. Copper corrosion in mildly alkaline water with the disinfectant monochloramine. *Corros. Sci.* 44, 2507–2528.