EFFECT OF DECHLORINATION TIME ON THE HALOGENATED DISINFECTION BYPRODUCTS IN CHLORINATED SALINE WASTEWATER EFFLUENTS

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Abstract
Due to the deficiency of fresh water resources, many coastal cities around the world may adopt the practice of using seawater for toilet flushing, which leads to saline wastewaters rich in bromide ions. During chlorination for inactivating pathogens in saline wastewater effluents, chlorine can react with bromide and organic matter in the effluents to form halogenated disinfection byproducts. Because of the toxicity of residual chlorine to aquatic species, chlorinated saline sewage effluents are required to be dechlorinated before being discharged into coastal marine water. In this work, by using a powerful precursor ion scan method with ultra performance liquid chromatography/electrospray ionization-triple quadrupole mass spectrometry, the effect of dechlorination time on the speciation and concentrations of halogenated disinfection byproducts in chlorinated secondary saline wastewater effluents was assessed.

Keywords: Disinfection byproducts, Saline wastewater, Chlorination, Dechlorination

1. INTRODUCTION
Numerous brominated disinfection byproducts (DBPs) are generated during chlorination of raw waters containing bromide (Richardson et al., 2003; Krasner et al., 2006). In a city where seawater is used for toilet flushing, the bromide concentration in the wastewater can be extremely high (up to 20 mg/L), which may lead to the formation of high levels of brominated DBPs as the wastewater effluent is chlorinated for inactivating pathogens. Brominated DBPs are generally more cytotoxic and genotoxic than their chlorinated analogues (Bull et al., 1995; Plewa et al., 2002; Echigo et al., 2004). Croue et al. (1989) studied the destruction of drinking water halogenated DBPs with sulfite by GC/MS. Recently, Zhang et al. (2008) developed a method for fast selective detection of polar brominated DBPs in drinking water with
electrospray ionization triple quadruple mass spectrometry (ESI-tqMS). This method is based on a useful function, precursor ion scan, in ESI-tqMS. By setting precursor ion scan of a fragment ion, all the precursor molecular ions that can generate the fragment ion can be selectively detected. Since only polar bromine-containing molecular ions can generate fragment bromide ions after colliding with argon gas in the collision chamber of tqMS, all the polar bromine-containing DBPs can be selectively detected by setting precursor ion scan of bromide ($m/z$ 79 or 81). In this study, by using the powerful precursor ion scan method with ESI-tqMS with/without ultra performance liquid chromatography (UPLC) preseparation, the effect of dechlorination time on the speciation and concentrations of halogenated DBPs in a chlorinated secondary saline wastewater effluent was assessed.

2. MATERIALS AND METHODS

2.1 Saline wastewater effluent chlorination and dechlorination

An undisinfected wastewater effluent sample was collected from a secondary biological treatment plant that treats saline wastewater. The wastewater effluent sample was stored at 4 °C in a cold room prior to use. The characteristics of the wastewater effluent sample were as follows: pH 7.8, bromide 20.0 mg/L, dissolved organic carbon 8.6 mg/L as C, and ammonia 1.26 mg/L as N. Six 2 L aliquots of the sample were disinfected with sodium hypochlorite at dose of 15 mg/L as Cl$_2$. After a 30 min chlorination contact time, except for one aliquot which was used immediately for total organic chlorine (TOCl), total organic bromine (TOBr), and mass spectrometry analyses, the other five aliquots were dechlorinated for residual chlorine with 0.1 M Na$_2$S$_2$O$_3$ at a Cl$_2$ to Na$_2$S$_2$O$_3$ mole ratio of 0.8 : 1.0; after dechlorination times of 5 min, 30 min, 4 h, 8 h, and 24 h, respectively, the five aliquots were used right away for TOCl, TOBr, and mass spectrometry analyses. The chlorinated aliquot without dechlorination was specified as “a dechlorination time of 0 min”.

2.2 TOCl/TOBr analysis

TOCl and TOBr were measured according to Standard Method 5320B except that an online ion chromatograph was used. Briefly, by using a three-channel adsorption module (TXA03C, Mitsubishi), a 100 mL aliquot of a sample was passed through two consecutive prepacked AC columns (Mitsubishi). Then the AC columns were rinsed by 10 mL of 5000 mg/L KNO$_3$ as NO$_3^-$ to remove inorganic halides and subsequently subjected to pyrolysis at 1000 °C with an AQF-100 automatic quick furnace (Mitsubishi). The Hydrogen halide and halogen gases were trapped by a 5 mL 0.003% H$_2$O$_2$ absorbent (freshly prepared daily) containing 1 mg/L phosphate serving as an internal standard to estimate the volume variation induced by GA-100 line washing. After absorption, the online ion chromatograph (ICS-90 Dionex) was triggered and 200 μL of the absorbent was injected. An IonPac analytical column (AS9-HC, Dionex) was used with a 9 mM Na$_2$CO$_3$ solution as the eluent at a flow rate of 1 mL/min. The concentrations of halides (i.e., chloride and bromide) were quantified by a conductivity detector.

2.3 (UPLC)/ESI-tqMS analysis

The chlorinated wastewater effluent aliquots with different dechlorination times were pretreated with the procedure by Zhang et al. (2008). The pretreated samples were analyzed
with an ESI-tqMS system (Waters Acquity TQD), which was optimized with a standard containing 1 mg/L each of nine commonly known haloacetic acids. By setting precursor ion scans of $m/z$ 79 and 81, all polar (i.e., electrospray-ionizable) bromine-containing compounds were expected to be detected. A Waters UPLC system was coupled to the Waters Acquity ESI-tqMS (UPLC/ESI-tqMS, Waters). For those brominated molecular ions detected by the precursor ion scans with relatively high intensities, the UPLC/ESI-tqMS multiple reaction monitoring (MRM) mode was applied to confirm the retention times (RTs) of the molecular ions. Then, product ion scans were conducted at the specific RTs to obtain some structural information of the molecular ions.

3. RESULTS AND DISCUSSION

Fig. 1 shows the TOBr and TOCl levels in the chlorinated wastewater effluent aliquots without or with the dechlorinating agent (Na$_2$S$_2$O$_3$). The TOBr concentration in the chlorinated aliquot without Na$_2$S$_2$O$_3$ was 0.51 mg/L. After dechlorination times of 5 min, 30 min, 4 h, 8 h, and 24 h with Na$_2$S$_2$O$_3$, the TOBr concentrations in the chlorinated aliquots decreased to 0.32, 0.30, 0.28, 0.27, and 0.23 mg/L, respectively. Also, less TOCl formed in the chlorinated aliquots with Na$_2$S$_2$O$_3$ than in the chlorinated aliquot without Na$_2$S$_2$O$_3$. However, no evident trend on the TOCl concentration was observed as the dechlorination time increased from 5 min to 24 h.

Fig. 2 shows the precursor ion scans of $m/z$ 79 of one chlorinated aliquot without Na$_2$S$_2$O$_3$ and three chlorinated aliquots with Na$_2$S$_2$O$_3$ for different dechlorination times. The y-axis scales of the four charts are set on the same maximum intensity. An interesting phenomenon was that, after the addition of Na$_2$S$_2$O$_3$, some significant odd-numbered ion peak/clusters (i.e., $m/z$ 261, 301/303/305, and 345/347/349) disappeared and some even-numbered ion peaks (i.e., $m/z$ 328, 356, and 370) showed up. Furthermore, as shown in Fig. 2b–d, increasing dechlorination time did not shift the speciation of DBPs. However, as contact time increased, the intensities of some peaks/peak clusters (i.e., $m/z$ 171/173, 205/207/209, 215/217, 249/251/253, 356, and 370) increased, which indicates that the concentration of each
corresponding brominated DBP increased. Fig. 3 shows the intensity variation of representative peaks subject to increasing trends with dechlorination time. As dechlorination time increased from 5 min to 4 h, the intensity increments ranged from 29.6% to 102.1%. Comparatively, the intensity increments, ranging from 4.6% to 81.2%, became less when dechlorination time increased from 4 to 24 h.

![Fig. 2 Precursor ion scan spectra of m/z 79 of the chlorinated wastewater effluent aliquots: (a) without Na2S2O3, (b) with Na2S2O3 for 5 min, (c) with Na2S2O3 for 4 h, and (d) with Na2S2O3 for 24 h](image)

![Fig. 3: Representative peaks following ascending intensity trends with dechlorination time](image)

A couple of new brominated DBPs that have not been previously reported were found in the chlorinated wastewater effluent aliquots with/without dechlorination with Na2S2O3. In the precursor ion scan spectra of m/z 79 and 81 of the chlorinated aliquot without Na2S2O3, both m/z 301/305/307 and 303/305/307 had an approximate abundance ratio of 3:4:1 (Fig. 4),
so pair (301/305/307, 303/305/307) should correspond to a compound with two bromine atoms and one chlorine atom.

Fig. 4: Precursor ion scan spectra of m/z (a) 79 and (b) 81 of the chlorinated wastewater effluent aliquot without Na2S2O3.

Fig. 5 shows the product ion scan spectra of m/z 301, 303, 305 and 307 at RT 1.97 min. The loss of 44 represented one carboxylic group. Therefore, a structure was tentatively proposed as shown in Fig. 5b.

Fig. 5: The chlorinated wastewater effluent aliquot without Na2S2O3: (a) product ion scan spectra of m/z 301, 303, 305 and 307 at RT 1.97 min, and (b) a tentatively proposed structure.
For pair (345/347/349, 347/349/351), there were three isotopic peaks with the abundance ratio of 1:2:1 in the precursor ion scan spectra of m/z 79 and 81 (Fig. 4), so this pair should correspond to a compound containing three bromine atoms.

Fig. 6: The chlorinated wastewater effluent aliquot without Na$_2$S$_2$O$_3$: (a) product ion scan spectra of m/z 345, 347, 349 and 351 at RT 1.97 min, and (b) a tentatively proposed structure

Pair (345/347/349, 347/349/351) was further analyzed with product ion scans at RT 1.97 min (Fig. 6). A loss of 44 represented one carboxylic group. Besides, it was observed that the RTs of ion clusters m/z 345/347/349/351 and m/z 345/347/349/351 were both around 1.97 min (Fig. 7), and these two ion clusters disappeared simultaneously after the dechlorinating agent was added, so the two DBPs might be related to each other. A structure is tentatively proposed as shown in Fig. 6b.
Fig. 7: UPLC/ESI-tqMS MRM chromatogram: (a) $m/z$ 301, 303, 305 and 307, (b) $m/z$ 345, 347, 349 and 351

Fig. 8: The chlorinated wastewater effluent aliquot that was dechlorinated with Na2S2O3 for 5 min: (a) UPLC/ESI-tqMS precursor ion scan spectra of $m/z$ 79 and 81 at RT 8.18 min, and (b) a tentatively proposed structure

Owing to the presence of ammonia and nitrogen-containing organic compounds in the wastewater effluent, nitrogenous brominated DBPs could be formed. Fig. 8 shows the UPLC (RT 8.18 min) precursor ion scan spectra of $m/z$ 79 and 81 of the chlorinated wastewater aliquot that was dechlorinated for 5 min. Both ion clusters $m/z$ 378/380/382/384 and 380/382/384/386 had an approximate abundance ratio of 1:3:3:1, so pair (378/380/382/384, 380/382/384/386) should correspond to a compound containing four bromine atoms. Also, the even-numbered $m/z$ values indicate that this compound contains one nitrogen atom. The
remaining part should be $378 - 79 \times 4 - 14 = 48$. The only reasonable composition for 48 is $C_4$, so this compound should be tetrabromopyrrole (Fig. 8b).

ACKNOWLEDGEMENTS

This work was supported by a grant from the Research Grants Council of the Hong Kong Special Administrative Region, China (Project No. HKUST622808).

REFERENCES