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Formation and speciation of haloacetamides and haloacetonitriles for chlorination, chloramination, and chlorination followed by chloramination

Huang Huang [a, b, c, *], Bo-Yi Chen [a], Zi-Ru Zhu [a]

[a] School of Environmental Science and Engineering, Sun Yat-sen University, Guangzhou, 510275, Guangdong, PR China
[b] Guangdong Provincial Key Laboratory of Environmental Pollution Control and Remediation Technology, Guangzhou, 510275, Guangdong, PR China
[c] Research Institute of Sun Yat-sen University in Shenzhen, Shenzhen, 518057, Guangdong, PR China

HIGHLIGHTS

- The Cl_2–NH_2Cl process formed more haloacetamides (HAcAms) and haloacetonitriles (HANs) than the Cl_2 and NH_2Cl processes.
- Bromine substitution factors (BSFs) of dihaloacetamides (DHAcAms) were higher than those of dihaloacetonitriles (DHANs).
- The order for the BSFs of DHAcAms and DHANs from highest to lowest was: Cl_2 process, Cl_2–NH_2Cl process, and NH_2Cl process.
- The Cl_2+NH_3 process formed more disinfection by-products than the NH_3+Cl_2 process for in situ chloramination.

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ABSTRACT

The formation of haloacetamides (HAcAms) and haloacetonitriles (HANs) from a solution containing natural organic matter and a secondary effluent sample was evaluated for disinfection by chlorination, chloramination, and chlorination followed by chloramination (Cl_2–NH_2Cl process). The use of preformed monochloramine (NH_2Cl) produced higher concentrations of HAcAms and lower concentrations of HANs than chlorination, while the Cl_2–NH_2Cl process produced the highest concentrations of HAcAms and HANs. These results indicate that the Cl_2–NH_2Cl process, which inhibited the formation of regulated trihalomethanes compared with chlorination, enhanced the formation of HAcAms and HANs. For disinfection in the presence of bromide, brominated dihaloacetamides and dihaloacetonitriles were formed, and the trends were similar to those observed for chlorinated species in the absence of bromide. The degrees of bromine substitution of dihaloacetamides and dihaloacetonitriles were highest for chlorination, followed by the Cl_2–NH_2Cl process and then by the NH_2Cl process. For the Cl_2–NH_2Cl process, HAN formation kept gradually increasing with prechlorination time increasing from 0 to 120 min, while HAcAm formation increased only until it reached a maximum at around 10–30 min. These results suggest that the prechlorination time could be reduced to control the formation of HAcAms and HANs. During chloramination, the formation of HAcAms and HANs was lower when using preformed NH_2Cl than when chloramines were formed in situ, with higher formation of HAcAms and HANs when chlorine was added before ammonia than vice versa for the secondary effluent; this finding suggests that preformed NH_2Cl could be used to inhibit the formation of HAcAms and HANs during chloramination.

1. Introduction

Because of water scarcity, water supply systems are increasingly exploiting water sources contaminated by municipal wastewater effluents and implementing reuse of municipal wastewater effluents for industrial and municipal use (Higgins et al., 2002; Westerhoff and Mash, 2002; Sun et al., 2016). Besides natural organic matter (NOM), such source waters contain wastewater effluent organic matter with high dissolved organic nitrogen (DON) concentrations, which is thought to act as an important precursor for nitrogenous disinfection by-products (DBPs) (Huang et al., 2016;

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* Corresponding author. School of Environmental Science and Engineering, Sun Yat-sen University, Guangzhou, 510275, Guangdong, PR China.
E-mail address: huangh46@mail.sysu.edu.cn (H. Huang).

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Hu et al., 2016). Haloacetonitriles (HANs) and haloacetamides (HAcAms) are commonly occurring classes of nitrogenous DBPs, and are of particular concern because they are reportedly more cytotoxic and genotoxic than regulated trihalomethanes (THMs) and haloacetic acids (HAAs) (Muellner et al., 2007; Plewa et al., 2008). Bromide ions are common in natural waters and wastewaters, where they affect the speciation of DBPs and promote the formation of brominated DBPs, which are associated with higher health risks than their chlorinated analogs (Richardson et al., 2007; Heeb et al., 2014). Most brominated HANs and HAcAms are more cytotoxic and genotoxic than their chlorinated analogs (Muellner et al., 2007; Plewa et al., 2008). Therefore, it is important for the water industry to control the formation of nitrogenous DBPs, and especially brominated nitrogenous DBPs, to reduce health risks.

To reduce the concentrations of regulated THMs and HAAs, utilities are increasingly using chloramines rather than chlorine for disinfection. There are some concerns regarding whether this switch could enhance the formation of certain nitrogenous DBPs. Previous research involving the application of chlorine and chloramines at the same doses and contact times to natural waters and secondary effluents showed that chloramination produced lower levels of dichloroacetonitrile (DCAN) but higher levels of dichloroacetamide (DCAcAm) than chlorination (Hayes-Larson and Mitch, 2010; Huang et al., 2012). In the presence of bromide, chloramination can reduce the formation of bromochloroacetonitrile (BCAN), which has been detected in chlorinated natural and treated waters (Bougeard et al., 2010; Tian et al., 2013). Few studies have compared the formation of brominated HAcAms during chlorination and chloramination. Chu et al. (2013) investigated the formation potentials of HAcAms, including brominated species, upon the chlorination and chloramination of several natural waters, and found that the relative importance of chlorination or chloramination for brominated HAcAm formation potential varied among the waters. However, the brominated HAcAm formation during chlorination and chloramination of wastewater effluent organic matter is unclear. Besides, since the formation potential tests involved application of different disinfectant doses for different time periods, there is a lack of comparison of brominated HAcAm formation over time between chlorination and chloramination based on the same disinfectant dose.

In practice, chloramines are mostly prepared in situ by the addition of ammonia and chlorine. One study indicated that chloramines formed in situ produced more DCAN over 1–2 days than produced by preformed monochloramine (NH_2Cl) (Hayes-Larson and Mitch, 2010). However, the influence of different chloramination disinfection schemes on HAcAm formation still needs to be explored.

Chlorination followed by chloramination (Cl_2–NH_2Cl process), which involves prechlorination followed by ammonia addition, is often used for disinfection because the chlorine is effective for bacterial inactivation and chloramines do not produce high concentrations of regulated DBPs (Zhang et al., 2007; Tian et al., 2013). Compared with chlorination in water with a high bromide content, the Cl_2–NH_2Cl process reduces the formation of THMs and HAAs but increases the formation of HANs (Tian et al., 2013). Performing chlorination before chloramination enhances the formation of HAcAms in water from natural sources (Chuang et al., 2015). Therefore, particular attention should be paid to the formation of nitrogenous DBPs in the Cl_2–NH_2Cl process.

The aim of this study was to evaluate the formation and speciation of HAcAms and HANs during chlorination, chloramination, and Cl_2–NH_2Cl process for solutions containing NOM both with and without bromide addition. These disinfection scenarios were also applied to secondary effluent to understand the processes that could occur in effluent-contaminated or reclaimed water. The effect of prechlorination time on the formation of nitrogenous DBPs was examined for the Cl_2–NH_2Cl process. The effects of different chloramination methods, including the use of preformed NH_2Cl or formation of chloramines in situ by addition of chlorine before ammonia addition and vice versa, on nitrogenous DBP formation were also investigated. The formation of THMs, a representative carbonaceous DBP, was measured simultaneously.

2. Materials and methods

2.1. Materials

The following four HAcAms and four HANs were detected in this study: DCAcAm, trichloroacetamide (TCAcAm), bromochloroacetamide (BCAcAm), and dibromacetamide (DBAcAm); DCAN, trichloroacetonitrile (TCAN), BCAN, and dibromoacetonitrile (DBAN). The brominated HAcAms were purchased from Cansyn Chem. Corp. (Toronto, Canada), the other HAcAms were purchased from Alfa Aesar, and the HANs were available in a standard mixture from Sigma Aldrich (USEPA 551B halogenated volatiles mixture). Trichloromethane (TCM), bromodichloromethane (BDCM), dibromochloromethane (DBCM), and tribromomethane (TBM) were available in a THM mixture obtained from Sigma Aldrich (USEPA 501/601).

Sodium hypochlorite (NaClO) stock solutions were prepared by adding NaClO (4.00–4.99%, Sigma Aldrich) to ultrapure water. Preformed NH_2Cl stock solutions were prepared daily by adding NaClO to ammonium chloride (99%, Vetec) solutions at 0.8 mol/mol (Mitch and Sedlak, 2002). Sodium bromide (99%, Alfa Aesar) was used for bromide-containing waters.

2.2. Water samples

A NOM stock solution was prepared by dissolving Suwannee River NOM solids (Cat. No. 2R101N, International Humic Substances Society) in ultrapure water and then filtering through a 0.45-μm membrane filter. The stock solution was diluted with ultrapure water to prepare a NOM solution for disinfection with a dissolved organic carbon (DOC) concentration of 5 mg/L. A secondary effluent sample was collected from a wastewater treatment plant in Guangzhou, China, which uses an inverted anaerobic–anoxic–oxic process. After collection, the sample was filtered through a 0.45-μm membrane and stored at 4 °C. The characteristics of the samples are shown in Table S1. The DOC and total nitrogen concentrations were measured using a total organic carbon (TOC) analyzer (TOC-VCPH, Shimadzu, Kyoto, Japan). The DON concentration was calculated by subtracting the concentrations of nitrogen present as nitrate, nitrite, and ammonia from the total nitrogen concentration. The ammonia concentration was measured by the salicylate-hypochlorite method, the nitrite concentration was measured by the *N*-(1-naphthyl)ethylenediamine dihydrochloride colorimetric method, and the nitrate concentration was measured by ion chromatography (Dionex ICS-2000) (Eaton et al., 2005; Huang et al., 2012).

2.3. Experimental procedures

The experiments were conducted under headspace-free conditions in 40-mL amber glass bottles shielded from the light at 25 °C. The pH of each solution was maintained at 7 using 20 mM phosphate buffer. For the chlorination (Cl_2 process) and chloramination (NH_2Cl process) experiments, NaClO and preformed NH_2Cl solutions, respectively, were added to the samples at 15 mg/L Cl_2. For the Cl_2–NH_2Cl process, the NaClO solution was added at 15 mg/L Cl_2, and after 30 min, ammonium chloride was added at 3.75 mg/L