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Degradation kinetics of organic chloramines and formation of disinfection by-products during chlorination of creatinine

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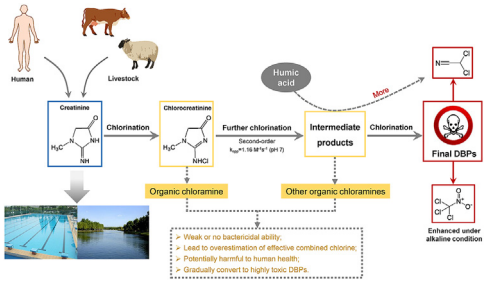
HIGHLIGHTS

- Creatinine is a typical precursor of organic chloramines during chlorination.
- The chlorination of chlorocreatinine can be described as a second-order model.
- C- and N-DBPs were generated and yields varied with pH in creatinine chlorination.
- Humic acid can enhance dichloroacetonitrile formation in creatinine chlorination.
- Some products of chlorocreatinine were also identified as organic chloramines.

GRAPHICAL ABSTRACT



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ABSTRACT

Organic chloramines can interfere with the measurement of effective combined chlorine in chlorinated water and are potential intermediate products of highly toxic disinfection by-products (DBPs). In order to know more about the degradation and transformation of organic chloramines, a typical organic chloramine precursor creatinine was selected for investigation and a corresponding individual organic chloramine chlorocreatinine was prepared in this study. The preparation condition of chlorocreatinine by chlorination was established as chlorine/creatinine = 1 M/M, reaction time = 2 h and pH = 7.0. Then the degradation kinetics of chlorocreatinine during further chlorination was studied, and a second-order rate constant of 1.16 (±0.14) M^{-1} s^{-1} was obtained at pH 7.0. Solution pH significantly influenced the degradation rate, and the elementary rate constants of chlorocreatinine with $HOCl+H^+$, HOCl, OCl^- and chlorocreatinine$^-$ with OCl^- were calculated as 2.43 (±1.55) × 10^4 M^{-2} s^{-1}, 1.05 (±0.09) M^{-1} s^{-1}, 2.86

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Disinfection by-products (DBPs)

(±0.30) M^{-1} s^{-1} and 3.09 (±0.24) M^{-1} s^{-1}, respectively. Besides, it was found that chlorocreatinine could be further converted into several C-DBPs (chloroform and trichloroacetone) and N-DBPs (dichloroacetonitrile (DCAN) and trichloronitromethane (TCNM)) during chlorination. The total yield of DBPs increased obviously with increasing pH, especially for TCNM. In addition, the presence of humic acid in creatinine solution could increase the formation of DCAN obviously during chlorination. Based on the UPLC-Q-TOF-MS analysis, the conversion pathways of chlorocreatinine were proposed. Several kinds of intermediate products were also identified as organic chloramines and some of them could even exist stably during the further chlorination.

1. Introduction

Currently, chlorination and chloramination are still the most common methods in water disinfection treatment. When these disinfectants react with the dissolved organic matter with amino groups in water, organic chloramines may be produced (Lee and Westerhoff, 2009; How et al., 2017a, b). Organic chloramines have been proved to be quite weak in oxidation and sterilization (Feng, 1966; Donnermair and Blatchley III, 2003; Heeb et al., 2017), but they are difficult to be distinguished from the inorganic chloramines (NH_2Cl, $NHCl_2$ and NCl_3) by the common *N,N*-diethyl-*p*-phenylenediamine (DPD) method (Lee et al., 2007; How et al., 2017a). Thus, their existence will lead to overestimation of the real disinfection efficacy in chlor(am)inated water. Besides, as a subclass of nitrogenous disinfection by-products (N-DBPs), organic chloramines have been proved to have potential adverse health impacts. For example, Laingam et al. (2012) found that some organic chloramines including *N*-chloroglycine, *N*-chlorolysine, *N*-chloroethanolamine and *N*-chlorohistamine had significant *in vitro* cytotoxicity and genotoxicity. In addition to the toxicity of organic chloramines themselves, organic chloramines can be converted to other more toxic N-DBPs, such as cyanogens chloride (CNCl), dichloroacetonitrile (DCAN) and trichloronitromethane (TCNM) during further chlor(am)ination (Fang et al., 2010; Yang et al., 2010, 2012; Zhang et al., 2016; How et al., 2017b). However, different organic chloramines showed different transformation rates. For instances, Huang et al. (2017) found that some organic chloramines produced from dipeptides could keep quite stable within even 240 h; Chen et al. (2017) investigated the changes of organic chloramines produced from *β*-*N*-methylamino-*L*-alanine (a cyanobacterial neurotoxin) and found that their degradation rates were also quite slow within 2 h in the presence of excess chlorine. But some organic chloramines were very unstable (half-life ≤ 15 min) after produced from the precursors, such as glutamine, aspartic acid, proline and so on (How et al., 2016). Besides, the conversion products of organic chloramines were also different due to the different organic functional groups (Zhang et al., 2016; How et al., 2017a, b; Yu and Reckhow, 2017), and some organic chloramines could even combined with other organic compounds to generate new organic chloramines and by-products (Deng et al., 2014). Therefore, attentions should be paid to the degradation and transformation of organic chloramines, which would affect the risk of water consumption.

Creatinine ($C_4H_7N_3O$) is an end-product of muscle metabolism in both human and animals, and is eliminated daily from body with urine and sweat (Bell et al., 1995). Its concentrations in normal human urine and sweet can reach 403.46 mg/L and 1.55 mg/L, respectively (Tabellen, 1981; Weng et al., 2012). Considering the arbitrary discharge of livestock wastewater in some places (Kolodziej et al., 2004) and aquatic animal metabolism (Golombieski et al., 2013), creatinine should widely exist in natural water. In particular, swimming pool water has been proved to contain a very high concentration level of creatinine due to its direct contraction with human fluids (Li and Blatchley, 2007; Weng et al., 2012, 2013). Besides, creatinine has been proved to be a precursor of organic chloramines (e.g. chlorocreatinine and chlorocreatine) for a long time (Alouini and Seux, 1988). The organic chloramines formed from creatinine were found to be stable and cytotoxic (Alouini and Seux, 1988; Wojtowicz, 2001; Weng et al., 2017). During further chlorination, these organic chloramines could decompose to some other products such as CNCl, CH_3NCl_2, NCl_3 and so on (Li and Blatchley, 2007; Weng et al., 2012, 2013). However, the degradation rates of these organic chloramines produced from creatinine have not yet been figured out. In addition, it is also unclear that whether these organic chloramines from creatinine can transform into other DBP species, particularly some highly toxic N-DBPs. Based on previous studies, the dominant organic chloramine species produced during creatinine chlorination is chlorocreatinine (Tachikawa et al., 2005; Weng et al., 2013, 2017). Therefore, the objectives of this study are (1) to investigate the chlorination kinetics of organic chloramine – chlorocreatinine and calculate its degradation rate, and (2) to study the formation of final DBPs and the transformation mechanism during creatinine chlorination.

2. Materials and methods

2.1. Materials and reagents

All chemicals used in this study were analytical grade unless otherwise noted. Creatinine (≥98%), NaOCl solution (available chlorine 4.00–4.99%), NH_4Cl (≥99.5%), NaOH (≥98%), KH_2PO_4 (≥99%) were purchased from Sigma-Aldrich (USA). H_2SO_4 was obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). The HPLC mobile phase methanol, acetonitrile and the extraction solvent methyl *tert*-butyl ether (MtBE) were obtained from J.T. Baker (USA). The DBP standard solutions (EPA 551A and 551B halogenated volatiles mix), including trihalomethanes (THMs), haloketones (HKs), haloacetonitriles (HANs) and trichloronitromethane (TCNM), were purchased from Sigma-Aldrich (USA). Suwannee River humic acid was obtained from the International Humic Substances Society, and the stock solution of humic acid was filtered through 0.45 μm cellulose acetate membranes (Anpel, China) before experiments. All solutions in the experiments were prepared with ultra-pure water produced from a Millipore filtration system (USA).

2.2. Experimental procedures

According to previous studies, only chlorocreatinine could be produced during the chlorination of creatinine with chlorine: precursor (Cl: P) ≤ 1 (molar ratio) and the reaction would terminate after chlorine was depleted (Tachikawa et al., 2005; Weng et al., 2013). So in this study the stock solution of chlorocreatinine was