Formation of organic chloramines during chlor(am)ination and UV/chlor(am)ination of algae organic matter in drinking water

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ABSTRACT

Surface water are frequently subjected to problems of algal blooms and release of algae organic matter (AOM) from the algae cells, which cause many water quality issues. This study investigated the formation of organic chloramines and nitrogenous disinfection by-products (N-DBPs) during chlor(am)ination and UV/chlor(am)ination of AOM in drinking water. AOM caused higher organic chloramine formation than humic acid and fulvic acid during chlor(am)ination. The formation of organic chloramines increased first and then decreased with the increase of free chlorine dosage, but kept increasing with the increase of NH_2Cl dosage. During AOM chlorination, the formation of organic chloramines kept decreasing as the reaction time went by, and the maximum organic chloramine proportion (79.1%) in total chlorine occurred at 8 h. However, during AOM chloramination, the formation of organic chloramines increased first, decreased in the following and then increased again as the reaction time went by, and the maximum organic chloramine proportion (22.1%) in total chlorine occurred at 24 h. UV irradiation pretreatment did not effectively influence organic chloramine formation during AOM chlor(am)ination, but accelerated the degradation of organic chloramines during chloramination. Besides, UV pretreatment enhanced the formation of N-DBPs during the subsequent chlor(am)ination of AOM, especially dichloroacetonitrile.

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1. Introduction

Chlorination and chloramination are two common disinfection methods used in drinking water treatment plants because of their low cost, effective sterilization and persistence for a long time in the distribution systems. With the presence of dissolved organic matter (DOM), organic chloramines can be produced by the substitution of hydrogen on the amino groups with chlorine during chlor(am)ination (Morris, 1967; Isaac and Morris, 1983; Lee and Westerhoff, 2009; Zhang et al., 2016). It was reported that organic chloramines possess little or no bactericidal activity (Feng, 1966; Wolfe et al., 1985; Donnermair and Blatchley III, 2003). However, the conventional N,N-diethyl-p-phenylenediamine (DPD) method cannot distinguish between organic chloramines from inorganic chloramines (NH_2Cl, $NHCl_2$ and NCl_3) (APHA, 1998; Lee et al., 2007;

Zhang et al., 2015). Therefore, the real disinfection efficacy will be overestimated when using DPD method for the measurement of total chlorine in water.

In addition, organic chloramines have been proven to be the intermediates of disinfection by-products (DBPs) during chlor(am)ination (Joo and Mitch, 2007; Fang et al., 2010a; Yang et al., 2010, 2012; Xu et al., 2011). For examples, Yang et al. (2010, 2012) reported that organic chloramines were the intermediates of nitrogenous disinfection by-products (N-DBPs) such as dichloroacetonitrile (DCAN), trichloronitromethane (TCNM) and cyanogens chloride (CNCl) during chlor(am)ination of organic-N precursors (e.g. glycine, glutamic acid, glycylglycine, etc.). In our previous study of chlortoluron chlorination, organic chloramines were also detected as intermediates of TCNM and DCAN (Xu et al., 2011). Meanwhile, it was found that the reaction rate constants (k) of free chlorine and amino acids/organic amines were higher than 10^4 M^{-1} s^{-1} at pH 7 (Morris, 1967; Yoon and Jensen, 1993), which were 2−80 times faster than that of free chlorine and ammonia (Morris, 1967; Yoon and Jensen, 1993). While during

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chloramination of amino acids/organic amines, the formation rate constants of organic chloramines ($k = 0.1$–15 M^{-1} s^{-1} at pH 7) are much slower than those during chlorination (Snyder and Margerum, 1982; Isaac and Morris, 1983). However, once formed, organic chloramines are stable in water with very small hydrolysis rate ($k < 10^{-5}$ M^{-1} s^{-1} at pH 7) (Yoon and Jensen, 1993) and long half-life (e.g. 34 h for *N*-Chloroisobutyraldimine in water (McCormlck et al., 1993)) and 35 and 58 h for *N*-Chlorophenylacetaldimine in water and wastewater, respectively (Conyers and Scully, 1993). In this way, the formation of organic chloramines delays the formation of DBPs, which will cause high risk of gradual DBP release in the water distribution systems. Therefore, understanding the distribution of organic chloramines is very crucial not only for pathogen disinfection and microbial regrowth prevention but also for DBP control in water distribution systems.

Blooms of cyanobacteria (or blue-green algae, e.g. *Microcystis aeruginosa*) happen commonly due to water eutrophication, which will cause water quality degradation (Yang et al., 2008; Zamyadi et al., 2013) as well as odor and taste problems (Henderson et al., 2008; Fang et al., 2010a; Li et al., 2012). Moreover, algae organic matter (AOM) generated by cyanobacteria, including intracellular organic matter (IOM) and extracellular organic matter (EOM), has been proven to be the cause of algae toxins (e.g. Microcystin-LR) (Daly et al., 2007; Zamyadi et al., 2013; Li et al., 2014). Several preoxidation processes, such as chlorination, ozonation, potassium permanganation and ultraviolet (UV) irradiation, have been widely applied for the removal of cyanobacteria cells (Sakai et al., 2009; Zamyadi et al., 2013; Li et al., 2014). However, after these processes, cyanobacteria cells will be damaged and release IOM (Daly et al., 2007; Zamyadi et al., 2010, 2013; Li et al., 2014). Both IOM and EOM are not easily to be removed by coagulation or preoxidation enhanced coagulation (Widrig et al., 1996; Ma et al., 2006), and their existence will cause many water quality issues during the subsequent chlor(am)ination. Previous studies have proven that AOM (especially IOM) is rich in organic-N matter, such as proteins, amino acids and aliphatic amines (Henderson et al., 2008; Fang et al., 2010a; Li et al., 2012). Organic-N matter with large amount of amino groups should be important precursors of organic chloramines during chlor(am)ination. Previous studies of organic chloramine formation mainly focused on the precursors of individual organic-N compounds (Nweke and Scully, 1989; McCormlck et al., 1993; Conyers and Scully, 1993; Takats et al., 2001) or the sources of raw water (Lee and Westerhoff, 2009). The research of Fang et al. (2010a,b) compared the production of organic chloramines between AOM from *Microcystis aeruginosa* and NOM from Suwannee River (Cat. No. 1R101N) during chlor(am)ination, but the detailed mechanisms of organic chloramine formation from AOM and other NOM species (e.g. humic acid or fulvic acid) remained unclear. Moreover, proteins produced by algal blooms have been proven to be contributed to DBP formation (Scully et al., 1988; Yang et al., 2010), and UV irradiation has been widely applied to remove algae (Sakai et al., 2009). Therefore, the roles of UV irradiation on the formation of organic chloramines and N-DBPs from AOM should be another important concern during chlor(am)ination of drinking water.

The objectives of this study were (1) to assess the effect of AOM in the formation of organic chloramines with influencing factors of free chlorine/NH_2Cl dosage and reaction time, (2) to investigate the relationship between organic chloramine and N-DBP formation, and (3) to study the effect of UV irradiation pretreatment on the formation of organic chloramine and N-DBPs during post-chlor(am)ination. The results could be useful for the operation in drinking water treatment plants to avoid the overestimation of real disinfection efficacy, to know the transformation of organic

chloramines to N-DBPs especially after UV pretreatment, and to find solutions to N-DBP control when algal blooms occur in the source water.

2. Materials and methods

2.1. Chemicals and reagents

The freshwater algae *Microcystis aeruginosa* (FACHB-315) was purchased from the Institute of Hydrobiology, Chinese Academy of Sciences and cultured in a light incubator at 25 °C with BG11 media. After growing to the stationary phase, the algae was centrifuged at 10,000 rpm for 10 min to obtain the cells. The separated cells were washed using Milli-Q water and centrifuged again, and the process was repeated for three times to remove the culturing media. Then the cells were re-suspended with Milli-Q water for three cycles of freeze/thawing to break down algae cells. Finally, the algal IOM could be obtained by filtering the thawed solution through 0.45 μm cellulose acetate membranes (Anpel Co. Led, Shanghai, China) (Daly et al., 2007; Li et al., 2012). IOM was selected as the representative of AOM in this study due to its more organic-N content and less ammonia interference than EOM (Li et al., 2012). Dissolved organic carbon (DOC), UV_{254} and the specific ultraviolet absorbance (SUVA) of the AOM stock solution were 135.7 mg-C/L, 0.624 cm^{-1} and 0.460 L/(m·mg), respectively. Two raw water samples were collected from the intakes of two drinking water treatment plants in Shanghai. One water source was from a reservoir in the center of Yangtze River, and the other was directly from Huangpu River. The water samples were stored at 4 °C in dark after being filtered through 0.45 μm cellulose acetate membranes (Anpel Co. Led, Shanghai, China) before experiments. The characteristics of the two collected raw water samples were shown in Table S1.

All chemical reagents were analytical grade. Trichloroacetonitrile (TCAN), DCAN and TCNM standards, sodium hypochlorite (NaOCl) solution (available chlorine 4.00–4.99%), ammonium chloride (NH_4Cl), NaOH ($\geq$98%), KH_2PO_4 ($\geq$99.0%) were obtained from Sigma-Aldrich (USA). Methyl *tert*-butyl ether (MtBE) was obtained from J.T. Baker (USA). H_2SO_4 was purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Because humic acid and fulvic acid are two important NOM species in natural water, Suwannee River humic acid and fulvic acid (International Humic Substances Society) were selected for the comparison experiments with AOM. Humic acid and fulvic acid stock solutions were also prepared after being filtered through 0.45 μm cellulose acetate membranes (Anpel Co. Led, Shanghai, China) and stored in the dark at 4 °C. NH_2Cl solution was freshly prepared by mixing aqueous NaOCl and NH_4Cl solutions with Cl_2/N molar ratio of 0.8 at pH 8.5 for 0.5–1 h. All solutions were prepared using Milli-Q water produced by a Millipore water purification system (USA).

2.2. Experimental procedures

The raw water samples were chlor(am)inated with 3 mg-Cl_2/L free chlorine or NH_2Cl directly at pH 7.0 with 10 mM phosphate buffer. While humic acid, fulvic acid and AOM samples were all diluted to 5 mg-C/L of DOC at first, and then chlor(am)inated with 5 mg-Cl_2/L free chlorine or NH_2Cl at pH 7.0 with 10 mM phosphate buffer. The raw water samples dosed with 3 mg-Cl_2/L oxidants was due to the low DOC value of Yangtze River (2.3 mg-C/L, Table S1), while 5 mg-Cl_2/L was used in NOM solutions to compensate the rapid disinfectant consumption by the 5 mg-C/L humic acid. In addition, the formation of organic chloramines is related with both DOC and dissolved organic nitrogen (DON) in raw water, but the DOC and DON of raw water samples are very different (see Table S1). It is impossible to set the oxidant dose at the same Cl_2/