WATER RESEARCH 46 (2012) 5491–5498

Available online at www.sciencedirect.com

SciVerse ScienceDirect

journal homepage: www.elsevier.com/locate/watres

The effects of selected preoxidation strategies on I-THM formation and speciation

Darryl B. Jones [a], Hocheol Song [b], Tanju Karanfil [a,*]

[a] Department of Environmental Engineering and Earth Sciences, Clemson University, 342 Computer Court, Anderson, SC 29625, USA
[b] Department of Environment and Energy, Sejong University, 98 Gunja-dong, Gwnagjin-gu, Seoul 143-747, South Korea

ARTICLE INFO

Article history:
Received 21 March 2012
Received in revised form
26 June 2012
Accepted 10 July 2012
Available online 24 July 2012

Keywords:
I-THM
THM
Bromide
Iodide
NOM
Preoxidation
Potassium permanganate
Chlorine dioxide
Hydrogen peroxide
Monochloramine

ABSTRACT

In this study, the impacts of three preoxidation strategies [i.e., using potassium permanganate ($KMnO_4$), chlorine dioxide (ClO_2), or hydrogen peroxide (H_2O_2)] before preformed monochloramine (NH_2Cl) addition on the formation and speciation of iodinated trihalomethanes (I-THMs) were evaluated at the Br^-/I^- mass ratio of 10 in two natural waters. The effects of preoxidant dose, Br^-/DOC, and I^-/DOC ratio were investigated. Preoxidation with $KMnO_4$ increased I-THM formation due to an increase in iodoform (CHI_3) and brominated I-THM (CHBrClI, $CHBrI_2$, $CHBr_2I$) formation. In contrast, preoxidation with ClO_2 sometimes reduced I-THM formation, primarily due to a reduction in CHI_3 formation. Preoxidation with H_2O_2 had no effect on I-THM formation or speciation. I-THM formation from each preoxidant alone was considerably less than the formation from NH_2Cl. Overall, preoxidant type, preoxidant/DOC, preoxidant/I^-, and I^-/DOC ratios are the important factors that water utilities should evaluate when assessing the impact of preoxidation for controlling I-THM formation.

1. Introduction

Preoxidants are used in water treatment for various reasons to: (i) control mussels in treatment plant intakes, (ii) reduce taste and odor problems, (iii) oxidize iron and manganese species, (iv) minimize algae growth in treatment tanks, (v) improve filtration, and/or (vi) enhance disinfection (Klerks and Fraleigh, 1991; Chen and Yeh, 2005; Alam et al., 2008; Liang et al., 2009). Potassium permanganate ($KMnO_4$), chlorine dioxide (ClO_2), and hydrogen peroxide (H_2O_2) are often considered as alternative preoxidants to chlorine (Cl_2) and ozone (O_3), which have been shown to form regulated halogenated disinfection byproducts (DBPs) and bromate (BrO_3^-), respectively (Krasner et al., 2006). While $KMnO_4$ and H_2O_2 do not form regulated DBPs, ClO_2 forms chlorite (ClO_2^-) and some levels of haloacetic acids (HAAs), two types of regulated DBPs in the United States (Arora et al., 2001). The formation of ClO_2^- may be controlled by limiting the ClO_2 dose application to less than 1.5 mg/L due to a 30–70% conversion rate of ClO_2 to ClO_2^- (Baribeau et al., 2002).

While the formation of regulated DBPs from the three alternative preoxidants is not a large issue, preoxidants may affect the subsequent DBP formation from post-disinfectants (i.e., chlorine or chloramines) by oxidizing precursors, or alternatively forming DBP precursors (Ma and Graham, 1996; Gallard and von Gunten, 2002). The extent of these effects also

* *Corresponding author*. Tel.: +1 864 656 1005; fax: +1 864 656 0672.
E-mail address: tkaranf@clemson.edu (T. Karanfil).
0043-1354/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.watres.2012.07.018

depends on the variations in the natural organic matter (NOM) characteristics of the source water (Chowdhury et al., 2008).

Chloramination, as a post-disinfection, has been a strategy more frequently used in recent years in the United States to control the formation of THMs and HAAs. Today, an increasing number of utilities are considering chloramination practices in order to comply with the increasingly stringent Stage 2 D/DBP rule. However, recent studies have shown that the formation of iodinated DBPs (I-DBPs), that have been shown to be more geno- and cyto-toxic than brominated and chlorinated DBPs (Plewa et al., 2004), may be particularly problematic during chloramination of source waters containing iodide (Bichsel and von Gunten, 2000; Hua and Reckhow, 2007a, 2008; Jones et al., 2011, 2012).

Bromide (Br^-) to iodide (I^-) ratio in natural waters is an important factor in the formation and speciation of I-THMs (Jones et al., 2012). An occurrence study of 23 cities showed that the ratio of Br^-/I^- in source waters was 10:1 on average (Richardson et al., 2008). While this ratio can vary, a study of six treatment plants showed that for all cases, Br^- was at a higher concentration than I^- (Weinberg et al., 2011). Since bromide and iodide levels have not been simultaneously characterized in natural waters until recently, previous research have not been conducted at typical Br^-/I^- mass ratios of natural waters (Leitner et al., 1998; Bichsel and von Gunten, 2000; Hua et al., 2006; Hua and Reckhow, 2007a,b, 2008).

While some previous work has shown that preoxidation affects the formation of regulated DBPs such as THMs and HAAs, studies are lacking about the effects of preoxidation on emerging iodinated DBPs. To the best of our knowledge, there are no studies that have investigated I-THM formation from $KMnO_4$ or H_2O_2, while there have been only two field studies that have observed I-THMs from ClO_2 followed by NH_2Cl (Weinberg et al., 2002; Richardson et al., 2003). In addition, Hua and Reckhow (2007a) observed I-THM formation from ClO_2 during laboratory investigations. However, they investigated ClO_2 only (not followed by NH_2Cl) at high iodide levels (200 μg/L) without correspondingly increasing Br^-; thus a much lower Br^-/I^- than typically found in natural waters.

The objective of this study was to examine the effect of preoxidation (i.e., using $KMnO_4$, ClO_2 or H_2O_2) as a strategy to control I-THM formation from chloramination. Typical preoxidant doses were applied to two waters (low-$SUVA_{254}$ [$SUVA_{254} = UV_{254}/DOC$] and high-$SUVA_{254}$) prior to preformed NH_2Cl addition. A representative Br^-/I^- mass ratio (10:1) for natural waters, and two Br^- and I^- concentrations (200 μg/L and 20 μg/L; 800 μg/L and 80 μg/L) were evaluated. Even though it has been shown previously that the formation of THMs is minimal from preformed NH_2Cl (Hong et al., 2007), THMs, due to their regulatory significance, were also monitored and compared with I-THMs.

2. Materials and methods

2.1. Source waters

Raw waters prior to any treatment were used in this study because preoxidants are often added at the intakes or beginning of water treatment plants (WTPs). Two source waters were selected because of differences in their $SUVA_{254}$ values, which indicate some differences in their NOM characteristics. The SJWD WTP located in Lyman, SC (inland) has a source water with low-$SUVA_{254}$, while the Hanahan WTP located in Charleston, SC (coast) uses a higher $SUVA_{254}$ source water (Table 1). Two different water batches were collected from each source and utilized in the experiments. Similar $SUVA_{254}$ values of two batches at each source (Table 1) and insignificant changes in I-THM formation from preformed NH_2Cl treatment (data not shown) suggested that the differences in the reactivity of NOM between the batches were minimal.

2.2. Preoxidants

The $KMnO_4$ solution was prepared by dissolving 30 mg of $KMnO_4$ crystals (Sigma–Aldrich) in 100 mL of distilled and deionized (DDI) water. The standard method (4500-$KMnO_4$), which measures the absorbance of MnO_4^- at 525 nm, was used to determine the $KMnO_4$ concentrations. The samples were filtered with 0.2 μm filters to avoid any interference due to any MnO_2 solids that may have formed.

ClO_2 was prepared via the slow acidification of a $NaClO_2$ solution with H_2SO_4. Details of the ClO_2 generation procedure are presented elsewhere (Jones, 2009). The ClO_2 stock solution was kept in an amber glass bottle with no headspace in the refrigerator and was freshly prepared every month. The concentration of ClO_2 was determined using the Lissamine Green B (LGB) and Horseradish Peroxidase method (HRP) (Dattilio et al., 2005; Wu et al., 2007).

H_2O_2 solutions were prepared from diluting a 30% solution of ACS grade H_2O_2. The H_2O_2 concentration was measured using a Hach Test Kit (model HYP-1).

2.3. Preformed NH_2Cl

Preformed NH_2Cl was prepared by slowly titrating a HOCl solution in a $(NH_4)_2SO_4$ solution to reach a Cl_2/NH_3 ratio of 3.5 (by weight), which is within the typical range of 3:1–5:1 used in practice. The prepared solution had no measurable free chlorine. The concentration of NH_2Cl was measured using the N,N-diethyl-p-phenylenediamine (DPD) method (Standard Method 4500).

2.4. Preoxidation–NH_2Cl experiments

Raw waters were buffered with $NaHCO_3$ (4 mM) at pH 7.5, and then calculated volumes of Br^- and I^- solutions were added to the waters to achieve the target concentrations (Br^-/I^-: 200/20

Table 1 – Selected characteristics of SJWD and Charleston waters.

Parameter	SJWD raw	Charleston raw
DOC (mg/L)	2.5 (1.9)[a]	6.4 (7.4)
$SUVA_{254}$ (L/mg-m)	2.6 (2.4)	3.8 (3.7)
Br^- (μg/L)	33 (22)	115 (78)
I^- (μg/L)	3 (<2)	<2 (<2)

a Values in parentheses are for the second batch of water from each source.