Enhanced formation of bromate and brominated disinfection byproducts during chlorination of bromide-containing waters under catalysis of copper corrosion products

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ABSTRACT

Copper corrosion products (CCPs) in water distribution pipes may catalyze the reactions among disinfectant, natural organic matter (NOM), and bromide (Br$^-$). This study investigated the simultaneous formation of bromate (BrO$_3^-$) and brominated disinfection byproducts (Br-DBPs) during chlorination of Br$^-$-containing waters in the presence of three CCPs (i.e., CuO, Cu$_2$O, and Cu^{2+}). In a synthetic water, both oxidant decay and BrO$_3^-$ formation were enhanced by CCPs, whereas the presence of humic acid (HA) significantly inhibited BrO$_3^-$ formation due to its competition for HOBr to form Br-DBPs. In the HOCl—Br$^-$—CuO system, the BrO$_3^-$ yield increased obviously with increasing CuO dose and initial Br$^-$ concentration, while the catalytic formation of Br-DBPs was rather limited. A molar conversion (Br$^-$ to BrO$_3^-$) of 22.1% was observed under CuO catalysis, compared with little conversion in the absence of CuO. In the HOCl—Br$^-$—Cu$_2$O/Cu^{2+} systems, Cu$_2$O or Cu^{2+} mainly enhanced the formation of Br-DBPs, with enhancement ratios of 69.9% and 50.1%, respectively. The degree of enhancement on Br-DBPs formation became more apparent with increasing pH, while that on BrO$_3^-$ formation reached maximal at pH 7.6. The catalytic formation of Br-DBPs and BrO$_3^-$ by CCPs was also verified in three filtered real waters, although to a lesser extent because of the water matrix effect. In mechanism, the CCPs promoted the formation of BrO$_3^-$ and Br-DBPs through catalyzing the HOBr disproportionation pathway and the reaction of HOBr toward HA, respectively.

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1. Introduction

To maintain the microbial stability in distributed water, chlorine is ubiquitously used as a disinfectant in drinking water distribution systems (Zhang and Andrews, 2012; Liu et al., 2013a). However, one major drawback of chlorinated water treatment is the formation of halogenated disinfection byproducts (DBPs) and other transformation byproducts resulting from the reactions of chlorine with various moieties of water matrix, which has been one of human health concerns over drinking water (Krasner et al., 2006; Heeb et al., 2014).

Natural organic matter (NOM) and bromide (Br$^-$) are two common components of water matrix relevant to oxidation processes (Heeb et al., 2014). Br$^-$ can be oxidized to hypobromous acid (HOBr) by free chlorine (HOCl) with a second-order rate constant of 1.55×10^3 M^{-1} s^{-1}, while no further reaction proceeds between HOCl and HOBr (Kumar and Margerum, 1987; Beckwith and Margerum, 1997; Margerum and Huff Hartz, 2002). Although the disproportionation of HOBr still occurs, bromate (BrO$_3^-$) formation during chlorination of Br$^-$-containing waters is usually insignificant because of the slow reaction rate ($<10^{-2}$ M^{-1} s^{-1}) (Liu et al., 2012). However, HOBr can react quickly with NOM to form brominated disinfection byproducts (Br-DBPs) (Cowman and Singer, 1996; Richardson et al., 2003; Zhao et al., 2012; Pan and Zhang, 2013), which are more carcinogenic than their chlorinated analogues (Nobukawa and Sanukida, 2000).

Because copper ions can inactivate certain bacterial species (Feng et al., 1996), copper has been extensively used in water distribution pipes throughout the world. The corrosion of copper pipes

leads to the formation of cupric oxide (CuO) and cuprous oxide (Cu$_2$O) on the inner surface as well as releases copper ions (Cu^{2+}) into the drinking water (Li et al., 2007; Xiao et al., 2007; Zhang and Andrews, 2012). Previous studies have reported that these copper corrosion products (CCPs) could catalytically enhance the formation of BrO$_3^-$ (Liu et al., 2012, 2013a) and halogenated DBPs (Blatchley et al., 2003; Li et al., 2008; Zhang and Andrews, 2012). For example, CuO could enhance the BrO$_3^-$ formation during water chlorination via a CuO-catalyzed HOBr disproportionation pathway as follows (Liu et al., 2012, 2013a):

$$3Br(I) \xrightarrow{CuO} 2Br(-I) + Br(V) \tag{1}$$

where Br(I), Br(-I) and Br(V) represent HOBr/OBr$^-$, Br$^-$, and BrO$_3^-$, respectively. Once formed, the Br$^-$ could be re-oxidized to HOBr/OBr$^-$ by HOCl, until most of Br$^-$ was eventually converted to BrO$_3^-$ as long as HOCl was present in excess. In addition, copper could also catalyze the formation of trihalomethanes (THMs) and haloacetic acids (HAAs) through complexing with precursor compounds to promote the oxidative decarboxylation and enolization of keto-groups (Blatchley et al., 2003; Li et al., 2008). Liu and Croue (2016) investigated the formation of BrO$_3^-$ and halogenated DBPs in the presence of CuO during chlorination of six dissolved organic matter isolates, and found that the formation of THM$_4$ and HAA$_5$ was enhanced in simulated distribution systems, particularly for low-SUVA$_{254}$ isolates. BrO$_3^-$, THM$_4$ and HAA$_5$ are regulated in drinking water with maximum contaminant levels of 10, 80 and 60 μg L^{-1} by US Environmental Protection Agency (USEPA, 2001), respectively.

This study aimed to investigate the catalysis of three different CCPs (i.e., CuO, Cu$_2$O, and Cu^{2+}) on the simultaneous formation of BrO$_3^-$ and Br-DBPs during chlorination of Br$^-$-containing waters. The effects of reaction time, solution pH, CCP dose, and initial Br$^-$ concentration on the formation of BrO$_3^-$ and Br-DBPs were examined in detail. Moreover, three filtered real waters (RWs) were used to evaluate the enhanced formation of Br-DBPs and BrO$_3^-$ under the catalysis of CCPs. Because copper pipe is commonly used in domestic plumbing systems, understanding the catalysis of CCPs on the formation of BrO$_3^-$ and Br-DBPs will help water utilities and households to develop the corresponding control strategies.

2. Materials and methods

2.1. Chemicals

All chemicals used were of analytical grade or higher. The pH of reaction solution was adjusted by borate buffer (1 mM) and NaOH/HNO$_3$ solutions. A humic acid (HA) stock solution was prepared by dissolving humic acid solids (Sigma-Aldrich, Shanghai, China) into deionized water and then filtering through 0.45-μm membrane filters. Sodium hypochlorite solution (NaOCl, >10%) was used as the source of chlorine and was periodically standardized. An initial free chlorine concentration of 14.2 mg L^{-1} (as Cl$_2$) was applied to achieve a detectable residual, which was particularly necessary under the catalysis of Cu$_2$O. Br$^-$ was added in the form of potassium bromide. An elevated initial Br$^-$ concentration of 2.0 mg L^{-1} was applied to achieve distinguishable catalytic effects of CCPs on the formation of BrO$_3^-$ and Br-DBPs. Cu^{2+} was added in the form of copper nitrate. NaOCl solution, potassium bromide, CuO, Cu$_2$O, and copper nitrate were all purchased from Sinopharm Chemical Reagent Company (Shanghai, China). The surface areas of CuO and Cu$_2$O were measured to be 4.7 and 11.5 m^2 g^{-1}, respectively, with an ASAP 2020 surface area and porosity analyzer (Micromeritics, USA).

2.2. Analytical methods

Residual oxidant (i.e., the sum of HOCl and HOBr formed through Br$^-$ oxidation by HOCl) concentrations were analyzed spectrophotometrically by the N, N-diethyl-p-phenylenediamine method at 515 nm (Rice, 2012). Free bromine (e.g., HOBr/OBr$^-$) was analyzed according to our earlier developed method (Qiang et al., 2012). BrO$_3^-$ and Br$^-$ were quantified by an ion chromatograph (Dionex-ICS2000) equipped with an Ionpac AS19 column (250 mm × 4.0 mm, 5.0 μm). KOH solution was used as the eluent with a flow rate of 1.0 mL min^{-1} and a gradient program as follows: 20 mM held for 1 min, and ramped linearly to 110 mM over the next 18 min. The limits of quantification for Br$^-$ and BrO$_3^-$ were 0.5 and 1.0 μg L^{-1}, respectively.

The dissolved copper content was determined by an Agilent 7500 inductively coupled plasma mass spectrometer. Cu$^+$ concentration was analyzed according to Chen et al. (2015) with certain modifications. In brief, 10 mM ethylenediamine was spiked into a water sample as a masking ligand to inhibit the interference of Cu^{2+}; 1 mM bathocuproine was added to form an orange complex with Cu$^+$; and the orange complex was measured by light absorbance at 484 nm on a Hach DR6000 spectrophotometer (Hach, USA).

Brominated trihalomethanes (Br-THMs), brominated haloacetic acids (Br-HAAs), and brominated haloacetamides (Br-HAcAms) were extracted according to Bougeard et al. (2010), and then analyzed with a gas chromatograph and an electron capture detector (GC/ECD) (Agilent 7890A) coupled with a DB-5ms separation column (30 m × 0.25 mm, 0.25 μm). The instrumental conditions for the analysis of Br-THMs and Br-HAcAms were as follows: injection volume of 2.0 μL (splitless), helium carrier gas with a flow rate of 2.0 mL min^{-1}, injector temperature of 180 °C, detector temperature of 300 °C, and initial oven temperature held at 40 °C for 5 min, ramped to 45 °C at 1 °C min^{-1} and held for 2 min, ramped to 115 °C at 10 °C min^{-1} and held for 1 min, and finally ramped to 220 °C at 15 °C min^{-1}. For the analysis of Br-HAAs, the instrumental conditions were as follows: injector temperature of 210 °C, detector temperature of 300 °C, and initial oven temperature held at 40 °C for 4 min, and ramped to 80 °C at 2 °C min^{-1}. The tested species of Br-THMs, Br-HAAs and Br-HAcAms are described in Text S1.

2.3. Reaction system

All experiments were performed in the dark and under magnetic agitation at ambient temperature (25 ± 2 °C). The reaction bottles (200 mL) had no headspace and were made chlorine demand free before use. Control experiments were conducted under the same conditions but without the addition of CCPs. Each experiment was performed in duplicate and the relative percent difference (RPD) was calculated.

The effects of reaction time, pH, CCP dose, and initial Br$^-$ concentration on the catalytic formation of BrO$_3^-$ and Br-DBPs were investigated systematically. Cu^{2+} was spiked at concentrations of 0.5, 1.0, and 2.0 mg L^{-1} because its concentration in water distribution systems could vary from 20 to 2020 μg L^{-1} (Zhang and Andrews, 2012). The doses of CuO (0.5, 1.0, and 2.0 g L^{-1}) and Cu$_2$O (0.2, 0.5, and 1.0 g L^{-1}) applied in this study were comparable to those adopted by Li et al. (2007). The reaction solution pH was adjusted to typical pH values (6.6, 7.6, and 8.6) in distribution systems. It was observed that the pH change was insignificant after the reaction. The initial Br$^-$ concentration varied from 0.2 to 2.0 mg L^{-1} when testing its effect on the catalysis of CCPs. After preselected time intervals, water samples were withdrawn, filtered immediately through 0.45-μm membrane filters, and analyzed for the residual oxidant. For the analysis of Br$^-$, BrO$_3^-$, and Br-DBPs, the