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Catalysis of copper corrosion products on chlorine decay and HAA formation in simulated distribution systems

Hong Zhang[*], *Susan A. Andrews*

Department of Civil Engineering, University of Toronto, Toronto, Ontario M5S 1A4, Canada

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ABSTRACT

This study investigated the effect of copper corrosion products, including Cu(II), Cu_2O, CuO and $Cu_2(OH)_2CO_3$, on chlorine degradation, HAA formation, and HAA speciation under controlled experimental conditions. Chlorine decay and HAA formation were significantly enhanced in the presence of copper with the extent of copper catalysis being affected by the solution pH and the concentration of copper corrosion products. Accelerated chlorine decay and increased HAA formation were observed at pH 8.6 in the presence of 1.0 mg/L Cu(II) compared with that observed at pH 6.6 and pH 7.6. Further investigation of chlorine decay in the presence of both Suwannee River NOM and Cu(II) indicated that an increased reactivity of NOM with dissolved and/or solid surface-associated Cu(II), rather than chlorine auto-decomposition, was a primary reason for the observed rapid chlorine decay. Copper corrosion solids [Cu_2O, CuO, $Cu_2(OH)_2CO_3$] exhibited catalytic effects on both chlorine decay and HAA formation. Contrary to the results observed when in the absence of copper corrosion products, DCAA formation was consistently predominant over other HAA species in the presence of copper corrosion products, especially at neutral and high pH. This study improves the understanding for water utilities and households regarding chlorine residuals and HAA concentrations in distribution systems, in particular once the water reaches domestic plumbing where copper is widely used.

1. Introduction

To maintain the microbial stability of distributed water, free chlorine is used as a secondary disinfectant in distribution systems. As chlorine may experience temporal and spatial degradation due to chemical and biological consumption that occurs in the bulk water and on the pipe wall, at least 0.2 mg/L of free chlorine residual should be maintained to reduce the possible occurrence of biological regrowth (USEPA, 1989).

Haloacetic acids (HAAs) are formed primarily by the chlorination of natural organic matter (NOM). In its simplest terms, NOM can be classified as either humic substances or non-humic compounds. However, humic substances are a mixture of many molecules, and the major functional groups which contribute to surface charge and reactivity of humic substances include carboxyl groups, some phenolic groups, alcohol groups, methoxyl groups, ketones, and aldehydes (Reckhow et al., 1990). Humic substances in the environment are capable of interacting with metal ions to form soluble complexes, colloidal substances and/or insoluble substances (Stevenson, 1994). Alvarez-Puebla et al. (2004a, b) have investigated possible retention mechanisms of Cu(II), Co(II) and Ni(II) on humic substances and found surface complexation and electrostatic retention played key roles in the retention of these metals on humic substances, and Cu(II) had a higher affinity for humic substances compared with

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[*] *Corresponding author*. Tel.: +1 416 9783220; fax: +1 416 978 3674.
E-mail address: irisy.zhang@utoronto.ca (H. Zhang).

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Co(II) and Ni(II). Furthermore, the humic substances studied displayed a great selectivity for different Cu(II) species, and the selectivity depended on pH.

Since the 1970s, considerable effort has been made to understand HAA formation mechanisms by using NOM or well-defined model compound precursors (Kanokkantapong et al., 2006; Morris, 1975; Reckhow et al., 1990). Reaction mechanisms involved in HAA formation have been found to generally include oxidation, substitution, addition, and hydrolysis (Morris, 1975). The reaction rates and HAA speciation are dependent on temperature, pH, chlorine dose and the nature of the organic compounds that contribute to NOM. Although there are nine HAA species, monochloroacetic acid (MCAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), monobromoacetic acid (MBAA) and dibromoacetic acid (DBAA) are commonly detected in drinking water, and DCAA and TCAA are normally dominant over other species. Due to the toxicological properties of HAAs, the Stage 2 Disinfectant/Disinfection Byproduct Rule (D/DBPR) has regulated a Maximum Contaminant Level (MCL) of HAA_5 (MCAA, DCAA, TCAA, MBAA, and DBAA) at 60 μg/L (USEPA, 2006). The Guidelines for Canadian Drinking Water Quality have established a Maximum Acceptable Concentration (MAC) for HAA_5 in drinking water at 80 μg/L, based on a locational running annual average of a minimum of quarterly samples taken in the distribution system (Health Canada, 2008).

Copper corrosion occurs as water containing a disinfectant residual travels through copper pipes. Copper ions [Cu(II)], cuprite [Cu_2O], tenorite [CuO], cupric hydroxide [$Cu(OH)_2$], and malachite [$Cu_2CO_3(OH)_2$] are dominant corrosion products of copper in drinking water systems (Xiao et al., 2007). Copper has no acute toxicity to humans except at high dose (>15 mg/day). An aesthetic objective of $\leq$1.0 mg/L has been established for copper in drinking water (Health Canada, 1992).

The catalytic potential of copper in many reaction processes has been widely investigated (Onuchukwu, 1994; Paidar et al., 1999; Pintar et al., 1997). Other studies have also demonstrated copper catalysis on free chlorine and monochloramine degradation and on THM formation (Blatchley et al., 2003; Fu et al., 2009a,b; Li et al., 2007, 2008). The mechanism of Cu-catalyzed THM formation proposed by Blatchley et al. (2003) was that copper could complex with THM precursor compounds and enhance the oxidative decarboxylation and enolization of the keto-groups.

Since HAA formation has been found to be concurrent with THM formation, with both DBP classes having similar organic precursors and some similarities in their formation mechanisms (Morris, 1975; Reckhow and Singer, 1985), it is hypothesized that copper will play a similar catalytic role in HAA formation. Li et al. (2008) have reported elevated formation of HAAs in copper pipes. However, they did not examine in detail the catalytic potential of Cu(II) and other corrosion products to affect chlorine degradation and HAA formation. Furthermore, a regulatory guideline for HAA_5 has recently been added to the "Guidelines for Canadian Drinking Water Quality" (Health Canada, 2008). This information, therefore, has increased the awareness of water utilities and households to minimize HAAs in their water systems. As such, the objective of this study was to investigate the effect of Cu(II) and its solid corrosion products on chlorine degradation and HAA formation, including HAA speciation, by applying different concentrations of copper corrosion products and under different pH conditions. Since copper is widely used in domestic plumbing systems, understanding the roles of copper and its corrosion products on the fate of HAAs will benefit utilities and households to minimize HAAs in their systems by adopting preventive strategies for their control.

2. Materials and methods

2.1. *Reagents and materials*

All chemicals used in this study were ACS grade or higher. The chlorine dosing solution (approximately 3500 mg/L as Cl_2) was prepared by diluting a concentrated solution of sodium hypochlorite (NaOCl, 6%, VWR) in Milli-Q water. The target chlorine concentration applied in the tests was achieved by spiking 3.5 mL chlorine dosing solution in 1 L test water. An initial free chlorine concentration of 10 mg/L as Cl_2 was applied to achieve a detectable 24-h residual of 0.2 mg/L as Cl_2, which was found to be necessary especially when the effects of Cu_2O were investigated. Phosphate buffer ($H_2PO_4^-/HPO_4^{2-}$) and borate buffer (H_3BO_3/NaOH) solutions were prepared and added to test solutions at 1 mM concentration to control reaction solution pH at desired levels. Sulfuric acid (H_2SO_4, 50%) and sodium hydroxide (NaOH, 20%) were also used for pH adjustment. L-Ascorbic acid ($\geq$99.0%, Sigma Aldrich) at 200 mg/L was applied to quench chlorine residuals before HAAs extraction. Over the reaction period, the pH was maintained at their specified target values (±0.1).

Unchlorinated post-filtration water was collected from the Mannheim Water Treatment Plant (MWTP), Ontario, for testing. Water quality parameters are listed in Table 1. In the tests to determine reaction pathways of Cu(II) catalysis on chlorine decay, synthetic water with similar inorganic chemical composition to the water from the MWTP was prepared. Suwannee River NOM (International Humic Substances Society) was dosed into synthetic water at the concentration of 2.4 mg/L and 4.7 mg/L.

2.2. *Experimental procedures*

All of the experiments were performed in 1 L amber bottles with PTFE-lined caps and at room temperature (21 ± 2 °C). The reaction bottles were made chlorine demand free before use.

Table 1 – Water quality parameters for post-filtration water from MWTP.

Parameters	Parameter values
pH	7.5 ± 0.2
UV_{254} (cm^{-1})	0.045 ± 0.015
TOC (mg/L)	3.9 ± 0.4
SUVA ($L/mg \cdot cm^{-1}$)	0.016 ± 0.004
Bromide (μg/L)	65.0 ± 15.5
Chloride (mg/L)	84.5 ± 2.5
Sulfate (mg/L)	35.0 ± 2.0
Cl^-:SO_4^{2-} ratio	2.4 ± 0.1