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

Jun Hu ^{a, b}, Zhimin Qiang ^{a, b, *}, Huiyu Dong ^{a, b}, Jiuhui Qu ^{a, b}

^a Key Laboratory of Drinking Water Science and Technology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, 18 Shuang-qing Road, Beijing 100085, China

^b University of Chinese Academy of Sciences, 19 Yu-quan Road, Beijing 100049, China

ARTICLE INFO

Article history:

Received 6 February 2016

Received in revised form

12 April 2016

Accepted 15 April 2016

Available online 19 April 2016

Keywords:

Copper corrosion products

Catalysis

Bromate

Brominated disinfection byproducts

Water pipe

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_2O , 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 $\text{HOCl}-\text{Br}^- - \text{CuO}$ 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 $\text{HOCl}-\text{Br}^- - \text{Cu}_2\text{O}/\text{Cu}^{2+}$ systems, Cu_2O 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.

© 2016 Elsevier Ltd. All rights reserved.

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 $1.55 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$, 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 ($< 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$) (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

* Corresponding author. Key Laboratory of Drinking Water Science and Technology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, 18 Shuang-qing Road, Beijing 100085, China.

E-mail address: qiangz@rcees.ac.cn (Z. Qiang).

leads to the formation of cupric oxide (CuO) and cuprous oxide (Cu₂O) on the inner surface as well as releases copper ions (Cu²⁺) 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 BrO₃⁻ (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 BrO₃⁻ formation during water chlorination via a CuO-catalyzed HOBr disproportionation pathway as follows (Liu et al., 2012, 2013a):

where Br(I), Br(-I) and Br(V) represent HOBr/OBr⁻, Br⁻, and BrO₃⁻, respectively. Once formed, the Br⁻ could be re-oxidized to HOBr/OBr⁻ by HOCl, until most of Br⁻ was eventually converted to BrO₃⁻ 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 BrO₃⁻ and halogenated DBPs in the presence of CuO during chlorination of six dissolved organic matter isolates, and found that the formation of THM₄ and HAA₅ was enhanced in simulated distribution systems, particularly for low-SUVA₂₅₄ isolates. BrO₃⁻, THM₄ and HAA₅ 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, Cu₂O, and Cu²⁺) on the simultaneous formation of BrO₃⁻ 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 BrO₃⁻ and Br-DBPs were examined in detail. Moreover, three filtered real waters (RWs) were used to evaluate the enhanced formation of Br-DBPs and BrO₃⁻ under the catalysis of CCPs. Because copper pipe is commonly used in domestic plumbing systems, understanding the catalysis of CCPs on the formation of BrO₃⁻ 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/HNO₃ 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 Cl₂) was applied to achieve a detectable residual, which was particularly necessary under the catalysis of Cu₂O. 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 BrO₃⁻ and Br-DBPs. Cu²⁺ was added in the form of copper nitrate. NaOCl solution, potassium bromide, CuO, Cu₂O, and copper nitrate were all purchased from Sinopharm Chemical Reagent Company (Shanghai, China). The surface areas of CuO and Cu₂O were measured to be 4.7 and 11.5 m² 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). BrO₃⁻ 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 BrO₃⁻ 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 Cu²⁺; 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 BrO₃⁻ and Br-DBPs were investigated systematically. Cu²⁺ 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 Cu₂O (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⁻, BrO₃⁻, and Br-DBPs, the

residual oxidant was quenched immediately by ascorbic acid. Three different RWs were collected from Danjiangkou Reservoir (DR, Hubei), Miyun Reservoir (MR, Beijing) and Beijing No. 9 Waterworks (NW, Beijing), filtered through 0.45- μm membrane filters, and used to evaluate the enhanced formation of Br-DBPs and BrO_3^- with various spiked Br^- concentrations (200 or 500 $\mu\text{g L}^{-1}$) in the presence of CCPs. Table S1 shows the major characteristics of these RWs post filtration.

3. Results and discussion

3.1. Oxidant decay and BrO_3^- formation

Batch experiments were performed to investigate the oxidant (i.e., $\text{HOCl} + \text{HOBr}$) decay and BrO_3^- formation in the presence and

absence of CCPs and HA. As shown in Fig. 1a, the total oxidant concentration remained quite stable in the absence of both CCPs and HA, with a slow pseudo-first-order decay rate of 0.0019 h^{-1} . Only a small amount of oxidants was consumed in the presence of Cu^{2+} (2.0 mg L^{-1}), whereas the addition of CuO (2.0 g L^{-1}) or Cu_2O (0.5 g L^{-1}) accelerated oxidant decay obviously. The oxidant decay rates were determined to be 0.0134, 0.0213 and 0.0053 h^{-1} in the presence of CuO , Cu_2O and Cu^{2+} , respectively. The released Cu^{2+} concentrations measured after 72 h were approximately 0.1 and 0.3 mg L^{-1} for the solutions containing 2.0 g L^{-1} CuO and 0.5 g L^{-1} Cu_2O , respectively, indicating that the acceleration of CuO and Cu_2O on the oxidant decay was not primarily attributed to the Cu^{2+} ions released from the copper oxides (Zhang and Andrews, 2012). In addition, after 5.0 mg L^{-1} HA was spiked, the oxidant concentration decreased more quickly as expected. It is noted that Cu^{2+} exhibited a more obvious catalytic impact on the oxidant decay than CuO , which is just opposite to the case in the absence of HA. This is probably due to the different catalytic capabilities of Cu^{2+} and CuO on the DBPs formation, which will be discussed later.

Due to the slow oxidant decay, the BrO_3^- formation in the absence of CCPs and was negligible (Fig. 1b). The presence of CCPs promoted the BrO_3^- formation at different levels, corresponding to the rates of oxidant decay. After HA was spiked, the BrO_3^- formation was suppressed significantly. It was reported that the HOBr disproportionation rates under CuO catalysis were 0.5 and $1.6 \text{ M}^{-1} \text{ s}^{-1}$ at pHs 6.6 and 7.6, respectively (Liu et al., 2012). The reaction rates of HOBr with organic compounds are generally greater than $10^2 \text{ M}^{-1} \text{ s}^{-1}$ (Pattison and Davies, 2004; Skaff et al., 2007; Lee and von Gunten, 2009), which are much higher than the CuO -enhanced HOBr disproportionation rates. Hence, HA could significantly compete for HOBr to form Br-DBPs, thus exerting an obvious suppression on the BrO_3^- formation.

3.2. Time-dependent formation profiles of Br-DBPs and BrO_3^-

To further elucidate the competition between the substitution reaction (to form Br-DBPs) and the disproportionation reaction (to form BrO_3^-) in the presence of both CCPs and HA, the time-dependent formation profiles of Br-DBPs and BrO_3^- were determined. Results indicate that in the absence of CCPs, the yields of Br-THMs and Br-HAAs kept increasing until nearly reaching a plateau after 48 h. By contrast, the Br-HAcAms yield reached the maximum at 24 h and then gradually decreased (Fig. S1). The initial formation and subsequent degradation of Br-HAcAms could be attributed to the hydrolysis of brominated acetonitriles to form Br-HAcAms, which could further hydrolyze to produce Br-HAAs (Chu et al., 2012). The presence of CCPs facilitated the formation of Br-DBPs to different extents. As shown in Fig. 2a, with the spike of Cu_2O and Cu^{2+} , the enhancement ratios on Br-DBPs formation reached 69.9% and 50.1% after 72 h, respectively. However, CuO could only slightly enhance the Br-DBPs formation. This result is consistent with the oxidant decay rates in the presence of HA mentioned above.

Being different from the quick formation of Br-DBPs, a lag phase appeared for the BrO_3^- formation within the first several hours (Fig. 2b). The HOBr disproportionation pathway consists of two steps to produce BrO_3^- , through a decisive intermediate, Br(III) (i.e., BrO_2^-) (Beckwith and Margerum, 1997):

It is seen that the production of BrO_2^- is a rate-limiting step. Hence, the reaction between HOBr and highly reactive HA moieties

Fig. 1. Oxidant decay (a) and BrO_3^- formation (b) in the presence or absence of copper corrosion products (CCPs) and humic acid (HA) in the synthetic water (SW). Experimental conditions: $[\text{Cl}_2]_0 = 14.2 \text{ mg L}^{-1}$ (0.2 mM), $[\text{Br}^-]_0 = 2.0 \text{ mg L}^{-1}$ (25 μM), $[\text{HA}]_0 = 5.0 \text{ mg L}^{-1}$, $[\text{CuO}] = 2.0 \text{ g L}^{-1}$, $[\text{Cu}_2\text{O}] = 0.5 \text{ g L}^{-1}$, $[\text{Cu}^{2+}] = 2.0 \text{ mg L}^{-1}$, pH = 7.6, reaction time = 48 h. Error bars represent the relative percent differences (RPDs, $n = 2$).

Fig. 2. Time-dependent formation of Br-DBPs (a) and BrO_3^- (b) in the presence of CCPs and HA in the SW. Experimental conditions: $[\text{Cl}_2]_0 = 14.2 \text{ mg L}^{-1}$, $[\text{Br}^-]_0 = 2.0 \text{ mg L}^{-1}$, $[\text{HA}]_0 = 5.0 \text{ mg L}^{-1}$, $[\text{CuO}] = 2.0 \text{ g L}^{-1}$, $[\text{Cu}_2\text{O}] = 0.5 \text{ g L}^{-1}$, $[\text{Cu}^{2+}] = 2.0 \text{ mg L}^{-1}$, pH = 7.6. Error bars represent the RPDs ($n = 2$).

could suppress the BrO_2^- formation and result in the lag phase for the BrO_3^- formation. Only after the highly reactive HA moieties were substantially consumed by HOBr (i.e., after 10 h) did BrO_3^- start to be formed quickly.

According to previous studies (Alvarez-Puebla et al., 2004; Deborde and von Gunten, 2008), Cu^{2+} could complex with the carbonyl and hydroxyl groups of NOM, thus facilitating the base-catalyzed enolization and hydrolysis reactions. Recently, Chen et al. (2015) found that Cu^{2+} was not merely a hydrolysis catalyst but also an oxidant for the transformation of benzylpenicillin in oxygen-rich aqueous solutions. The degradation of benzylpenicillin involved the oxidation by Cu^{2+} through Cu^+ . Cu^{2+} could be regenerated via the oxidation of Cu^+ by dissolved oxygen (DO) with a short half-life of less than 1 min in freshwater (Pham et al., 2012), which sustained the continuous degradation of benzylpenicillin. Hence, Cu^{2+} may also activate certain HA fractions to induce a higher reaction rate between HOBr and HA. In this study, Cu^+ was measured only at a very low concentration level in the $\text{HOCl}-\text{Br}^- - \text{Cu}^{2+}$ system (Fig. S2). A possible explanation is that the standard oxidation-reduction potential of chlorine ($E^\circ_{\text{Cl}_2/\text{Cl}^-} = 1.36 \text{ V}$) is much higher than that of DO ($E^\circ_{\text{O}_2/\text{OH}^-} = 0.4 \text{ V}$), so chlorine can more easily convert Cu^+ to Cu^{2+} . As for the copper oxides (i.e., CuO and Cu_2O), heterogeneous reactions could occur. Gallard et al. (2009) reported that the iodine species (i.e., HOI and I_2) were catalytically converted to iodinated organic byproducts on the surface of $\delta\text{-MnO}_2$. Likewise, the bromine in HOBr/OBr^- could also be polarized by CuO/ Cu_2O (Lewis acids) to increase its reactivity toward HA.

In summary, the BrO_3^- formation was primarily promoted in the $\text{HOCl}-\text{Br}^- - \text{CuO}$ system, whereas the formation of studied Br-DBPs (i.e., the sum of Br-THMs, Br-HAAs, and Br-HACams) was primarily

promoted in the $\text{HOCl}-\text{Br}^- - \text{Cu}_2\text{O}$ and $\text{HOCl}-\text{Br}^- - \text{Cu}^{2+}$ systems. Fig. 3 shows the bromine mass balance in the absence or presence of CCPs. Results indicate that without the addition of CCPs, 0.04% and 24.6% of Br^- (on a molar basis) were converted to BrO_3^- and the studied Br-DBPs, respectively. By contrast, the conversion ratios of Br^- to BrO_3^- increased to 22.1%, 8.6% and 9.1% in the presence of CuO, Cu_2O and Cu^{2+} , respectively; and meanwhile, the conversion ratios of Br^- to the studied Br-DBPs reached 24.7%, 36.0% and 30.6%, correspondingly. It is also noted that a considerable amount of bromide (29.7–44.9%) was incorporated in organic byproducts which could not be identified (i.e., unknown Br-DBPs).

3.3. Effect of pH

The effect of pH on the catalytic formation of Br-DBPs and BrO_3^- was tested in the pH range of 6.6–8.6. As shown in Fig. S3, without the addition of CCPs, the formation of Br-THMs and Br-HAAs decreased with increasing pH, while the Br-HACams formation maximized at pH 7.6. Chu et al. (2012) found that the difference between the hydrolysis rates of dichloroacetonitrile and dichloroacetamide at pH 7.0–8.0 was higher than those at other pH levels. In the presence of Cu^{2+} , the catalytic formation of Br-DBPs was notably dependent on pH, and the degree of enhancement became more apparent at a higher pH (Fig. 4a). A previous study reported that the Cu^{2+} -catalyzed enolization and hydrolysis of NOM were accelerated with increasing pH (Deborde and von Gunten, 2008). Furthermore, the deprotonation of NOM functional groups (e.g., carboxyl and hydroxyl groups), which is more favorable at a higher pH, may make electron transfer to Cu^{2+} easier, leading to the reduction of Cu^{2+} to Cu^+ and the concurrent oxidation of NOM. The catalytic promotion of CuO/ Cu_2O on the Br-DBPs formation showed a similar tendency with increasing pH. One possible explanation is that the deprotonation of HOBr to OBr^- favored the electrostatic interactions with the positively charged CuO/ Cu_2O surface (Liu et al., 2012), thus comparatively enhancing the Br-DBPs formation.

In Fig. 4b, the trend of BrO_3^- formation was similar for each of the three catalysts, which maximized at pH 7.6. However, Liu et al. (2012) reported that the BrO_3^- yield reached the maximum at pH 8.6 in the $\text{HOBr}-\text{CuO}$ system. The difference lies in the fact that the reaction in this study was initiated by HOCl, which was present in large excess of Br^- . At pHs 6.6 and 7.6, Br^- was quickly oxidized to HOBr so that the BrO_3^- formation was facilitated. According to the conceptual model proposed by Liu et al. (2012), the rate constant estimated for the $\text{CuO}-\text{OBr}^-$ complex reacting with HOBr was two orders of magnitude higher than that estimated for the $\text{CuO}-\text{HOBr}$ complex. Thus, the $\text{CCP}-\text{OBr}^-$ complex was also likely to react with HOBr more quickly for BrO_3^- formation at pH 7.6 than at pH 6.6.

3.4. Effect of CCP dose

The effect of CCP dose on the catalytic formation of Br-DBPs and BrO_3^- is manifested in Fig. S4. Results indicate that as the CCP dose increased, the formation of Br-HAAs and Br-HACams was slightly enhanced, whereas a significant enhancement on the Br-THMs formation was observed. The CCPs played a catalytic role through complexation with HA, thus the formation of Br-DBPs was generally enhanced with increasing CCP dose. On the whole, the formation of Br-DBPs was considerably affected by the doses of Cu_2O and Cu^{2+} , while only changed slightly with increasing CuO dose (Fig. 5). Analogously, the BrO_3^- formation was also enhanced with increasing CCP doses because of the availability of more reactive sites (or ions) interacting with HOBr/OBr^- . Nevertheless, the BrO_3^- yield was affected by the CuO dose more significantly than by the doses of Cu_2O and Cu^{2+} (Fig. 5). The results further confirm that BrO_3^- formation was primarily promoted in the $\text{HOCl}-\text{Br}^- - \text{CuO}$

Fig. 3. Bromine mass balance in the presence of CCPs and HA during chlorination of SW. Experimental conditions: $[\text{Cl}_2]_0 = 14.2 \text{ mg L}^{-1}$, $[\text{Br}^-]_0 = 2.0 \text{ mg L}^{-1}$, $[\text{HA}]_0 = 5.0 \text{ mg L}^{-1}$, $[\text{CuO}] = 2.0 \text{ g L}^{-1}$, $[\text{Cu}_2\text{O}] = 0.5 \text{ g L}^{-1}$, $[\text{Cu}^{2+}] = 2.0 \text{ mg L}^{-1}$, pH = 7.6, reaction time = 72 h.

Fig. 4. Effect of pH on the catalytic formation of Br-DBPs (a) and BrO_3^- (b) in the SW. Experimental conditions: $[\text{Cl}_2]_0 = 14.2 \text{ mg L}^{-1}$, $[\text{Br}^-]_0 = 2.0 \text{ mg L}^{-1}$, $[\text{HA}]_0 = 5.0 \text{ mg L}^{-1}$, $[\text{CuO}] = 2.0 \text{ g L}^{-1}$, $[\text{Cu}_2\text{O}] = 0.5 \text{ g L}^{-1}$, $[\text{Cu}^{2+}] = 2.0 \text{ mg L}^{-1}$, reaction time = 72 h. Error bars represent the RPDs ($n = 2$).

system, whereas Br-DBPs formation was primarily promoted in the $\text{HOCl-Br}^- \text{--Cu}_2\text{O}$ and $\text{HOCl-Br}^- \text{--Cu}^{2+}$ systems.

3.5. Effect of initial Br^- concentration

Bromine utilization factor (BUF) and bromine incorporation factor (BIF) were calculated to examine the effect of initial Br^- concentration on the catalytic formation of Br-DBPs. BUF refers to the percentage of Br^- that is utilized in forming Br-DBPs, and BIF is used as an index to describe the proportion of Br-DBPs that is partially or totally substituted by bromine. The equations used to calculate the BUF and BIF values are shown in Text S2. The BUF values range from 0 to 1. For example, a BUF value of 0.5 for Br-THMs indicates that half of Br^- was utilized to produce Br-THMs. The BIF values range from 0 (all chlorinated DBPs) to 3 (all Br-DBPs). For example, a BIF value of 2 for THMs means that the typical THM species is dibromochloromethane on average.

As expected, no matter whether CCPs were present or absent, the formation of Br-DBPs always increased with increasing Br^- concentration (Fig. 6a). The specific formation of Br-THMs, Br-HAAs and Br-HAcAms is presented in Fig. S5. The BIFs exhibited a similar trend as well. However, the BUFs decreased with increasing Br^- concentration. For example, when the Br^- concentration increased from 0.2 to 2.0 mg L^{-1} , the Br-THMs formation increased from 276.6 to 638.4 g L^{-1} , and the BIF for Br-THMs increased from 0.52 to 2.20, while the BUF for Br-THMs decreased from 0.40 to 0.26 in the presence of Cu_2O , respectively. The increased BIF implies that there was more bromine incorporated into tribromomethane with increasing Br^- concentration, while the decreased BUF implies that the utilized Br^- in forming Br-THMs did not increase in proportion to the initial Br^- concentration.

Fig. 5. Effect of CCP dose on the catalytic formation of Br-DBPs and BrO₃⁻ in the SW. Experimental conditions: [Cl₂]₀ = 14.2 mg L⁻¹, [Br⁻]₀ = 2.0 mg L⁻¹, [HA]₀ = 5.0 mg L⁻¹, pH = 7.6, reaction time = 72 h. Error bars represent the RPDs (n = 2).

In addition, the BrO₃⁻ formation was also enhanced with increasing Br⁻ concentration (Fig. 6b). For example, as the Br⁻ concentration increased from 0.2 to 2.0 mg L⁻¹, the BrO₃⁻ yield increased from 14.2 to 616.2 μg L⁻¹ in the presence of CuO. Due to a significant competition from HA, the majority of HOBr/OBr⁻ was converted to Br-DBPs at low Br⁻ concentrations. However, at a high Br⁻ concentration, the excessive HOBr/OBr⁻ could be transformed to BrO₃⁻ via the disproportionation pathway under the catalysis of CCPs.

3.6. Effect of real water characteristics

Three different RWs (i.e., MR, DR and NW) were used post filtration to evaluate the effect of water matrix on the catalytic formation of Br-DBPs and BrO₃⁻. As shown in Fig. S6, although the CCPs catalytically enhanced the formation of Br-THMs, Br-HAAs and Br-HAcAms in the RWs, the degree of enhancement were relatively lower than that in the SW. For an instance, at the Br⁻ concentrations of 0.5 mg L⁻¹, the enhancement ratios on Br-DBPs formation under Cu₂O catalysis were 47.4% and 60% in the MR water and SW, respectively (Fig. 7a). The BrO₃⁻ formation presented a similar trend. For example, at the Br⁻ concentration of 0.5 mg L⁻¹, the BrO₃⁻ concentrations under CuO catalysis were 37.3 and 80.5 μg L⁻¹ in the MR water and SW, respectively (Fig. 7b). Despite of the similar SUVA₂₅₄ values of the three RWs, the dissolved organic carbon

Fig. 6. Effect of Br⁻ concentration on the catalytic formation of Br-DBPs (a) and BrO₃⁻ (b) in the SW. Experimental conditions: [Cl₂]₀ = 14.2 mg L⁻¹, [HA]₀ = 5.0 mg L⁻¹, [CuO] = 2.0 g L⁻¹, [Cu₂O] = 0.5 g L⁻¹, [Cu²⁺] = 2.0 mg L⁻¹, pH = 7.6, reaction time = 72 h. Error bars represent the RPDs (n = 2).

(DOC) concentration impacted the catalytic formation of BrO₃⁻ and Br-DBPs to different extents in the presence of CCPs. The BrO₃⁻ formation was suppressed more significantly with increasing DOC concentration than the Br-DBPs formation. For an instance, at the Br⁻ concentration of 0.5 mg L⁻¹, the enhancement ratios on Br-DBPs formation under Cu₂O catalysis were 47.4%, 44.0% and 42.9%, while the BrO₃⁻ yields under CuO catalysis were 37.3, 40.7 and 54.6 μg L⁻¹, corresponding to the DOC concentrations of 5.34, 4.17 and 2.48 mg L⁻¹ in the MR, JR and NW waters, respectively. It was reported that inorganic ions (e.g., phosphate and sulfate) could be absorbed onto metal oxides (Liu et al., 2013b), thus inhibiting the catalytic activity by blocking the reactive sites. Moreover, inorganic compounds (e.g., ammonia and iodide) could react with bromine (Heeb et al., 2014), resulting in less HOBr available for the disproportionation and substitution reactions. This result indicates that water matrix had an important impact on the formation of BrO₃⁻ and Br-DBPs in the presence of CCPs.

4. Conclusions

This study investigated the catalytic enhancement of CCPs on the formation of BrO₃⁻ and Br-DBPs simultaneously during the chlorination of Br⁻-containing waters. Based on the experimental results obtained, the following conclusions are drawn:

- The oxidant decay and BrO₃⁻ formation were enhanced at different degrees in the presence of CCPs, while the presence of HA significantly suppressed the BrO₃⁻ formation due to its strong competition for HOBr.

Fig. 7. Catalysis of CCPs on the formation of Br-DBPs (a) and BrO₃⁻ (b) in three different real waters (RW) collected from Miyun Reservoir (MR, Beijing), Danjiangkou Reservoir (DR, Hubei), and Beijing No. 9 Waterworks (NW, Beijing). Experimental conditions: [Cl₂]₀ = 14.2 mg L⁻¹, [CuO] = 2.0 g L⁻¹, [Cu₂O] = 0.5 g L⁻¹, [Cu²⁺] = 2.0 mg L⁻¹, pH = 7.6, reaction time = 72 h. Error bars represent the RPDs (n = 2).

- The BrO₃⁻ formation was primarily promoted in the HOCl–Br⁻–CuO system, while the Br-DBPs formation was primarily promoted in the HOCl–Br⁻–Cu₂O/Cu²⁺ systems.
- The catalytic formation of BrO₃⁻ and Br-DBPs was highly dependent on pH. The degree of enhancement on the Br-DBPs formation became more apparent under an alkaline condition, while the BrO₃⁻ formation reached the maximum under a nearly neutral condition.
- The characteristics of the real waters, such as organic compositions, had an important impact on the formation of BrO₃⁻ and Br-DBPs in the presence of CCPs.

Acknowledgements

This study was financially supported by the National Natural Science Foundation (51290281, 51525806, 51408590) and the Ministry of Housing and Urban-Rural Development (2012ZX07404-004) of China.

Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.watres.2016.04.033>.

References

- Alvarez-Puebla, R.A., Valenzuela-Calahorra, C., Garrido, J.J., 2004. Retention of Co(II), Ni(II), and Cu(II) on a purified brown humic acid. Modeling and characterization of the sorption process. *Langmuir* 20, 3657–3664.
- Beckwith, R.C., Margerum, D.W., 1997. Kinetics of hypobromous acid disproportionation. *Inorg. Chem.* 36, 3754–3760.
- Blatchley, E.R., Margetas, D., Duggirala, R., 2003. Copper catalysis in chloroform formation during water chlorination. *Water Res.* 37 (18), 4385–4394.
- Bougeard, C.M., Goslan, E.H., Jefferson, B., Parsons, S.A., 2010. Comparison of the disinfection by-product formation potential of treated waters exposed to chlorine and monochloramine. *Water Res.* 44 (3), 729–740.

- Chen, J.B., Sun, P.Z., Zhou, X.F., Zhang, Y.L., Huang, C.H., 2015. Cu(II)-catalyzed transformation of benzylpenicillin revisited: the overlooked oxidation. *Environ. Sci. Technol.* 43, 7003–7009.
- Chu, W.H., Gao, N.Y., Krasner, S.W., Templeton, M.R., Yin, D., 2012. Formation of halogenated C-, N-DBPs from chlor(am)ination and UV irradiation of tyrosine in drinking water. *Environ. Pollut.* 161, 8–14.
- Cowman, G.A., Singer, P.C., 1996. Effect of bromide ion on haloacetic acid speciation resulting from chlorination and chloramination of aquatic humic substances. *Environ. Sci. Technol.* 30, 16–24.
- Deborde, M., von Gunten, U., 2008. Reactions of chlorine with inorganic and organic compounds during water treatment – kinetics and mechanisms: a critical review. *Water Res.* 42 (1–2), 13–51.
- Feng, Y., Teo, W.K., Siow, K.S., Tan, K.L., Heih, A.K., 1996. The corrosion behaviour of copper in neutral tap water. *Corros. Sci.* 38 (3), 369–385.
- Gallard, H., Allard, S., Nicolau, R., von Gunten, U., Croue, J.P., 2009. Formation of iodinated organic compounds by oxidation of iodide-containing waters with manganese dioxide. *Environ. Sci. Technol.* 43, 7003–7009.
- Heeb, M.B., Criquet, J., Zimmermann-Steffens, S.G., von Gunten, U., 2014. Oxidative treatment of bromide-containing waters: formation of bromine and its reactions with inorganic and organic compounds – a critical review. *Water Res.* 48, 15–42.
- Krasner, S.W., Weinberg, H.S., Richardson, S.D., Pastor, S.J., Scimanti, M.J., Onstad, G.D., Thurston, A.D., 2006. Occurrence of a new generation of disinfection byproducts. *Environ. Sci. Technol.* 40, 7175–7185.
- Kumar, K., Margerum, D.W., 1987. Kinetics and mechanism of general-acid-assisted oxidation of bromide by hypochlorite and hypochlorous acid. *Inorg. Chem.* 26 (16), 2706–2711.
- Lee, Y., von Gunten, U., 2009. Transformation of 17 α -ethinyl estradiol during water chlorination: effects of bromide on kinetics, products, and transformation pathways. *Environ. Sci. Technol.* 43, 480–487.
- Li, B., Qu, J.H., Liu, H.J., Hu, C.Z., 2007. Effects of copper(II) and copper oxides on THMs formation in copper pipe. *Chemosphere* 68 (11), 2153–2160.
- Li, B., Liu, R.P., Liu, H.J., Gu, J.N., Qu, J.H., 2008. The formation and distribution of haloacetic acids 9 in copper pipe during chlorination. *J. Hazard. Mater.* 152 (1), 250–258.
- Liu, C., Croue, J.P., 2016. Formation of bromate and halogenated disinfection byproducts during chlorination of bromide-containing waters in the presence of dissolved organic matter and CuO. *Environ. Sci. Technol.* 50, 135–144.
- Liu, C., von Gunten, U., Croue, J.P., 2012. Enhanced bromate formation during chlorination of bromide-containing waters in the presence of CuO: catalytic disproportionation of hypobromous acid. *Environ. Sci. Technol.* 46, 11054–11061.
- Liu, C., von Gunten, U., Croue, J.P., 2013a. Chlorination of bromide-containing waters: enhanced bromate formation in the presence of synthetic metal oxides and deposits formed in drinking water distribution systems. *Water Res.* 47 (14), 5307–5315.
- Liu, C., von Gunten, U., Croue, J.P., 2013b. Enhanced chlorine dioxide decay in the presence of metal oxides: relevance to drinking water distribution systems. *Environ. Sci. Technol.* 47, 8365–8372.
- Margerum, D.W., Huff Hartz, K.E., 2002. Role of halogen(I) cation-transfer mechanisms in water chlorination in the presence of bromide ion. *J. Environ. Monit.* 4 (1), 20–26.
- Nobukawa, T., Sanukida, S., 2000. The genotoxicity of by-products by chlorination and ozonation of the river water in the presence of bromide ions. *Water Sci. Technol.* 42 (3–4), 259–264.
- Pan, Y., Zhang, X., 2013. Four groups of new aromatic halogenated disinfection byproducts: effect of bromide concentration on their formation and speciation in chlorinated drinking water. *Environ. Sci. Technol.* 47, 1265–1273.
- Pattison, D.I., Davies, M.J., 2004. Kinetic analysis of the reactions of hypobromous acid with protein components: implications for cellular damage and use of 3-bromotyrosine as a marker of oxidative stress. *Biochemistry* 43, 4799–4809.
- Pham, A.N., Rose, A.L., Waite, T.D., 2012. Kinetics of Cu(II) reduction by natural organic matter. *J. Phys. Chem. A* 116 (25), 6590–6599.
- Qiang, Z.M., Jiang, Y.J., Ben, W.W., Adams, C., Dong, H.Y., 2012. Monitoring free chlorine and free bromine in aquarium seawater treated by ozone. *Anal. Methods* 4, 3646–3652.
- Rice, E.W., 2012. Standard Methods for the Examination of Water and Wastewater. American Public Health Association, Washington, D.C.
- Richardson, S.D., Thurston, A.D., Rav-Acha, C., Groisman, L., Popilevsky, I., Juraev, O., Glezer, V., Mackague, A.B., Plewa, M.J., Wagner, E.D., 2003. Tribromopyrrole, brominated acids, and other disinfection byproducts produced by disinfection of drinking water rich in bromide. *Environ. Sci. Technol.* 37, 3782–3793.
- Skaff, O., Pattison, D.I., Davies, M.J., 2007. Kinetics of hypobromous acid-mediated oxidation of lipid components and antioxidants. *Chem. Res. Toxicol.* 20 (12), 1980–1988.
- USEPA, 2001. National Primary Drinking Water Regulations. Washington D.C.
- Xiao, W.Z., Hong, S.K., Tang, Z.J., Seal, S., Taylor, J.S., 2007. Effects of blending on surface characteristics of copper corrosion products in drinking water distribution systems. *Corros. Sci.* 49 (2), 449–468.
- Zhang, H., Andrews, S.A., 2012. Catalysis of copper corrosion products on chlorine decay and HAA formation in simulated distribution systems. *Water Res.* 46 (8), 2665–2673.
- Zhao, Y., Anichina, J., Lu, X., Bull, R.J., Krasner, S.W., Hrudey, S.E., Li, X.F., 2012. Occurrence and formation of chloro- and bromo-benzoquinones during drinking water disinfection. *Water Res.* 46 (14), 4351–4360.