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Iodinated trihalomethane formation during chloramination of iodate-containing waters in the presence of zero valent iron

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ABSTRACT

Iodide (I^-) and iodinated X-ray contrast media (ICM) are the primary iodine sources for the formation of iodinated disinfection byproducts (I-DBPs), and iodate (IO_3^-) is believed to be a desired sink of iodine in water. This study found that highly cytotoxic iodinated trihalomethanes (I-THMs) also can be generated from iodate-containing waters (without any other iodine sources) in the presence of zero valent iron (ZVI) during chloramination, which could be a big issue in the wide usage of iron pipes. The effect of major factors including ZVI dosage, NH_2Cl and IO_3^- concentrations, initial pH, Br^-/IO_3^- molar ratio, phosphate concentration, iron corrosion scales (goethite and hematite) on the formation of I-THMs were investigated. Formation of I-THMs from IO_3^- increased with the increase of ZVI dosage, IO_3^- and NH_2Cl concentrations. Chloramines can also remarkably accelerate the reduction of IO_3^- by ZVI. Peak I-THM formation was found at pH 8. As the Br^-/IO_3^- molar ratio increased from 0 to 20, I-THM formation considerably enhanced, especially for the bromine-incorporated species. Goethite and hematite enhanced the formation of I-THMs in the presence of ZVI. Additionally, a significant suppression on I-THM formation was observed with the addition of phosphate. Considering that a large number of water distribution networks contain unlined cast iron pipes, transformation of IO_3^- in the presence of ZVI during chloramination may contribute to the formation of I-THMs in such systems.

1. Introduction

The disinfection of drinking-water has been named as a public health triumph of the twentieth century (Richardson, 2003). Before it had been used widely, millions of people died from waterborne illnesses. However, chemical disinfection has also raised an unintended health hazard due to the genotoxic and cytotoxic effects associated with disinfection by-products (DBPs) (Richardson et al., 2007). Over the past decades, regulated DBPs including trihalomethanes (THMs), haloacetic acids (HAAs), bromate and chlorate have aroused wide public concern. However, other emerging iodinated DBPs (I-DBPs) are reported to be more cytotoxic and genotoxic in mammalian cells compared to their chlorinated and brominated analogues (Plewa et al., 2004). For example, iodoacetic acid was reported as the most cytotoxic, genotoxic, and potential carcinogenic DBP in mammalian cells (Richardson et al., 2008; Duirk et al., 2011; Richardson and Postigo, 2012; Wei et al., 2013). Additionally, iodinated trihalomethanes (I-THMs) were reported to be attributed to the issues of medicinal or pharmaceutical taste and odor. For instance, the odor and taste threshold concentrations of iodoform are 0.02 and 5 μg/L, respectively (Cancho et al., 2000; Hansson et al., 1987). Therefore, the formation of I-DBPs has raised great concern in recent years (Richardson et al., 2003; Ye et al., 2013; Wang et al., 2014; Zhang et al., 2016). Bichsel and Von Gunten (1999, 2000) reported that chloramination of iodate containing water can form a significant amount of I-THMs due to the formation of active hypolodous acid (HOI) that can react with natural organic matter (NOM), causing the formation of I-THMs.

It is a common consensus that the main iodine species in water are iodide (I^-), iodate (IO_3^-) and iodinated organic compounds such as iodinated X-ray contrast media (ICM) (Bichsel and Von Gunten, 1999; Duirk et al., 2011; Hansen et al., 2011). IO_3^- is preferentially

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recommended as an additive to salt for its stability by most health authorities to prevent iodine deficiency (Burgi et al., 2001) because it can rapidly be reduced to I^- in vivo by glutathione and will not cause toxicological problems (Taurog et al., 1966; Smith et al., 2010). Therefore, IO_3^- is a preferred sink of iodine in drinking water (Allard et al., 2013) and has been detected in tap waters with concentrations at level of several to dozens of μg-I/L (Snyder et al., 2005; Gong and Zhang, 2013; Zhang et al., 2016). One of the optimal approaches proposed to mitigate the formation of I-DBP is to ensure full oxidation of the iodinated precursors, such as I^- (Bichsel and Von Gunten, 1999, 2000) and organo-iodine (Seitz et al., 2008; Wang et al., 2014), to IO_3^- (Allard et al., 2015).

Large amounts of unlined cast iron pipes have been used in water distribution systems for several centuries throughout the world (Mcneiill and Edwards, 2001; Tang et al., 2006; Husband and Boxall, 2011). However, they are very prone to corrosion, causing the release of ferrous and ferric ions as well as the formation of iron oxides, such as goethite (α-FeOOH) and hematite (Fe_2O_3), on the top layer of red rust (Tang et al., 2006; Zhu et al., 2014). Recently, chloramines have been utilized as a secondary disinfectant for their long-term stability and less formation of regulated DBPs (Diehl et al., 2000; Seidel et al., 2005; Shen and Andrews, 2011). Humic acid (HA), a major component of NOM, is also ubiquitous in drinking water (Li et al., 2016). Hence, it is an interesting scientific question to understand whether IO_3^- can react with zero valent iron (ZVI) and/or its corrosion scales in the presence of chloramine and NOM to form iodinated trihalomethanes (I-THMs). Although IO_3^- is widely perceived as nontoxic and stable, the possible transformation of IO_3^- to I^- by ZVI might make a contribution to the formation of I-THMs in source waters. At present, little is known about which parameters, if any, would affect the formation of I-THM in the presence of chloramine and ZVI. This information is significant to realize the formation of I-THM in both natural and engineered systems.

The primary aim of this research was therefore to investigate the formation of I-THMs from IO_3^- during chloramination in the presence of ZVI and/or its corrosion scales. Key parameters including ZVI dosage, NH_2Cl and IO_3^- concentrations, initial pH, Br^-/IO_3^- molar ratio and phosphate concentration were studied systematically.

2. Materials and methods

2.1. Chemicals and reagents

All chemicals were at least of analytical grade except as noted. Commercial 4–4.99% sodium hypochlorite (NaOCl), iodoform (CHI_3, 99.0%), ammonium chloride (NH_4Cl), NaOH (≥98%), KH_2PO_4 (≥99.0%), KIO_3 (≥99.0%), α-FeOOH, phenol (≥99.0%), 2-iodophenol (≥98.0%) and 4-iodophenol (≥99.0%) and Fe_2O_3 (≥99.0%) were purchased from Sigma-Aldrich (USA). The ZVI (≥99.99%) powder and humic acid (HA) used as the model NOM source in this study were also supplied by Sigma-Aldrich (St Louis, Missouri, USA). Five I-THM standards, including chlorodiiodomethane ($CHClI_2$, 90–95%), dichloroiodomethane ($CHCl_2I$, ≥ 95%), bromochloroiodomethane (CHBrClI, ≥ 95%), dibromoiodomethane ($CHBr_2I$, 90–95%) and bromodiiodomethane ($CHBrI_2$, 90–95%) were obtained from CanSyn Chemical Corp (Toronto, ON, Canada). Methyl tertbutyl ether (MtBE) was purchased from J.T. Baker (USA). $Na_2S_2O_4$, $Na_2S_2O_3$, KBr and H_2SO_4 were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) without further purification. All solutions were prepared with ultra-pure water produced using a Milli-Q water purification system (Millipore, USA). A monochloramine (NH_2Cl) solution was freshly prepared by adding NaOCl solution slowly into a stirred ammonium chloride (NH_4Cl) solution with the Cl_2/N molar ratio of 0.8 at pH 8.5 for 0.5–1 h (Xu et al., 2012).

2.2. Experimental procedures

Batch experiments were performed in duplicate under headspace-free conditions in 40-mL glass screw-cap amber vials with PTFE-lined septa. The vials were then placed into a constant-temperature shaker bath (25 ± 1 °C, 150 rpm) in dark for 3 d. After the designed reaction time, 10 mL of the solution was withdrawn with a 20 mL gas-tight syringe into a 25 mL vial and filtered immediately through a glass fiber filter (GF/F, Whatman, USA) to remove ZVI particles before analysis. The filtered solution was quenched using $Na_2S_2O_3$ with 20% excess of the initial NH_2Cl concentration, and the samples were then extracted using MtBE immediately to avoid any chance of I-THM decomposition.

Factors including ZVI dosage (0–2.0 g/L), NH_2Cl and IO_3^- concentrations (0 - 20 mg-Cl_2/L and 0–6.35 mg-I/L (0–50 μM), respectively), Br^-/IO_3^- molar ratio (0–20), initial pH (4–10) and phosphate concentration (0–10 mM) on I-THM formation from IO_3^- were investigated. Typical experiments were conducted using 50 mL humic acid solutions prepared at DOC concentration of 5.0 mg-C/L and then being spiked with IO_3^-, NH_2Cl and ZVI to the designed concentrations without pH buffer to avoid any potential interference in the reactions (Fan et al., 2006; Xie, 2005; Xie and Shang, 2005). For the experiments regarding the effect of phosphate concentration on I-THM formation, the initial pH of solutions were adjusted to 7 using small amounts of H_2SO_4 or NaOH to prevent the change of pH due to the addition of phosphate. For investigating the mass balance of IO_3^- transformation by ZVI, IO_3^- and ZVI initial concentrations were increased to 12.7 mg-I/L (100 μM) and 5 g/L, respectively, to get the signals higher than the detection limits of I^- and HOI (see Section 2.3). In order to evaluate the risk of I-DBP formation under real drinking water treatment conditions, raw waters from Huangpu River (HR) and Taihu lake as well as the treated water (after coagulation and ultrafiltration but prior to disinfection) from a drinking water treatment plant (DWTP) were collected. The characteristics of the collected water samples were distinctively different, which were summarized in Table S1. The collected samples were filtered through 0.45 μm cellulose acetate membranes (Millipore Corp., Billerica, MA) and stored at 4 °C in dark. Only 12.7 μg-I/L (0.1 μM) IO_3^- was spiked in the real water samples.

2.3. Analytical methods

DOC was measured using a TOC-VCSH analyzer (Shimadzu, Japan) with the detection limit was 0.1 mg-C/L. Solution pH was measured using a pH meter (FE20-FiveEasy, Mettler Toledo, Switzerland), which was calibrated regularly with standard buffer solutions (pH = 4.01, 7.00, 9.21, Mettler Toledo). Iodate (IO_3^-), iodide (I^-) and hypolodous acid (HOI) were analyzed using a UPLC (Waters, USA) equipped with an XTerra® MS C18 column (4.6 × 250 mm i.d., 5 μm film thickness, Waters, USA) and a UV detector. IO_3^- was analyzed with the mobile phase of 35% acetonitrile and H_3PO_4 solution (0.1%), flow rate of 0.80 mL/min, column temperature of 25 °C at the wavenumber of 209 nm (Sajonz et al., 2006). The mobile phase for I^- measurement was consisted of 2%/98% (v/v) acetonitrile and KH_2PO_4 solution (0.09 M) at a flow rate of 0.80 mL/min and the wavenumber 223 nm (Tian et al., 2014). HOI was measured using excess phenol to form 2-iodophenol and 4-iodophenol, which could be detected using UPLC (Bichsel and Von Gunten, 2000). The retention times for IO_3^-, I^-, 2-iodophenol and 4-iodophenol were 3.24, 4.21, 10.89 and 13.02 min. The injection volume was 10 μL, and the detection limits of IO_3^-, I^- and HOI were 10, 5 and 10 μg-I/L, respectively.