Chemosphere 196 (2018) 25–34

Contents lists available at ScienceDirect

Chemosphere

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

Impact of ClO_2 pre-oxidation on the formation of CX_3R-type DBPs from tyrosine-based amino acid precursors during chlorination and chloramination

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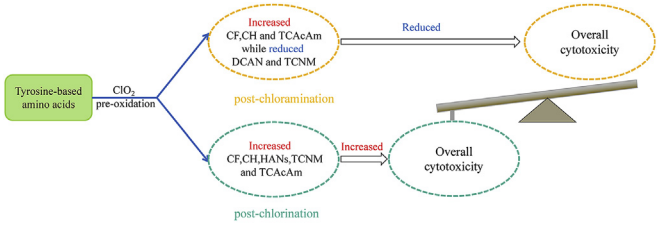
HIGHLIGHTS

- ClO_2 pre-oxidation increased CF and CH during chlor (am)ination of tyrosine-based amino acids.
- During chlorination, introduction of ClO_2 increased HANs, TCNM and TCAcAm.
- During chloramination, introduction of ClO_2 decreased DCAN and TCNM.
- CTI during chlorination were higher than that during chloramination.
- ClO_2 pre-oxidation increased CTI in chlorination but reduced it in chloramination.

GRAPHICAL ABSTRACT



ClO_2 pre-oxidation increased the overall cytotoxicity of DBPs produced during chlorination of tyrosine-based amino acids while reduced the overall cytotoxicity during chloramination.

ARTICLE INFO

Article history:
Received 19 September 2017
Received in revised form
17 December 2017
Accepted 22 December 2017
Available online 26 December 2017

Handling Editor: W. Mitch

Keywords:
Chlorine dioxide
CX_3R-type disinfection by-products
Drinking water
tyrosine
Cytotoxicity

ABSTRACT

ClO_2 is frequently used as a pre-oxidant in water treatment plants. However, the effects of ClO_2 pre-oxidation on disinfection by-product (DBP) formation, especially the highly toxic nitrogenous DBPs, during subsequent chlor (am)ination have not been studied thoroughly. There is also limited information about DBP formation from combined amino acids (AAs), which are more abundant than free AAs in source waters. Many typical DBPs (including representative N-DBPs) have a similar structure of "CX_3R" (X = H, Cl, Br or I). In the study, tyrosine and forms representing its reactivity in combined AAs (tyrosine *tert*-butyl ester and Boc-tyrosine) were selected as model precursors. The formation of various regulated and unregulated CX_3R-type DBPs from ClO_2 pre-oxidation and subsequent chlor (am)ination were studied at a wide-range of ClO_2 and chlor (am)ine doses (ClO_2/precursors and chlor (am)ine/precursors are at the range of 0–2.5 and 1–20 [Mol/Mol], respectively). Chloroform and chloral hydrate (CH) yields increased with chlorine dose, while haloacetonitrile and haloacetamide maximized at median chlorine dose (Cl_2/Precursors = 10). All DBP yields increased with chloramine dose. ClO_2 pre-oxidation increased chloroform, haloacetonitrile, trichloronitromethane and CH yields during chlorination, but ClO_2

Abbreviations: AAs, Amino acids; CF, Chloroform; CH, Chloral hydrate; ClO2, Chlorine dioxide; CTI, Cytotoxicity index; DBPs, Disinfection by-products; DCAN, Dichloroacetonitrile; DOC, Dissolved organic carbon; DON, Dissolved organic nitrogen; DWTPs, Drinking water treatment plants; HAAs, Haloacetic acids; HALs, Haloacetaldehydes; HAcAms, Haloacetamides; HANs, Haloacetonitriles; HNMs, Halonitromethanes; MCAN, Chloroacetonitrile; MTBE, Methyl-t-butyl ether; C-DBPs, Carbonaceous DBPs; N-DBPs, Nitrogenous DBPs; THMs, Trihalomethanes; TCAN, Trichloroacetonitrile; TCNM, Trichloronitromethane; Tyr, Tyrosine; Tyr-OtBu, Tyr tert-butyl ester.

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https://doi.org/10.1016/j.chemosphere.2017.12.143
0045-6535/

increased chloroform, CH, trichloroacetamide while decreased dichloroacetonitrile and trichloronitromethane yields during chloramination. The overall toxicity of the formed DBPs was evaluated by cytotoxicity index (CTI). ClO_2 pre-oxidation increased CTI from all precursors during post-chlorination while reduced it during post-chloramination. Results imply that ClO_2 is probably more suitable for use in combination with chloramination disinfection, rather than chlorination, in the integrated control of CX_3R-type DBPs from source waters abundant in AAs.

1. Introduction

The use of chlorine and chloramines in drinking water treatment plants (DWTPs) can effectively reduce microbial risk of drinking water by inactivating water-borne pathogens (Sedlak and von Gunten, 2011). However, chlorine may also reacts with organic and inorganic matter to produce undesirable disinfection by-products (DBPs), resulting in adverse health effects (Plewa and Wagner, 2015). Since the first discovery of chloroform (CF) in 1974 by two research teams (Bellar and Kroner, 1974; Rook, 1974), a long list of DBPs have been identified in drinking water (Krasner et al., 2006; Richardson et al., 2007; Richardson and Ternes, 2014). In recent ten years, nitrogenous DBPs (N-DBPs) have been of particular concern because of their high toxicity within the overall DBP field (Richardson et al., 2003; Muellner et al., 2007; Shah and Mitch, 2012; Plewa et al., 2017). Three groups of halogenated N-DBPs, namely the haloacetonitriles (HANs), halonitromethanes (HNMs) and haloacetamides (HAcAms), presented comparable but typically lower concentrations than the trihalomethanes (THMs), which was the most abundant class of carbonaceous DBPs (C-DBPs) (Krasner et al., 2006; Richardson et al., 2007). More importantly, these three groups of N-DBPs have significantly higher cyto- and geno-toxicity than THMs (Plewa et al., 2008a, 2008b). Additionally, haloacetaldehydes (HALs) are an important class of unregulated C-DBPs (Richardson and Postigo, 2012), which were found to be the third largest DBP class by weight (Krasner et al., 2006). The recent toxicity study found HALs exhibited higher cytotoxicity (cytotoxicity index value = 144) than HANs (cytotoxicity index value = 16.0) and HNMs (cytotoxicity index value = 75.0), but lower than HAcAms (cytotoxicity index value = 302) based on the mean LC_{50} value of all the individual compounds of a single class of DBPs (Jeong et al., 2015; Postigo et al., 2015). Notably, whether they are typical C-DBPs, or the emerging N-DBPs, the above mentioned DBPs (THMs, HALs, HANs, HAcAms and HNMs) all have a simple and similar molecular structure "CX_3R" (X = H, Cl, Br or I) (Fig. SM1), which may be regarded as CX_3R-type DBPs. And their concentration has a high proportion in all known halogenated DBPs in the real chlorinated and chloraminated drinking water (Weinberg et al., 2002; Krasner et al., 2006).

Due to the lack of high-quality source water, utilities have been exploiting source waters impaired by wastewater effluents or algal blooms. These source waters feature higher dissolved organic carbon (DOC) and dissolved organic nitrogen (DON) that serves as a source for CX_3R-type DBPs, including C-DBPs and N-DBPs (Westerhoff and Mash, 2002; Shah and Mitch, 2012; Xue et al., 2014; Li et al., 2017), and traditional drinking water treatment processes such as coagulation, sedimentation and filtration incompletely remove these precursor compounds (Chu et al., 2015a) unless additional treatments are added (e.g. advanced oxidation) (Zhang et al., 2017).

In order to meet the more stringent regulations for the regulated CX_3R-type DBPs (e.g., THMs), many DWTPs are switching disinfectants from chlorine to alternative disinfectants (e.g., chloramine and chlorine dioxide [ClO_2]). Although chloramine disinfection reduces the formation of THMs, it can increase concentrations of certain unregulated N-DBPs (Chu et al., 2012; Shah and Mitch, 2012). Application of ClO_2 does not form appreciable levels of CX_3R-type DBPs under typical conditions although it does not provide a residual chlorine in the distribution system (Li et al., 1996; Yang et al., 2013a). Therefore, ClO_2 is usually used as a pre-oxidant in combination with chlorine or chloramines to oxidize organic contaminants or to improve the disinfection performance. However, the effect of ClO_2 pre-oxidation on DBP formation (especially N-DBPs) during subsequent chlor (am)ination is not clear.

Amino acids (AAs) comprise an important portion of the DON pool (Westerhoff and Mash, 2002; Shah and Mitch, 2012) and have been highlighted as key precursors in the formation of a variety of CX_3R-type DBPs, including THMs, HALs, HANs, HAcAms and HNMs (Scully and White, 1991; Bond et al., 2012; Shah and Mitch, 2012). It is known that tyrosine (Tyr) can form both C-DBPs and N-DBPs during chlor (am)ination and therefore acts as a representative model precursor of N-DBPs (Chu et al., 2012; Chang et al., 2016). However, free AAs account for only a small proportion (<6%) of the DON pool; on the contrary, combined AAs comprise the largest identifiable part, especially in algae- and wastewater-impaired waters (e.g., in raw water of 16 full-scale water treatment plants in the United States, the average concentration of free AAs was 0.69 μg/L N, while the concentration of combined was 40.41 μg/L N [14.75% of the DON] (Westerhoff and Mash, 2002; Dotson and Westerhoff, 2009; Huang et al., 2012; Chu et al., 2015b). In the present work, free Tyr and two artificial amino acid derivatives Tyr *tert*-butyl ester (Tyr-OtBu) and Boc-Tyr (representing combined AAs, Fig. SM2) were therefore selected as model precursors. Tyr-OtBu and Boc-Tyr were selected as carboxyl- and amino-protected amino acids (i.e., amino protection with a *tert*-butoxycarbonyl group, and carboxyl protection with a *tert*-butyl ester group) mimicking peptide bonds) (Chu et al., 2014, 2015b). Similarly, Boc-lysine has previously been used as a model compound for polypeptides, as the "Boc" group protects the amino group from oxidation reactions (McCurry et al., 2016).

The aim of this study was to examine the effect of ClO_2 pre-oxidation on the formation of some typical CX_3R-type DBPs during subsequent chlor (am)ination of free and combined Tyr-based AAs. Of note, the effects of both ClO_2 dose and chlor (am) ine dose were simultaneously investigated in the hope the information gained will be helpful for minimizing CX_3R-type DBPs during disinfection.

2. Materials and methods

2.1. Materials

The standards of THMs, HALs, HANs, HNMs and three AA precursors (Tyr, Tyr-OtBu, Boc-Tyr) were all supplied from