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Formation of iodinated disinfection by-products during oxidation of iodide-containing waters with chlorine dioxide

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ABSTRACT

This study was to explore the formation of iodinated disinfection by-products (I-DBPs), including iodoform (CHI_3), iodoacetic acid (IAA) and triiodoacetic acid (TIAA), when iodide-containing artificial synthesized waters and raw waters are in contact with chlorine dioxide (ClO_2). Among the investigated I-DBPs, CHI_3 was the major species during ClO_2 oxidation in artificial synthesized waters. Impact factors were evaluated, including the concentrations of ClO_2, iodide (I^-), dissolved organic carbon (DOC) and pH. Formation of CHI_3, IAA and TIAA followed an increasing and then decreasing pattern with increased ClO_2 or DOC concentration. I-DBPs yield was significantly affected by solution pH. High concentrations of I-DBPs were generated under circumneutral conditions with the maximum formation at pH 8. The increase of I^- concentration can increase I-DBPs yields, but the increment was suppressed when I^- concentration was higher than 50 μM. When 100 μg/L $I^-$and ClO_2 (7.5–44.4 μM) were spiked to the raw water samples from Yangshupu and Minhang drinking water treatment plant, certain amounts of CHI_3 and IAA were found under pH 7 and the concentrations were strongly correlated with ClO_2 dosage and water qualities, however, no TIAA was detected. Finally, we investigated I-DBPs formation of 18 model compounds, including 4 carboxylic acids, 5 phenols and 8 amino acids, treating with ClO_2 when I^- was present. Results showed that most of these model compounds could form a considerable amount of I-DBPs, especially for propanoic acid, butanoic acid, resorcinol, hydroquinone, alanine, glutamic acid, phenylalanine and serine.

1. Introduction

Due to concerns about potential cancer risks of disinfection by-products (DBPs) including two most abundant groups trihalomethanes (THMs) and haloacetic acids (HAAs) produced during chlorination (Singer, 1994; Richardson, 2003), the US Environmental Protection Agency (USEPA) has established a maximum contaminant level (MCL) of 80 μg/L for four THMs and 60 μg/L for five HAAs (USEPA, 2006). To comply with these regulations, many drinking water utilities have to adjust their treatment processes (Lykins et al., 1990), which leads to the exploration of many alternative disinfectants, including chlorine dioxide (ClO_2). This owes much to the reason that ClO_2 does not produce THMs and total HAAs to a significant

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extent comparing to chlorine (Richardson et al., 1994; Hua and Reckhow, 2007a). In addition, the biocidal efficiency of ClO_2 is equal or superior to chlorine over a wide pH range (Aieta and Berg, 1986; USEPA, 1999; White, 1992). ClO_2 is effective in controlling tastes and odors (White, 1992; Edwards and Amirtharajah, 1993) as well as eliminating iron and manganese (Aieta and Berg, 1986; White, 1992). Moreover, ClO_2 could possess the same disinfection efficiency as chlorine does with a smaller dosage and less reaction time (White, 1992; Narkis et al., 1995; USEPA, 1999).

When iodide (I^-) (from natural sources, sea-water intrusion or brines) is present, the oxidation of I^- to hypoiodous acid (HOI) during oxidative drinking water treatment and its further reaction with natural organic matter (NOM) can lead to the formation of iodinated DBPs (I-DBPs) (Bichsel and von Gunten, 2000; Plewa et al., 2004; Richardson et al., 2008). Because iodinated THMs (I-THMs) can cause taste and odor issues and I-DBPs are generally more cytotoxic and/or genotoxic in mammalian cell assays than their chlorinated and brominated analogues, formation of I-DBPs has caused more and more concerns recently (Hansson et al., 1987; Karpel Vel Leitner et al., 1998; Richardson et al., 2008; Plewa and Wanger, 2009). Past studies have reported formation of I-DBPs by oxidative treatment of iodide-containing waters with chlorine (Brass et al., 1977; Karpel Vel Leitner et al., 1998; Bichsel and von Gunten, 2000; Cancho et al., 2000; Hua et al., 2006; Ding and Zhang, 2009), chloramines (Hansson et al., 1987; Bichsel and von Gunten, 2000; Hua et al., 2006; Richardson et al., 2008; Jones et al., 2012a,b), ozone (Bichsel and von Gunten, 2000; Smith et al., 2010), manganese dioxide (MnO_2) (Gallard et al., 2009), lead oxide (Lin et al., 2008) and potassium permanganate ($KMnO_4$) (Jones et al., 2012a; Ye et al., 2012). For typical concentration of disinfectants applied in drinking water treatment plants, I^- is quickly oxidized to HOI by oxidation with chlorine, chloramines, or ozone. Chloramination favors the formation of I-DBPs because chloramines can oxidize I^- to HOI without further oxidizing to iodate (IO_3^-), which is an inert and non-toxic form of iodine (Bichsel and von Gunten, 1999, 2000). Chlorination can result in both IO_3^- and CHI_3 formation. As chlorine concentration increases, CHI_3 formation decreases while IO_3^- formation increases (Bichsel and von Gunten, 2000; Hua et al., 2006). No iodo-trihalomethanes (I-THMs) were detected during ozonation, and greater than 90% of present I^- was oxidized to IO_3^- (Bichsel and von Gunten, 2000). When iodide-containing waters are treated with manganese dioxide, iodinated organic compounds can be produced in pH range of 5–7 because of the oxidation of I^- to iodine (I_2) and the polarization of I_2 by MnO_2 as a catalyst (Gallard et al., 2009). Lead oxide is also a very powerful oxidant and can oxidized iodide to triiodide (I_3^-), leading to the formation of I-DBPs in the presence of NOM (Lin et al., 2008). Potassium permanganate could oxide iodide to reactive iodine species, including HOI, I_2 and I_3^-, which could then react with NOM and form I-DBPs (Ye et al., 2012).

Although the formation of chlorinated and brominated DBPs during water treatment with ClO_2 have been deeply investigated (Aieta and Berg, 1986; Werdehoff and Singer, 1987; Richardson et al., 1994; Li et al., 1996; Chang et al., 2000a,b; Richardson et al., 2003), there is only a few literature that addressed the formation of I-DBPs when treating iodide-containing waters with ClO_2 (Richardson et al., 2003; Hua and Reckhow, 2007a; Jones, 2009; Jones et al., 2012a). The fate of I-radicals formed in the presence of ClO_2 is still unclear (Bichsel and von Gunten, 1999), however, Hua and Reckhow (2007a) reported the formation of a substantial amount of CHI_3 but only a small amount of IO_3^-. They proposed that I^- was oxidized to I_2 without quickly further oxidized to IO_3^-, and I_2 may play a significant role in the formation of I-DBPs when treating iodide-containing waters with ClO_2 (Hua and Reckhow, 2007a). Moreover, HOI and I_3^-, which are reactive iodine species, were also identified by Lengyel et al. (1996) as significant intermediates in the chlorine dioxide/chlorite–iodide reaction.

The objectives of this study were (1) to examine the impact of initial concentration of ClO_2, I^- and DOC as well as solution pH on the formation of I-DBPs, including CHI_3, IAA and TIAA, (2) to evaluate the effect of raw water composition on the formation of I-DBPs during oxidation by ClO_2 in the presence of I^-, and (3) to investigate I-DBPs formation of 18 model compounds including carboxylic acids, phenols and amino acid during oxidation by ClO_2 in the presence of I^-.

2. Materials and methods

2.1. *Chemicals*

All chemicals were at least of analytical grade except as noted. CHI_3 (99%) and IAA (≥99.0%) standard solutions as well as potassium iodide (KI ≥ 99.0%) were obtained from Sigma–Aldrich (USA). TIAA (90%) standard solution was purchased from Toronto Research Chemicals Inc. (Canada). Methyl *tert*-butyl ether (MtBE) and methanol were purchased from J.T. Baker (USA).

The 0.3% of ClO_2 stock solution was prepared by adding two powder reagents, component A (5 g, power composition containing sodium chlorite and additives) and component B (5 g, power composition containing sodium bisulfate monohydrate and additives) which were obtained from TwinOxide®(De Tongelreep, Netherlands), into 250 mL water sequentially. After around two hours' reaction, the prepared stock solution was kept in a sealed amber glass bottle in dark at 4 °C. The 0.3% of ClO_2 stock solution was freshly prepared every month and this method can provide certified 99.9× % pure ClO_2 solution without by-products (Manufacturers report). Humic acid (HA) was obtained from Sigma–Aldrich and used as a model NOM source in this study. HA stock solution was prepared by dissolving 100 mg HA into 250 mL Milli-Q water with the addition of 0.1 M NaOH to facilitate HA dissolution. After 2 h mixing, the completely dissolved solution was transferred to a 1000-mL volumetric flask, filled with Milli-Q water to 1000 mL, filtered through 0.45 μm cellulose acetate membranes (Anpel Co. Ltd, Shanghai, China) to eliminate suspended solids and then kept at 4 °C in the dark until use. All other chemicals were obtained from Sinopharm Chemical Reagent Co., Ltd. (China) without further purification. All solutions were prepared with ultra-pure water produced from a Milli-Q water purification system (Millipore, USA).