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Detection, identification and formation of new iodinated disinfection byproducts in chlorinated saline wastewater effluents

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ABSTRACT

The use of seawater for toilet flushing introduces high levels of inorganic ions, including iodide ions, into a city's wastewater treatment systems, resulting in saline wastewater effluents. Chlorination is widely used in disinfecting wastewater effluents owing to its low cost and high efficiency. During chlorination of saline wastewater effluents, iodide may be oxidized to hypoiodous acid, which may further react with effluent organic matter to form iodinated disinfection byproducts (DBPs). Iodinated DBPs show significantly higher toxicity than their brominated and chlorinated analogues and thus have been drawing increasing concerns. In this study, polar iodinated DBPs were detected in chlorinated saline wastewater effluents using a novel precursor ion scan method. The major polar iodinated DBPs were identified and quantified, and their organic precursors and formation pathways were investigated. The formation of iodinated DBPs under different chlorine doses and contact times was also studied. The results indicated that a few polar iodinated DBPs were generated in the chlorinated saline primary effluent, but few were generated in the chlorinated saline secondary effluent. Several major polar iodinated DBPs in the chlorinated saline primary effluent were proposed with structures, among which a new group of polar iodinated DBPs, iodo-trihydroxybenzenesulfonic acids, were identified and quantified. The organic precursors of this new group of DBPs were found to be 4-hydroxybenzenesulfonic acid and 1,2,3-trihydroxybenzene, and the formation pathways of these new DBPs were tentatively proposed. Both chlorine dose and contact time affected the formation of iodinated DBPs in the chlorinated saline wastewater effluents.

1. Introduction

To lower the local freshwater demand and conserve the limited freshwater resources, Hong Kong has implemented the use of seawater for toilet flushing territory-wide since the 1950s (Tang et al., 2007). A few other coastal cities or countries, including Avalon City, Marshall Islands and Kiribati, have also adopted this practice (Boehm et al., 2009; Mirti and Davies, 2005). But seawater toilet flushing introduces high levels of inorganic ions, including bromide and iodide ions, into the wastewater treatment systems, resulting in saline wastewater

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effluents. Chlorination is the most widely used method of disinfecting wastewater effluents owing to its low cost and high efficiency. In chlorination of saline wastewater effluents, bromide/iodide ions can be oxidized by chlorine or chloramines to hypobromous/hypoiodous acid, which may further react with effluent organic matter (EfOM) to form brominated/iodinated disinfection byproducts (DBPs) (Ding et al., 2013). When the brominated/iodinated DBPs are discharged into marine water, they may pose adverse impacts on the marine ecosystem (Yang and Zhang, 2013; Liu and Zhang, 2014). A previous study has reported the formation of brominated DBPs in chlorination of saline wastewater effluents (Ding et al., 2013), but the formation of iodinated DBPs in chlorinated saline wastewater effluents has never been reported.

Recently, iodinated DBPs have been drawing increasing concerns due to their relatively high toxicity. Previous studies have reported that iodinated DBPs are generally several to hundreds of times more cytotoxic and genotoxic than their brominated and chlorinated analogues (Plewa et al., 2008; Cemeli et al., 2006; Richardson et al., 2007, 2008). Our group has shown recently that iodinated DBPs (including emerging iodinated phenolic DBPs) presented substantially higher developmental toxicity and growth inhibition than their brominated and chlorinated analogues (Yang and Zhang, 2013; Liu and Zhang, 2014). Therefore, iodinated DBPs in chlorinated saline wastewater effluents are of great toxicological significance to the marine ecosystem and should be investigated.

Gas chromatography-electron capture detection and gas chromatography-mass spectrometry have been used for detecting and identifying iodinated DBPs in drinking waters (Bichsel and von Gunten, 2000; Plewa et al., 2004; Krasner et al., 2006; Hua and Reckhow, 2007; Richardson et al., 2008; Duirk et al., 2011; Jones et al., 2012). However, since these techniques are less amenable to polar/semi-polar iodinated DBPs, only a few iodinated DBPs have been detected and identified in drinking waters, including mainly iodo-trihalomethanes, iodo-acids and iodo-amides (Brass et al., 1977; Bichsel and von Gunten, 2000; Cancho et al., 2000; Plewa et al., 2004, 2008; Richardson, 2003; Richardson et al., 2008; Duirk et al., 2011; Chu et al., 2012). Owing to the complex constituents of EfOM in saline wastewater effluents (Ding et al., 2013), new polar iodinated DBPs may be generated in chlorinated saline wastewater effluents and they may escape detection by both techniques. Recently, a novel precursor ion scan (PIS) method has been developed for the fast selective detection of polar iodinated DBPs using an electrospray ionization-triple quadrupole mass spectrometer (ESI-tqMS) (Ding and Zhang, 2009). By setting PIS of *m/z* 126.9, almost all polar iodinated DBPs in a sample can be selectively detected. The principle of the PIS method is illustrated in Supplementary Information (SI) Section 1. Further, by coupling it with ultra performance liquid chromatography (UPLC) for preseparation, the ESI-tqMS can be used for identifying unknown polar iodinated DBPs. Total organic iodine (TOI) is another important collective parameter indicating the formation of all (nonpolar and polar) iodinated DBPs as a whole. A new TOI measurement approach involving UPLC/ESI-MS for detection of iodide has recently been developed by Pan and Zhang (2013).

The purposes of this study were thus to detect polar iodinated DBPs in chlorinated saline wastewater effluents, to identify the major polar iodinated DBPs, to quantify those iodinated DBPs, to determine their organic precursors and formation pathways, and to study the formation of iodinated DBPs under different chlorine doses and contact times.

2. Materials and methods

2.1. Chemicals and reagents

Potassium iodide (100%) was purchased from BDH. Ammonium chloride (≥99.5%) and potassium nitrate (≥99.0%) were purchased from Riedel-deHaën. A sodium hypochlorite stock solution was purchased from Sigma–Aldrich and it was diluted to around 2000 mg/L as Cl_2 and standardized by the N,N-diethyl-p-phenylene diamine ferrous titrimetric method every month (APHA et al., 1995). 4-Hydroxybenzenesulfonic acid solution (65% wt. in H_2O) and 1,2,3-trihydroxybenzene (≥99%) were purchased from Sigma–Aldrich. All other chemicals used in this study were purchased at the highest purities available from Sigma–Aldrich. Ultrapure water (18.2 MΩ cm) was supplied by a NANOpure Diamond purifier system (Barnstead).

2.2. Preparation of solutions

A potassium iodide solution (100 mg/L as I), an ammonium chloride solution (1.0 g/L as N), a sodium sulfite solution (12.6 g/L), and a sodium arsenite solution (13.0 g/L) were prepared. They were stored in amber glass bottles at 4 °C and newly prepared every week. Stock solutions of 4-hydroxybenzenesulfonic acid (100 mg/L) and 1,2,3-trihydroxybenzene (100 mg/L) were prepared just before use.

Iodoacetic acid was dissolved in ultrapure water to prepare standard solutions with TOI concentrations of 5, 10, 20, 50 and 100 μg/L as I. A potassium nitrate solution (5000 mg/L as NO_3^-) was prepared as the rinsing solution for removing inorganic halides from activated carbon in TOI measurement.

2.3. Collection, characterization and storage of the saline wastewater effluents

Two undisinfected saline wastewater effluent samples (24-h composite) were collected from a saline primary wastewater treatment plant and a saline secondary wastewater treatment plant. For the two wastewater treatment plants, their influents were the same or similar as they both were domestic wastewater. The collected effluent samples were immediately transported to the lab in ice packs. Some chemical characteristics of the collected saline wastewater effluents were measured immediately. The pH, dissolved organic carbon (DOC), ammonium and bromide concentrations were measured with a pH meter (Thermo Orion), a total organic carbon analyzer (Shimadzu), a fast injection analyzer (QuickChem), and an ion chromatograph (Dionex), respectively. The iodide concentration was measured following the method by Gong and Zhang (2013). The collected saline wastewater effluents were adjusted to pH 2 with sulfuric acid and stored at 4 °C to minimize changes in components. Before the experiment, they were brought to room temperature, adjusted to