Chemosphere 149 (2016) 70–75

Contents lists available at ScienceDirect

Chemosphere

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

Formation and toxicity of halogenated disinfection byproducts resulting from linear alkylbenzene sulfonates

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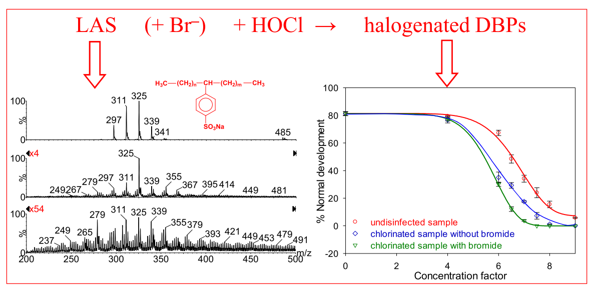
HIGHLIGHTS

- The formation of halogenated DBPs resulting from LAS was studied.
- The major polar halogenated DBPs resulting from LAS were proposed with structures.
- The formation pathways of the major polar halogenated DBPs were proposed.
- The developmental toxicity of different scenarios of LAS samples was evaluated.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 30 September 2015
Received in revised form
13 January 2016
Accepted 16 January 2016
Available online 3 February 2016

Handling Editor: Shane Snyder

Keywords:
Disinfection byproducts
DBPs
Halogenated DBPs
Linear alkylbenzene sulfonates
Chlorination

ABSTRACT

Linear alkylbenzene sulfonates (LAS) are an important group of organic pollutants in urban wastewater effluents. The practice of using seawater for toilet flushing results in saline wastewater effluents, which contain high levels of bromide ions. Chlorine is most commonly used in wastewater disinfection. During chlorination of freshwater or saline wastewater effluents, some halogenated disinfection byproducts (DBPs) resulting from LAS could be formed. In this study, the overall formation of halogenated DBPs resulting from LAS was quantified by total organic halogen (TOX) measurement. Polar halogenated DBPs resulting from LAS were detected with a novel precursor ion scan method. The structures and formation pathways of the major ones were tentatively proposed. The overall toxicity of different scenarios of LAS samples was evaluated with embryos of a marine polychaete *Platynereis dumerilii*. The results demonstrate that chlorinated DBPs were generated during chlorination of LAS without bromide, while brominated DBPs were generated during chlorination of LAS with bromide. The TOX concentrations were relatively low, indicating that LAS were not quite reactive with halogen. The major polar chlorinated and brominated DBPs resulting from LAS were proposed to be 2,6-dichloro-3,5-dihydroxy-4-dodecylbenzenesulfonic acid and 2,6-dibromo-3,5-dihydroxy-4-dodecylbenzenesulfonic acid, which belong to a group of DBPs with similar structures but different halogen atoms, and their formation pathways were tentatively proposed. The results also reveal that the undisinfected LAS sample was the least toxic, followed by the chlorinated LAS sample without bromide, and the chlorinated LAS sample with bromide was the most toxic.

1. Introduction

Linear alkylbenzene sulfonates (LAS) are a group of compounds

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http://dx.doi.org/10.1016/j.chemosphere.2016.01.067

which contain a benzene ring attached to a linear alkyl chain and sulfonated at the para position (Fig. 1d). The linear alkyl chain typically has 10 to 14 carbon atoms. LAS are the most commonly used surfactants in both industrial and domestic detergents with a global production of 2.4 million tons per year, which account for 40% of all surfactants (Riu et al., 2001). Commercial LAS are a mixture of more than 20 components, which are closely related isomers and homologues with different alkyl chain lengths and various benzene ring positions along the linear alkyl chain. But the ratio of various isomers and homologues is relatively constant, with an average carbon number in the alkyl chain between 11.7 and 11.8 (OECD SIDS, 2005). After use, LAS are discharged through the sewage infrastructures to wastewater treatment works. During wastewater treatment, LAS can be removed by two processes: biodegradation by microorganisms and adsorption by suspended particles or sediments (Takada and Ogura, 1992; Corcia et al., 1999), while biodegradation is regarded as the major removal pathway (Takada and Ogura, 1992). The removal efficiency of LAS depends on the operating conditions of wastewater treatment works. It has been reported that LAS concentrations in influents of wastewater treatment works were in the range of 2.4–6.7 mg/L (Clara et al., 2007), while their concentrations in effluents ranged from 5 to 1600 μg/L (Riu et al., 2001). In our study, it was found that LAS were present as an important group of organic components in three undisinfected wastewater effluents in Hong Kong and the experimental details are illustrated in Section 1 in the Supporting Information (SI). The full scan spectra of the three wastewater effluents are shown in Fig. 1a–c. Commercial LAS are mainly comprised of five components, which have a common structure shown in Fig. 1d with 10, 11, 12, 13 or 14 carbon atoms in the linear alkyl chain. The molecular ions of the five major components in the electrospray ionization (ESI) negative mode should be with *m/z* values of 297, 311, 325, 339 and 353, respectively. In the full scan spectra of the three effluent samples, the major peaks were with *m/z* values of 297, 311, 325, 339 and 353, which corresponded to the five major components of commercial LAS, indicating that LAS were present in all the three undisinfected wastewater effluents and were an important group of components of effluent organic matter (EfOM). Notably, the peak intensities of these ions in the secondary effluents were significantly lower than those in the primary effluent. Since biodegradation is the major removal pathway of LAS (Takada and Ogura, 1992), LAS might be removed to a large extent during secondary biological treatment, resulting in lower levels of LAS in the secondary effluents.

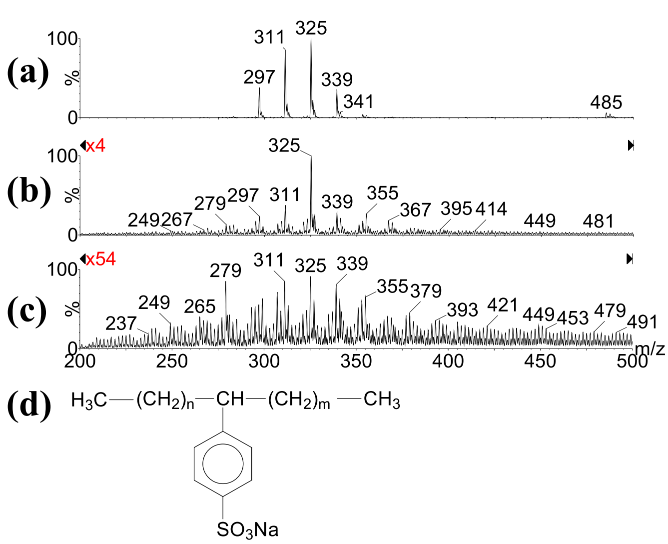

Fig. 1. Full scan spectra of (a) a saline primary effluent, (b) a saline secondary effluent, and (c) a freshwater secondary effluent. The spectra are on the same y-axis scale. (d) The chemical structure of LAS.

To reduce the local freshwater demand, seawater toilet flushing has been applied in Hong Kong on a large scale since the 1950s (Tang et al., 2007). Some other circumlittoral regions have also used seawater for toilet flushing (Mirti and Davies, 2005). Due to the lack of freshwater resources, toilet flushing with seawater can be an effective alternative for a large number of coastal cities or countries all over the world. However, the use of seawater for toilet flushing results in saline wastewater effluents, which contain high levels of bromide ions (SI Table S1). Commonly, urban wastewater effluents are freshwater effluents with low levels of inorganic ions (SI Table S1). When it comes to disinfection, bromide is an important ion of concern since it involves in the formation of brominated disinfection byproducts (DBPs) (Richardson et al., 1999; Chang et al., 2001; Shi et al., 2013).

Nowadays, wastewater effluents are extensively disinfected before discharge to inactivate the microorganisms therein. Chlorine is most commonly used in wastewater disinfection. During chlorination of wastewater effluents, chlorine reacts with EfOM and some inorganic ions (e.g., bromide ions) to form halogenated DBPs (Ding et al., 2013; Bulloch et al., 2015). Since LAS are an important group of components of EfOM, some halogenated DBPs resulting from LAS could be formed during chlorination of wastewater effluents. For freshwater effluents, chlorinated DBPs resulting from LAS could be formed. For saline effluents, chlorinated and brominated DBPs resulting from LAS could be formed due to the presence of bromide ions. When these halogenated DBPs pour into the receiving water body, they may have negative effects to the organisms in the receiving water body (Yang and Zhang, 2013, 2014; Liu and Zhang, 2014; Yang et al., 2015). Therefore, halogenated DBPs resulting from LAS are of great toxicological significance to the receiving water body and thus need to be studied.

In most of previous studies, detection and identification of halogenated DBPs was implemented by gas chromatography-electron capture detection (GC-ECD) and gas chromatography-mass spectrometry (GC–MS) (Xie, 2001; Richardson et al., 2007; Huang et al., 2013). Owing to the chemical structures of LAS molecules (containing a polar sulfo group on the benzene ring), some polar halogenated DBPs resulting from LAS may be formed, which can hardly be detected by GC-ECD or GC–MS. Recently, researchers reported methods for selectively detecting polar halogenated DBPs by ESI-triple quadrupole mass spectrometry (ESI-tqMS) (Zhang et al., 2008; Pan et al., 2014; Yang and Zhang, 2014). By setting precursor ion scans (PISs) of *m/z* 35/37 and *m/z* 79/81, practically all polar chlorinated and brominated DBPs can be selectively detected. The principle of the PIS method is detailed in the SI (Section 2). Also in recent years, total organic halogen (TOX) has been gaining popularity in DBP studies because it is a collective parameter to indicate the overall formation of both polar and nonpolar halogenated DBPs (Hua and Reckhow, 2006; Li et al., 2010; Kristiana et al., 2015). TOX generally consists of total organic chlorine (TOCl) and total organic bromine (TOBr).

Previously, Yang and Zhang (2013) adopted and improved a bioassay method to sensitively evaluate the developmental toxicity of DBPs by using embryos of a marine polychaete *Platynereis dumerilii*. In the method, by counting the numbers of normal and total embryos with a stereo microscope, the percent normal development can be calculated. Further, by plotting the curve of the percent normal development versus the DBP concentration (i.e., a concentration–response curve), the median effective concentration (EC_{50}) of the DBP (i.e., the DBP concentration at which 50% of the embryos developed normally) can be obtained. It has been demonstrated that the method was rather precise with a very low