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Insight into the formation of iodinated trihalomethanes during chlorination, monochloramination, and dichloramination of iodide-containing water

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ABSTRACT

In this study, the formation of iodinated trihalomethanes (I-THMs) was systematically evaluated and compared for three treatment processes - (i) chlorination, (ii) monochloramine, and (iii) dichloramination - under different pH conditions. The results demonstrated that I-THM formation decreased in the order of monochloramination > dichloramination > chlorination in acidic and neutral pH. However, the generation of I-THMs increased in the dichloramination < chlorination < monochloramination order in alkaline condition. Specifically, the formation of I-THMs increased as pH increased from 5 to 9 during chlorination and monochloramination processes, while the maximum I-THM formation occurred at pH 7 during dichloramination. The discrepancy could be mainly related to the stability of the three chlor (am) ine disinfectants at different pH conditions. Moreover, in order to gain a thorough insight into the mechanisms of I-THM formation during dichloramination, further investigation was conducted on the influencing factors of DOC concentration and Br^-/I^- molar ratio. I-THM formation exhibited an increasing and then decreasing trend as the concentration of DOC increased from 1 to 7 mg-C/L, while the yield of I-THMs increased with increasing Br^-/I^- molar ratio from 5:0 to 5:10. During the three processes mentioned above, similar I-THM formation results were also obtained in real water, which indicates that the

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excessive generation of I-THMs should be paid special attention during the disinfection of iodide-containing water.

Introduction

Because of the invention and application of disinfectants, many water-borne diseases have been controlled and eliminated (Richardson, 2003). Usually, disinfectants can not only effectively kill pathogenic microorganisms (Shang and Blatchley, 1999) but also oxidize micro-pollutants and inorganic ions (such as bromine and iodine) in groundwater (Han and Zhang, 2018) and swimming pool water (Fletcher and Link, 1933; Richardson, 2014). At present, the most widely used disinfectant is chlorine, and chloramine is sometimes being used as a substitute for chlorine (Allard et al., 2015). However, disinfectant will also react with the natural organic matter (NOM) in the raw water during the disinfection process and generate disinfection by-products (DBPs) (Rook, 2002). Since the 1970s, DBPs have been discovered by scientists for the first time and they have posed a threat to human health (Karanfil et al., 2008). Zoeteman et al. had conducted a statistical analysis displaying a positive correlation between chlorinated DBPs and gastric and esophageal cancer for males (Zoeteman et al., 1982). In the past fifty years, many experts and scholars have conducted extensive and in-depth research on the regulated DBPs (iodotrihalomethanes and haloacetic acids) of chlorination and chloramination disinfection, such as the formation mechanism, control strategy, toxicity, etc (Richardson et al., 2007). However, stronger cytotoxicity and genotoxicity lead to the emerging iodinated DBPs (I-DBPs) attracting special attention than the chlorinated and brominated analogas from the social and scientific fields (Criquet et al., 2012; Karanfil et al., 2008; Plewa et al., 2004, 2008, 2010). In addition, it has been reported that the odor threshold of the I-DBPs are very low, ranging from 0.03 to 8.9 μg/L, of which iodoform (CHI$_3$) has the lowest odor threshold of 0.03 μg/L (Cancho et al., 2001; Criquet et al., 2012). Besides, medicinal and chemical pungent odors produced by them will also greatly cause sensory discomfort to public (Hansson et al., 1987).

The intrusion of seawater in some coastal cities in winter and spring when river water level was below sea level, and the use of seawater to flush toilets in the cities lacking water will directly cause a significant increase in the concentration of iodide ions in the waters (Gong and Zhang, 2015). As environmental condition changes, such as pH, the species of iodine will undergo a series of changes Eqs. (11)–(19). Therefore, drinking water or sewage treatment plants in coastal cities that use chlorine or chloramine as disinfectants will face a great danger of exceeding the limit value of I-DBPs. Based on previous researches, the formation of I-DBPs can be attributed to the oxidiation of the iodine species, including iodide (I$^-$), iodate (IO$_3^-$), and iodide organics in water by disinfectants (Bichsel and von Gunten, 1999; Xia et al., 2017) to produce hypoiodic acid (HOI), which can oxidize NOM to generate I-

THMs (Bichsel and von Gunten, 2000). Inorganic chloramines are highly efficient oxidants due to their high redox potential, which can oxidize a variety of substances (Kinani et al., 2012). According to previous reports, in the water treatment process, chlorine and chloramine can oxidize I$^-$ in water to HOI. During chlorination, the more reactive HOI can continue to be oxidized to the stabler IO$_3^-$, while during chloramination with less oxidizing ability will just oxidize I$^-$ to HOI (Hua and Reckhow, 2006), which will lead to more I-THM yield. Therefore, the chloramination process will produce more I-DBPs, but the influence of NOM concentration and reactivity still cannot be ignored (Bichsel and von Gunten, 2000).

It is worth noting that during the preparation of monochloramine (NH$_2$Cl), dichloramine (NHCl$_2$) and trichloramine (NCl$_3$) will be produced as by-products and coexist with NHCl$_2$ in the system (Boudenne et al., 2021; Kinani et al., 2012). Meanwhile, hypochlorous acid (HOCl) can react with ammonia in water to form chloramines, including NH$_2$Cl, NHCl$_2$, and NCl$_3$ (Ibanez et al., 2008). The formation mechanisms of the three chloramines can be expressed in the following reactions Eqs. (22), (25) and (28) (Deborde and von Gunten, 2008; Péter et al., 2019; Qiang Adams, 2004). Therefore, in the disinfection process with chlorine and NH$_2$Cl, it is inevitable that NHCl$_2$ and NCl$_3$ will appear simultaneously (Kinani et al., 2012). In addition, NHCl$_2$ and NCl$_3$ also have pungent odors with threshold of 0.15 and 0.02 mg-Cl$_2$/L, respectively, (Heeb et al., 2017). The distribution of chloramine species will be affected by solution pH and the molar ratio of chlorine (Cl) to nitrogen (N) (Cl/N ratio) (Scully et al., 2002), the main types of chloramines will be different. When it comes to pH, acidic condition is suitable for the formation of NHCl$_2$ (pH 4-6) and NCl$_3$ (pH<4.4), while the optimum pH for NH$_2$Cl formation is in the range of 7.5-9.0 (Heeb et al., 2017; Shang et al., 1999; Valentine and Jafvert, 1988). On the other hand, Cl/N ratio also affects the distribution and transformation of chloramines (Jafvert and Valentine, 1992), for instance, the larger the Cl/N ratio, the more it can strengthen the oxidation of ammonia in the water (Vikesland and Jafvert, 2001). According to the results of a previous study, when the mass ratio of Cl/N range changes from 3.0:1 to 5.0:1, it is suitable to the formation of NH$_2$Cl. An increase of the Cl/N mass ratio to 5.0:1-7.6:1 is the better range of NHCl$_2$, and further increase of the ratio will significantly increase the amount of NCl$_3$ (Kinani et al., 2012).

However, there are rare reports regarding the derivatization of I-THMs from NHCl$_2$. In order to fill the knowledge gaps, further research with a systematic comparison of the generation and speciation of I-THMs during three above-mentioned chlor (am) ine processes is required. Therefore, the primary purpose of this study was to compare I-THM formation in the chlorination, monochloramination, and dichloramination processes at acidic, neutral and alkaline pH values and systematically explore the influence of key parameters including dissolved organic carbon (DOC) concentration and

Br$^-$/I$^-$ molar ratio in the dichloramination. In addition, we also conducted experiment in real water and detect the changes of the three-dimensional fluorescence characteristics. The experimental results can provide a reference for the mechanism of generating I-THMs when iodine-containing water is disinfected with chlor (am) ine in the actual operation of water treatment plants, so as to control the water quality safety risks in engineering applications.

1. Materials and methods

1.1. Materials and reagents

All reagents used in the experiment are of analytical grade or above unless otherwise specified. Iodotrihalomethane standards (≥99.0%), including dichloroiodomethane (CHCl$_2$I), dibromoiodomethane (CHBr$_2$I), chlorodiiodomethane (CHClI$_2$), bromodiiodomethane (CHBrI$_2$), chlorobromoiodomethane (CHClBrI) and triiodomethane (CHI$_3$) were all obtained from J&K Scientific, (Shanghai, China). And ascorbic acid (≥99.0%) were purchased from Aladdin (Shanghai, China). Ammonium chloride (NH$_4$Cl, ≥99.0%), potassium bromide (KBr, ≥99.5%), potassium iodide (KI, ≥99.0%), humic acid (HA), sodium hypochlorite (NaOCl) with available chlorine of 4.00%-4.99% and sodium hydroxide (NaOH, ≥99.0%) were all purchased from Sigma-Aldrich. Methyl tert-butylether (MtBE) was supplied by J.T. Baker (USA). Phosphoric acid (H$_3$PO$_4$≥99.0%) and sulfuric acid (H$_2$SO$_4$) reaching the purity level >98.0% were supplied by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Real water filtered by 0.22 μm cellulose acetate filter membrane, was sampled from the artificial lake, Sanhaowu, Tongji University, Shanghai, China. The real and filter water parameters were shown in Appendix A Table S1. And the ultrapure water used in this study was prepared by an Milli-Q water purification apparatus (Millipore, USA).

1.2. Experimental procedures

NaOCl solution (5 mg/L Cl$_2$) was freshly prepared by diluting the NaOCl standard solution. The monochloramine (NH$_2$Cl) stock solution was obtained through adding NaOCl into the NH$_4$Cl solution drop by drop at the molar Cl/N ratio of 0.8 with vigorous stirring at a pH greater than 8.5 controlled by NaOH (Liu et al., 2020; Zhang et al., 2016). After the dropwise addition of NaOCl was finished, the stirring speed was reduced, and continued for one hour and the prepared NH$_2$Cl solution was used within 4 hr (Xu et al., 2012). The preparation process of NHCl$_2$ was the same as that for the preparation of NH$_2$Cl, but increased the Cl/N molar ratio to 1:1.03 and lowered pH at 3.7 (±0.02) with H$_3$PO$_4$, then kept stirring for 1 hr (Yin et al., 2020). The I-THM formation experiments were carried out immediately after the solution was prepared. The pH values of water samples were pre-adjusted with 5 mmol/L phosphate buffer and H$_2$SO$_4$ or NaOH, then I$^-$ (5 μmol/L) were added, and finally NaOCl, NH$_2$Cl, and NHCl$_2$ stock solutions were dosed, respectively. During the experiment, the pH values of samples can be stabilized within ±0.2. The mixed solution was stirred and

mixed well for 3 at 150 r/min. For the experiments with other influencing factors, such as DOC concentration and Br$^-$/I$^-$ molar ratio, the corresponding experimental conditions were pre-adjusted, and then the pre-prepared NHCl$_2$ solution was added.

The I-THM formation experiments were conducted in duplicate in 40 mL amber glass vials under headspace-free condition. Then these vials were put in a constant temperature incubator (temperature 25 ± 1 °C) for 3 days. Finally, the chlorine was quenched with ascorbic acid (Moore et al., 2021) with concentration 20% excess of the chlorine dose. The samples were immediately extracted with MtBE to prevent volatilization and loss of I-THMs and analyzed by a gas chromatograph (GC).

1.3. Analytical methods

The pH of the solution was measured with a pH meter (FE20-FiveEasy, Mettler Toledo, Switzerland), and the deviation was within 99%±0.2%, calibrated with standard solution (pH = 4.01, 7.00, 9.21, Mettler Toledo, USA) before each experiment. The DOC concentration is detected by a TOC-VCSH analyzer (Shimadzu, Japan), including HA solution and real water. UV$_{254}$ was detected by a UV spectrophotometer (UNICO SQ-4802, China). The determination of the fluorescence spectrum was using the HORBA Fluorometer. NaOCl standard solution was calibrated with the DPD (N,N-diethyl-p-phenylenediamine) method. I$^-$ and IO$_3^-$ were measured by an ion chromatography (Dionex Aquion, ICS-2000) coupled with an anion analysis column (Dionex, AS19) using potassium hydroxide (30 mmol/L) as the eluent with the flow rate of 1 mL/min and detector current of 75 mA. NH$_2$Cl concentration was measured with the MonochlorF method (Lee and Westerhoff, 2009) through 5 min of reaction in the dark. The absorbance was detected by an ultraviolet spectrophotometer, and then the concentration of NH$_2$Cl was calculated using a predetermined standard curve (Appendix A Fig. S1) which accurately quantified NH$_2$Cl instead of NHCl$_2$ and organic chloramines. Because the absorbance at 665 nm of green indophenol produced by the reaction of NH$_2$Cl with phenol or substituted phenol has a linear relationship with the concentration of NH$_2$Cl (Lee et al., 2007). When the pH is less than 4, NHCl$_2$ can exist stably and occupy an absolute dominant position (Kinani et al., 2012) and the total chlorine was also accurately measured by the DPD method. The concentration of NHCl$_2$ is the difference between the total chlorine and the concentration of NH$_2$Cl obtained by the MonochlorF method (Lee and Westerhoff, 2009) method. It can be concluded that the ratio of dichloramine exceeds 95%.

The concentration of I-THMs was quantified by a Shimadzu gas chromatography (GC-2010) equipped with an electron capture detector (ECD) (Kyoto, Japan) according to the USEPA Method 551.1. A FluoroMax-4 fluorescence spectrophotometer (Horiba Jobin Yvon, Edison, NJ, USA) was used to measure the fluorescence spectrum of DOM. The excitation (Ex) and the emission (Em) wavelength range are set to 200-550 nm with an interval of 5 nm.
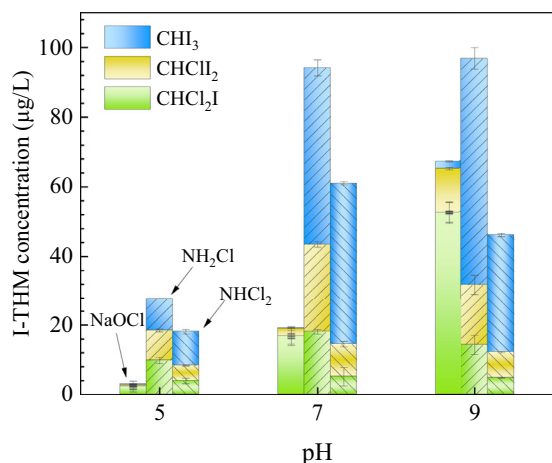
Fig. 1 – Comparison of I-THMs formation and speciation during chlorination (NaOCl), monochloramination (NH₂Cl), and dichloroamination (NHCl₂) at different initial pH values in HA solutions. Conditions: initial [I⁻] = 5 μmol/L, [NaOCl] = 5 mg-Cl₂/L, [NH₂Cl] = 5 mg-Cl₂/L, [NHCl₂] = 5 mg-Cl₂/L, [DOC] = 5 mg-C/L, reaction time = 72 hr, and temperature = 25 ± 1 °C.

2.   Results and discussion

2.1.   Comparison of I-THM formation and speciation during chlorination, monochloramination and dichloramination at different initial pH values

The I-THM formation and speciation during chlorination, monochloramination and dichloramination processes at different initial pH values (5–9) are displayed in Fig. 1. According to a previous study, both the distribution of iodine and the reaction with NOM are related to pH (Warner et al., 2000). The distribution of inorganic chloramines, including NH_2Cl, $NHCl_2$ and NCl_3, depends largely on the pH parameter (NH_2Cl prefers alkaline condition, $NHCl_2$ prefers acidic condition), three representative pH values of 5, 7 and 9 were selected as the experimental pH background parameter. With the increase of pH from 5 to 9, the I-THM yield surged from 2.91 to 67.28 μg/L during chlorination. And the main substances of chlorine and iodine in the system changed. I^- was oxidized to HOI and HOCl hydrolyzed to ClO^-. The pKa values of HOCl and HOI are 7.54 and 10.40, respectively (Von Gunten and Bichsel, 2000). Therefore, during chlorine process, the dominant species are HOCl and HOI at acidic and neutral conditions, while at alkaline conditions, the dominant species become OCl^- and HOI. Therefore, at pH 7, sufficient chlorine can oxidize I^- to form HOI, which is a reactive iodine species, and then can incorporate with NOM to produce I-THMs with $CHCl_2I$ as the main product (88.08%), followed by $CHClI_2$ and CHI_3. However, excessive HOCl can further oxidize HOI to IO_2^- according to Eq. (4), or even IO_3^- according to Eq. (9) (as shown in Table 1) (Ye et al., 2013), resulting in a decrease of reactive iodine species concentration and therefore the concentration of I-THMs displayed a reduction. In particular, at pH 5, this property of HOCl is more prominent so that I-THMs generated

reduced to the minimum. As pH increased to 9, I-THM yield raised rapidly to the maximum of 67.28 μg/L, mainly because HOI can still exist stably in the range of pH less than 10.40 and which further promote the reaction of HOI with NOM in HA.

The trend of increasing I-THM generation with increasing pH during monochloramination, from 27.75 μg/L (pH 5) to 96.87 μg/L (pH 9), is similar to that of chlorination, but the distribution of I-THM species was significantly different, which was also reported in a previous study (Liu et al., 2017). Based on the pH-dependant stability of inorganic chloramine, at pH ≥ 8.5, the dominant species of chloramine is NH_2Cl (Kinani et al., 2012). Therefore, the highest generation of I-THMs can be explained by that NH_2Cl oxidized I^- to form the reactive HOI, while not the stable IO_2^- or IO_3^-.

It is notable that dichloramination is significantly different from the above-mentioned free chlorine and NH_2Cl processes in the aspects of formation and speciation. At proper Cl/N mass ratio (5.0:1-7.6:1), acidic pH is favorable for the formation and stability of $NHCl_2$ (Kinani et al., 2012). With the increase of pH (from 5 to 9), as the initial total chlorine dosage was kept at 5 mg-Cl₂/L, the amount of I-THMs significantly increased from 18.07 μg/L to the maximum of 61.04 μg/L at pH 7, while a slightly decrease to 45.99 μg/L at pH 9. This phenomenon could be explained as that based on the strong oxidizing properties of $NHCl_2$, I^- could be oxidized to HOI and further to IO_3^-, according to Appendix A Fig. S2. This process was affected by both the oxidative reactivity of $NHCl_2$ and the stability of HOI (pKa = 10.40). At acidic conditions, $NHCl_2$ exists stably, but HOI will self-disproportionate reaction to form I^- and IO_3^- (Lengyel et al., 1993; Liu et al., 2014; Zhao et al., 2016), according to Eq. (20). While at neutral and alkaline conditions, $NHCl_2$ will hydrolyze and transform into other chlorine species, such as NH_2Cl (Jafvert and Valentin, 1987) and HOCl (Eq. (26)). Moreover, with the further increase of pH, byproducts such as N_2 will be produced (Eq. (27)), which will further reduce the concentration of available chloramines and the production of I-THMs. It could also be observed that during monochloramination and dichloramination processes at pH 5-9, the yield of I-THMs species both decreased in the order of $CHI_3 > CHClI_2 > CHCl_2I$ (Fig. 1). CHI_3 continuously occupied the position of the most abundant product, and this superiority was more prominent when the total quantity of I-THMs reached the maximum (pH 7), accounting for 76.23%. This phenomenon has the consistency of the results in a previous study that when chloramine was used as an oxidant to react with iodine, CHI_3 accounted for about 80% of the total yield of I-THM (Bougeard et al., 2010).

From the other side of the comparison, at the condition of pH 5, the order of I-THMs yield was $NH_2Cl > NHCl_2 > HOCl$. However, at pH 7, the monochloramination process produced the most I-THMs, but the I-THMs produced by the dichloramination process significantly surpassed the chlorination process, which could be attributed to the strong oxidizing property of $NHCl_2$ and the higher activity of reacting with I^-. At higher pH (pH 9), the phenomenon had reached a turning point that the total amount of I-THMs produced by the dichloramination process was lower than that of the chlorination process, while the yield of the chloramination process still ranked first, with dominant product CHI_3 and $CHCl_2I$, respectively. Therefore, the experimental results clarify that under

Table 1 – Possible reactions of inorganic chloramine and iodine/bromine substances at temperature 25 ± 2°C.

No.	Reaction	Rate constant ($(\text{mol/L})^{-1}\,\text{sec}^{-1}$)	Refs.
1	$H^+ + OCl^- \rightarrow HOCl$	5.00×10^{10}	Liu et al. (2017)
2	$HOCl \rightarrow H^+ + OCl^-$	1.20×10^3	Liu et al. (2017)
3	$HOCl + I^- \rightarrow HOI + Cl^-$	4.30×10^8	Bichsel and von Gunten (1999)
4	$HOCl + HOI \rightarrow IO_2^- + Cl^- + 2H^+$	8.20	Bichsel and von Gunten (1999)
5	$OCl^- + HOI \rightarrow IO_2^- + Cl^- + H^+$	52.0	Bichsel and von Gunten (1999)
6	$H^+ + OI^- \rightarrow HOI$	5.00×10^{10}	Wang et al. (2020)
7	$HOI \rightarrow H^+ + OI^-$	1.99	Wang et al. (2020)
8	$HOI + OI^- \rightarrow IO_2^- + I^-$	3.00×10^{-1}	Bichsel and von Gunten (1999)
9	$HOCl + IO_2^- \rightarrow IO_3^- + Cl^- + H^+$	1.00×10^6	Chen et al. (2020)
10	$OCl^- + IO_2^- \rightarrow IO_3^- + Cl^-$	1.00×10^6	Bichsel and von Gunten (1999)
11	$HOI + I^- \rightarrow I_2OH^-$	5.00×10^9	Jones et al. (2012)
12	$I_2OH^- \rightarrow I_2 + OH^-$	6.90×10^5	Lengyel et al. (1993)
13	$I_2 + OH^- \rightarrow I_2OH^-$	8.00×10^8	Lengyel et al. (1993)
14	$I_2 + I^- \rightarrow I_3^-$	6.20×10^9	Lengyel et al. (1993)
15	$I_3^- \rightarrow I_2 + I^-$	8.50×10^6	Liu et al. (2017)
16	$I_2OH^- + H^+ \rightarrow I_2 + H_2O$	2.20×10^{10}	Lengyel et al. (1993)
17	$I_2OH^- + H^+ \rightarrow HOI + I^-$	1.30×10^6	Lengyel et al. (1993)
18	$HOI + I^- + H^+ \rightarrow I_2 + H_2O$	3.67×10^9	Wang et al. (2020)
19	$I_2 + H_2O \rightarrow HOI + I^- + H^+$	5.52×10^{-2}	Lengyel et al. (1993)
20	$3HOI \rightarrow IO_3^- + 2I^- + 3H^+$	6.00×10^{-11}	Lengyel et al. (1993)
21	$NH_2Cl + H_2O \rightarrow HOCl + NH_3$	2.10×10^{-5}	Liu et al. (2017)
22	$HOCl + NH_3 \rightarrow NH_2Cl + H_2O$	4.20×10^6	Qiang et al. (2004)
23	$NH_2Cl + NH_2Cl \rightarrow NHCl_2 + NH_3$	7.00×10^{-4}	Jafvert et al. (1992)
24	$NHCl_2 + NH_3 \rightarrow NH_2Cl + NH_2Cl$	6.00×10^4	Hand and Margerum (1983)
25	$NH_2Cl + HOCl \rightarrow NHCl_2 + H_2O$	3.50×10^2	Qiang et al. (2004)
26	$NHCl_2 + H_2O \rightarrow NH_2Cl + HOCl$	6.38×10^{-7}	Jafvert and Valentine (1992)
27	$NH_2Cl + NHCl_2 \rightarrow 3HCl + N_2$	1.52×10^{-2}	Liu et al. (2017)
28	$NHCl_2 + HOCl \rightarrow NCl_3 + 2H_2O$	N.A.	Qiang et al. (2004)
29	$I^a + NHCl_2 \rightarrow HOCl + N_2 + HCl$	2.78×10^4	Liu et al. (2014)
30	$HOBr + I^- \rightarrow HOI + Br^-$	5.00×10^9	Criquet et al. (2012)
31	$NH_2Cl + I^- \rightarrow HOI + I^a$	$2.40 \times 10^{10} \times [H^+]M^{-1}$	Bichsel and von Gunten (1999)

I^a: Unidentified intermediate product.
N.A.: Not available.

circumneutral pH, special attention required to be paid on the disinfection process when iodine-containing water is disinfected with chloramine which contains NH_2Cl and $NHCl_2$ produced by hydrolysis conversion, Eqs. (23) and (27).

2.2. Key factors of I-THM formation during dichloramination process

2.2.1. Effect of DOC concentration on I-THM formation and speciation

The concentration of organic matter in natural waters which ranges from 0.1 to 20 mg/L varies with water pollution and geographic locations (Volk et al., 2002). Few current researches have explored the I-THM formation and related influencing factors during the dichloramination process. Therefore, the DOC concentration of 1 to 7 mg-C/L was selected to explore its effect on I-THM production under dichloramination process, and the results are displayed in Fig. 2. The total yield of I-THMs increased and reached the maximum of 34.74 µg/L as the DOC concentration increased from 1 to 3 mg-C/L. Since sufficient $NHCl_2$ in the solution can react with I^- to produce HOI which has stronger oxidizing ability than HOCl and further lead to the incorporation with NOM to generate I-THMs with CHI_3 as dominant product. However, when further increased the DOC concentration from 5 to 7 mg-C/L, the forma-
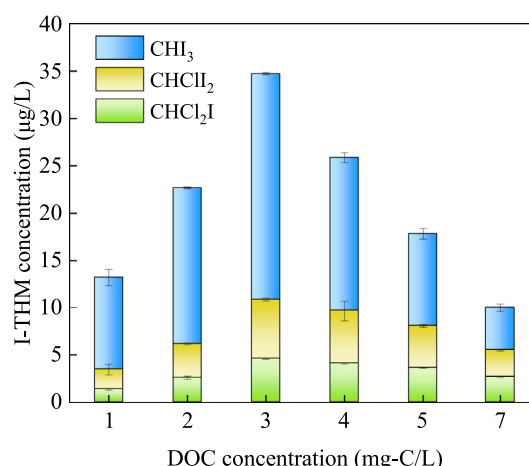

Fig. 2 – Effect of DOC concentration on the formation and speciation of I-THMs in HA solutions. Conditions: initial $[I^-]$ = 5 µmol/L, $[NHCl_2]$ = 5 mg-Cl_2/L, [DOC] = 5 mg-C/L, pH = 5, reaction time = 72 hr, and temperature = 25 ± 1 °C.

tion of I-THMs gradually decreased. Initially, sufficient NOM interacted with $NHCl_2$ so that caused rapid consumption of $NHCl_2$, as displayed in Appendix A Fig. S3. Considering hydrol-
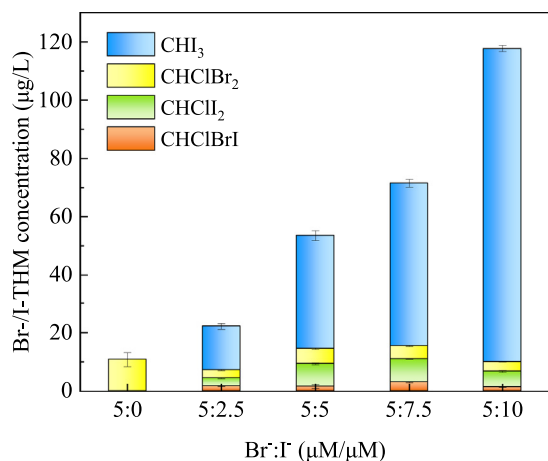
Fig. 3 – Effect of bromide to iodide ratio on the formation and speciation of I-THMs in HA solutions. Conditions: initial [I⁻] = 0-10 μmol/L, [Br⁻] = 5 μmol/L, [NHCl₂] = 5 mg-Cl₂/L, [DOC] = 5 mg-C/L, pH = 5, reaction time = 72 hr, and temperature = 25 ± 1 °C.

Fig. 4 – Comparison of I-THM formation and speciation during NaOCl, NH₂Cl, and NHCl₂ at different initial pH values in raw water. Conditions: initial [I⁻] = 5 μmol/L, [NaOCl] = 5 mg-Cl₂/L, [NH₂Cl] = 5 mg-Cl₂/L, [NHCl₂] = 5 mg-Cl₂/L, [DOC] = 5.57 mg-C/L, reaction time = 72 hr, and temperature = 25 ± 1 °C.

ysis of NH₂Cl in the case of coexistence with NOM (Duirk et al., 2005), it could be speculated that NHCl₂ might also undergo hydrolysis to produce HOCl at neutral pH according to Eq. (26) (Duirk et al., 2002), which could quickly oxidize I⁻ into HOI, and then oxidize it to IO₃⁻, thereby reduced the I-THM formation (Bichsel and von Gunten, 1999). On the other hand, as the reaction proceeds, the macromolecular substances in NOM are oxidized and converted into other micromolecular substances, resulting in a decrease in the precursor of I-THMs, thus limiting the generation of I-THMs. In short, the content of HOI and NOM both decreased, so the production of I-THMs showed a decline. In practical situation, DOC concentration in drinking water sources is usually below 3.5 mg-C/L (the average value of DOC of in a reservoir in Beijing is 2.61 mg-C/L (Chen et al., 2020)). Therefore, when the amount of iodine and iodides in real water increase in the case of seawater inversion, etc. and NH₂Cl is used as the disinfectant, inorganic chloramines will undergo interconversion as pH changes, resulting of a great risk of excessive I-THMs.

2.2.2. Effect of bromide on I-THM formation and speciation

Bromide (Br⁻) is one of the common ions in water in coastal areas suffering seawater inversion, with the concentration ranging from 0.4 to 1120 μg/L in some areas of China (Xia et al., 2017) and 24 to 1120 μg/L in some cities of the USA and Canada (Yang and Zhang, 2013). Moreover, Br⁻ and I⁻ often appear in drinking water sources at the same time in seawater intrusion season. The interaction between Br⁻ and I⁻ has been extensively studied by other scholars (Bougeard et al., 2010), but in the information regarding the oxidation of Br⁻ and I⁻ by NHCl₂ and the potential for the generation of Br-/I-THMs has not been reported. This study selected five representative Br⁻ to iodide molar ratio (Br/I = 5:0, 5:2.5, 5:5, 5:7.5, 5:10) to conduct experiments to explore their effect on the generation of I-THMs. The results are displayed in Fig. 3. When the Br/I molar ratio was 5:0, only a brominated THM (CHClBr₂) was generated, which might be due to that similar to the ionization of
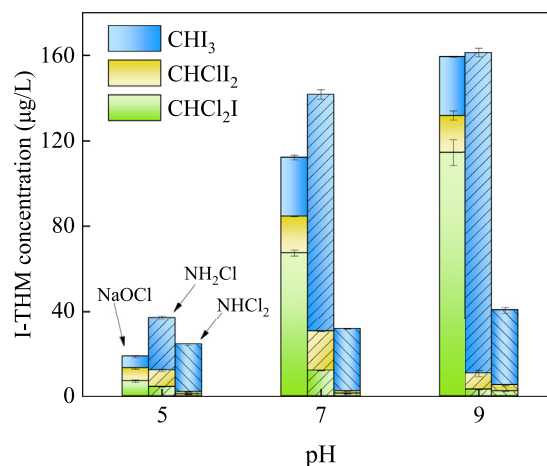
NH₂Cl (Xia et al., 2017), bromine replaced chlorine in NHCl₂ to produce NHClBr and NHBr₂. At the same time, NHClBr and NHBr₂ underwent hydrolysis and substitution reactions to generate hydrobromic acid (HOBr). Finally, NHClBr, NHBr₂ and HOBr reacted with NOM to generate brominated THMs (Jones et al., 2012). With the addition of I⁻, CHClI₂, CHClBrI, and CHI₃ were also produced and the amount of CHClBr₂ decreased sharply. In addition, the organic bromine amines will also promote the brominated I-THM production (Wang et al., 2020; How et al., 2017). This phenomenon indicated that sufficient iodine source reacted more efficiently than bromide with NHCl₂ to generate HOI instead of HOBr, and HOI was more likely to react with THM precursor in HA to generate I-THMs. According to a report, iodide has a lower oxidation-reduction potential 1.33 V than so that it is more likely to be oxidized by NHCl₂ than chloride (2.41 V) and bromide (1.62 V) (Huie et al., 1991). Based on a previous research (Criquet et al., 2012), NHCl₂ can oxidize Br⁻ and I⁻ to HOBr and HOI, respectively, and HOBr can also convert I⁻ to HOI, Eq. (30). As the I⁻ concentration gradually increased, the conversion of HOBr to HOI could also lead to a decrease in the production of CHClBr₂.

It is worth noting that as the molar ratio of I⁻ continued to increase, the Br-/I-THM product held a more dominant advantage than the Cl-THMs product. This observation indicates that bromine has a stronger reactivity and faster reaction rate with I-THM precursor in HA than chlorine, which can be further confirmed that bromine compared to chlorine is a better electrophilic substitution addition agent (Allard et al., 2015; Heeb et al., 2014; Olbregts, 1974).

Besides, CHI₃ was the predominant product in the formed I-THMs (Fig. 3). It could be explained by two reasons. The first reason was that sufficient I⁻ were oxidized by NHCl₂ to form HOI which is an important component that reacts with NOM to generate I-THMs. Another reason is that HOI produced by the reaction of NHCl₂ and I⁻ had a longer half-life (Dong et al., 2019), and could fully undergo substitution reaction with
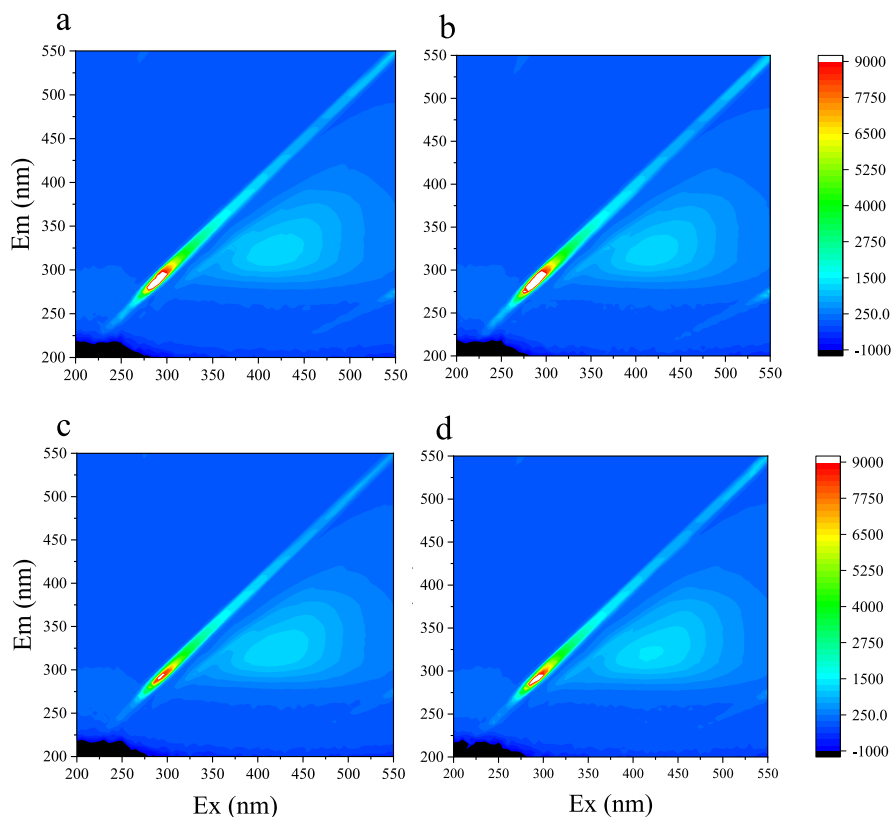
Fig. 5 – Three-dimensional fluorescence characterization of organic components of the raw water during (a) NaOCl, (b) NH₂Cl, (c) NHCl₂ and (d) blank. Conditions: initial [I⁻] = 5 µmol/L, [NaOCl] = 5 mg-Cl₂/L, [NH₂Cl] = 5 mg-Cl₂/L, [NHCl₂] = 5 mg-Cl₂/L, [DOC] = 5.57 mg-C/L, pH = 9, reaction time = 72 hr, and temperature = 25 ± 1 °C.

THM precursor in HA. Therefore, as the proportion of I⁻ increased from 5:7.5 to 5:10, the mono- and di-substituted I-THMs were further transformed into tri-substituted I-THMs.

2.3. I-THM formation in real water samples

2.3.1. I-THM formation and speciation in real water during chlorination, monochloramination and dichloramination at different initial pH values

In order to investigate the I-THM generation and distribution mechanism in natural water, chlorine, NH₂Cl, and NHCl₂ processes were also conducted at pH 5-9. As shown in Fig. 4, during chlorination and monochloramination, the increase of pH led to the increase of I-THMs with CHCl₂I and CHI₃ as the dominant product, respectively. And the maximum reached 159.41 µg/L and 161.29 µg/L, respectively. While the increase of pH only caused slightly increase of I-THM formation during dichloramination, the maximum of 40.44 µg/L at pH 9, which can be explained by the oxidization of I⁻ to stable IO₃⁻ by NHCl₂ to reduce the production of I-THMs.

Compared with the I-THM formation of HA, the real water used in the experiment presented a greater risk, especially under chlorination condition. The main influencing factors can be credited to SUVA₂₅₄ defined as the ratio of UV₂₅₄ absorbance value to DOC value and is often used as a surrogate of the aromatic content in NOM in water (Deborde and von

Gunten, 2008). It has been reported that NOM with a lower SUVA₂₅₄ (lower aromaticity) has less active sites to react with HOCl (Allard et al., 2015), but due to the stronger selectivity and reactivity of HOI with THM precursors than HOCl, so more I-THMs will be produced (Allard et al., 2015; Lee et al., 2005). But for dichloramination process, although the water formulated with HA has a higher SUVA₂₅₄ of 7.82 L/mg-m than that of real water 2.84 L/mg-m (Appendix A Table S1), NHCl₂ has stronger oxidizing and reactivity to compete with HOI to preemptively react with THM precursors in real water, resulting in a smaller amount of I-THMs yield than HA. For the distribution of I-THMs which was consistent with the previous Section 2.1, the experimental results in the case of real water showed that CHI₃ was still the dominant product during monochloramination and dichloramination.

In the case of filter water (Appendix A Fig. S4), the generation of I-DBPs increased and reached the maximum of 1075.01 ng/L and 2412.90 ng/L, respectively, and CHI₃ was still the dominant product during monochloramination and dichloramination. But the difference from the case of real water is that more CHBrI₂ was produced which can be attributed to higher Br⁻ concentration in the filter water (Appendix A Table S1). And the increase of pH did not significantly affect the yield of I-DBPs in the dichloramination process, which reached the maximum of 713.23 ng/L at pH 7. Compared with the I-THM formation of HA and the real water used in the experiment, it is obvious that the filter water produced less I-

DBPs after disinfection, which is mainly because the DOC concentration of the filter water (2.30 mg-C/L) is lower than that of HA and the real water so that the content of I-DBPs precursors provided is also less.

2.3.2.   Three-dimensional fluorescence characterization of organic components in real water during chlorination, monochloramination and dichloramination

Dissolved organic matter (DOM) usually considered as the main precursor of DBPs in the disinfection process and is highly heterogeneous. Three-dimensional fluorescence spectroscopy, also known as excited emission spectroscopy matrix (EEM), is a new type of spectroscopy technique used in recent years to explore the characteristics of DOM. The analytical results of the real water during chlorine, NH_2Cl, and $NHCl_2$ processes as well as dark control are shown in Fig. 5.

In order to compare and highlight the effects of different oxide species on water quality components and thereby affect the production of I-THMs, the condition of pH 9 was selected for discussion. In general, three-dimensional fluorescence spectra can be divided into 5 regions: the region (I and II) corresponding to the simple structure of aromatic proteins is the area with wavelength less than 250 nm and emission light wavelength below 380 nm; when excitation wavelengths below 250 nm and emission wavelengths more than 380 nm, the region is correspond to fulvic acid-like (III); the excitation wavelength of 250–280 nm is the region correspond to soluble microbial by-product samples (IV) and emission wavelengths greater than 380 nm correspond to humic acid-like (V).

It can be clearly observed from Fig. 5 that the real water contains almost no protein and soluble microbial metabolites, and the main components are humic acid-like and fulvic acid-like substances. After chlorination (Fig. 5a), monochloramination (Fig. 5b), and dichloramination (Fig. 5c), the fluorescence intensity of humic acid-like and fulvic acid-like are enhanced. In particular, the effect of $NHCl_2$ is more obvious. The reason may be that certain oxidation activated substances with strong fluorescence intensity or oxidized macromolecular organic substances were transformed into certain substances with high fluorescence response, which could become the precursors of I-THMs, resulting of the formation of I-THMs. However, during dichloramination process (Fig. 5c), the amount of I-THMs produced was negatively correlated with the enhance in fluorescence intensity, which could be attributed to the oxidization of I^- to stable IO_3^- by $NHCl_2$. This reminds us that the interaction mechanism between $NHCl_2$ and DOM in other conditions requires further research.

3.   Conclusions

Chlorination, monochloramination and dichloramination of iodine-containing water can lead to the formation of I-THMs, and chlorination and dichloramination produces a smaller amount of I-THMs than monochloramination. As the pH increased from 5 to 9, the I-THMs produced in the chlorination and monochloramination processes increased accordingly, but during the dichloramination process, the maximum happened at pH 7. The formation of I-THMs displayed a trend which is first increasing and then decreasing, reaching the maximum at 3 mg/L of DOC. The presence of bromine will increase the formation of Br-THMs, but iodoform is still the product with the largest proportion. At real water condition with lowe $SUVA_{254}$ value, the I-THMs produced by NaOCl and NH_2Cl as oxidants are both increased, but the dichloramination process results in significant I-THMs decline at neutral (pH 7) and alkaline (pH 9) conditions, which is relevant to the humic acid-like and fulvic acid-like groups detected by the three-dimensional fluorescence in the real water. In conclusion, this study systematically compared and explored the formation and speciation of I-THMs during chlorination, monochloramination and dichloramination, and the effects of influencing parameters on the products of iodine-containing water. In addition, further research about the effect of $NHCl_2$ on DBPs based on other conditions, such as aromatic and high-nitrogen water, is also required.

Appendix A Supplementary data

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jes.2022.05.011.

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