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Impact of pre-ozonation on disinfection by-product formation and speciation from chlor(am)ination of algal organic matter of *Microcystis aeruginosa*

Mingqiu Zhu [a,b], Naiyun Gao [a,*], Wenhai Chu [a,*], Shiqing Zhou [c], Zhengde Zhang [d], Yaqun Xu [d], Qi Dai [d]

[a] State Key Laboratory of Pollution Control and Resource Reuse, College of Environment Science and Engineering, Tongji University, Shanghai 200092, China
[b] Jiangsu post & telecommunications planning and designing institute CO., LTD, Nanjing 210019, China
[c] Department of Water Engineering and Science, College of Civil Engineering, Hunan University, Changsha 410082, China
[d] Yixing Jiubin Waterworks, Yixing 214200, China

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ABSTRACT

The increasing use of algal-impacted source waters is increasing concerns over exposure to disinfection byproducts (DBPs) in drinking water disinfection, due to the higher concentrations of DBP precursors in these waters. The impact of pre-ozonation on the formation and speciation of DBPs during subsequent chlorination and chloramination of algal organic matter (AOM), including extracellular organic matter (EOM) and intracellular organic matter (IOM), was investigated. During subsequent chlorination, ozonation pretreatment reduced the formation of haloacetonitriles from EOM, but increased the yields of trihalomethanes, dihaloacetic acid and trichloronitromethane from both EOM and IOM. While in chloramination, pre-ozonation remarkably enhanced the yields of several carbonaceous DBPs from IOM, and significantly minimized the nitrogenous DBP precursors. Also, the yield of 1,1-dichloro-2-propanone from IOM was decreased by 24.0% after pre-ozonation during chloramination. Both increases and decreases in the bromine substitution factors (BSF) of AOM were observed with ozone pretreatment at the low bromide level (50 μg/L). However, pre-ozonation played little impact on the bromide substitution in DBPs at the high bromide level (500 μg/L). This information was used to guide the design and practical operation of pre-ozonation in drinking water treatment plants using algae-rich waters.

1. Introduction

Cyanobacterial blooms frequently occur in lakes and reservoirs, and have become a global problem. Due to the population growth and rising water demand, the drinking water treatment plants (DWTPs) are increasingly treating source waters which are more polluted with blue-green algae (e.g. *Microcystis aeruginosa*) (Graham et al., 2010; Zhang et al., 2011). The undesirable algal organic matter (AOM) released from algal cells, including extracellular organic matter (EOM) and intracellular organic matter (IOM), causes a series of problems in drinking water treatment processes. Especially, AOM contains numerous carbohydrate, amino acids and proteinaceous compounds, all of which are potential disinfection by-product (DBP) precursors (Fang et al., 2010b; Li et al., 2012; Plummer and Edzwald, 2001; Yang et al., 2011). Also, many of these potential DBP precursors are characterized by more hydrophilic content and/or low molecular weight, and therefore likely to be poorly removed by conventional DWTPs using coagulation–sedimentation–filtration (Bond et al., 2012; Chang et al., 2013; Chu et al., 2011; Richardson et al., 2007). Consequently, these may react with disinfectants (e.g., Cl_2 or NH_2Cl) to form carbonaceous DBPs (C-DBPs) and nitrogenous DBPs (N-DBPs). Since their first discovery in 1974, DBPs have been the focus of drinking water regulations, research and WTP operations. Over the last 40 years, the number of DBP classes identified in drinking waters has grown from initially the trihalomethanes (THMs) to now a long list of halogenated and non-halogenated organic and inorganic compounds (Richardson et al., 2007). In the last ten years, N-DBPs have received increased attention, because some studies found that some N-DBPs have higher toxicity than the currently regulated

* Correspondence to: College of Environmental Science and Engineering, Tongji University, Room 308, Mingjing Building, 1239 Siping Road, Yangpu District, Shanghai 200092, China. Fax: +86 021 65986313.
E-mail addresses: gaonaiyun1@126.com (N. Gao), waterman@tongji.edu.cn (W. Chu).

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C-DBPs (Plewa et al., 2007; Richardson et al., 2007). Therefore, in the polluted source waters featuring high cyanobacteria, specific pretreatment processes are necessarily applied to control the formation of C, N- DBPs by reducing their precursors prior to disinfection.

As known, ozone is a powerful oxidant, which is commonly used in the drinking water and wastewater treatment. Some studies reported the effect of pre-ozonation on DBPs formation from natural organic matter (NOM) and/or model compounds (Chu et al., 2012b; Hua and Reckhow, 2007; Yang et al., 2012a; Yang et al., 2008; Zamyadi et al., 2012). However, relatively little studies examined the impact of pre-ozonation on the formation of DBPs from the chlorination and chloramination of AOM. Plummer and Edzwald (2001) reported that pre-ozonation increased the formation of chloroform during chlorination from algae species. Coral et al. (2013) also observed that the formation of THMs and haloacetic acids (HAAs) were increased by 174% and 65%, respectively, when the *Anabaena flos-aquae* suspensions was oxidized by ozone at pH 8. Additionally, a recent study examined that the effect of ozonation and permanganate pretreatment on cyanobacterial cell integrity and chlorinated DBP formation (Xie et al., 2013). However, the impact of pre-ozonation on the formation of C-DBPs and N-DBPs during both chlorination and chloramination of AOM was less investigated. Moreover, in the presence of bromide, the speciation of brominated C-DBPs and N-DBPs in AOM containing water with pre-ozonation and subsequent chlor(am)ination remains unclear.

The objectives of this research were to compare the changes of characteristics of AOM before and after pre-ozonation, and to evaluate the effect of pre-ozonation on the formation and speciation of DBPs from both EOM and IOM during subsequent chlorination and chloramination disinfection. Both regulated DBPs, including three THMs and six HAAs, and emerging DBPs, including two haloacetonitriles (HANs), two haloketones (HKs), and trichloronitromethane (TCNM), were investigated.

2. Materials and methods

2.1. Algae cultivation and reagents

M. aeruginosa (FACHB-912), purchased from Institute of Hydrobiology, Chinese Academy of Sciences (Wuhan, China), was cultured in batch cultivation using BG11 medium at 25 °C for 45 days to allow algal cells to grow into the stationary growth phase (2.57×10^7 cell/mL). The incubator was illuminated by tubular fluorescent lamps with a 12-h diurnal cycle. Algae solution was centrifuged at 7000 rpm for 10 min. The supernatants were filtered through 0.45 μm GF/F membranes (Whatman, UK) and the organic matters in the filtrate represented EOM (Fang et al., 2010b). The deposited algal cells in the centrifuge tubes were washed twice and re-suspended in the Milli-Q water (Daly et al., 2007). The cells were then subjected to three freeze/thawing cycles before centrifuged at 10,000 rpm for 5 min and filtered through 0.45 μm GF/F membranes (Li et al., 2012). The organic matters in the filtrate were referred to IOM.

All reagents and solvents were analytical grade at least. A free chlorine stock solution was prepared from sodium hypochlorite (NaOCl) (free chlorine $>5\%$, Sinopharm Chemical Reagent Co., Ltd., China) and standardized by DPD/FAS titration. Preformed monochloramine (NH_2Cl) was freshly prepared before each test by reacting ammonium chloride and sodium hypochlorite at a molar ratio of [NH_4Cl] / [NaOCl] equaling 1.2:1 for 1 h with rapid stirring. The pH of the solution was adjusted to 8.5 using hydrochloric acid or sodium hydroxide before mixing (Hua and Reckhow, 2013).

2.2. Experimental procedures

Ozonation was conducted by the ozone generator (KT-OZ-3G, Shanghai CONT Environment Protection Technology Co., Ltd., China) bubbling ozone through 600 mL sample in a glass reactor. Ozone was added to samples to achieve the desired concentrations of 1.5 or 3.0 mg/L, and then the samples were stored at 4 °C for no more than 24 h before the chlorination or chloramination experiments (Hua and Reckhow, 2013). In addition, samples were spiked with levels of bromide ion (Br^-) to reach a final concentration of 50 or 500 μg/L, and then the impact of pre-ozonation on the formation of the DBPs was examined. Chlorination and chloramination experiments were carried out at pH 7 and pH 8, respectively. Chlorination experiments were conducted following the method of Xu et al. (2007) and the initial weight ratio of NaOCl (as Cl_2) to total organic carbon (TOC) for each sample was 5. The required dosages of monochloramine in chloramination experiments were adopted from Chu et al. (2012a) and the initial weight ratio of NH_2Cl to TOC for each test was 3. After being dosed with chlorine or monochloramine, samples were sealed in 50 mL amber glass bottles at 25 ± 1 °C in the dark for 3 days (Xie et al., 2013; Yang et al., 2012a). Ascorbic acid at a concentration of 40 mg/L was used to quench chlorine and monochloramine residual before DBPs analysis (Bougeard et al., 2010).

2.3. Analytical methods

TOC and total nitrogen (TN) concentrations were measured using a TOC analyzer equipped with a TNM total nitrogen detection unit (TOC-V_{CPH}, Shimadzu, Japan). Inorganic nitrogen concentrations in the cultivation media were removed by electrodialysis prior to analysis (Vandenbruwane et al., 2007). Then DON concentrations were determined by subtracting the measured nitrite, nitrate, and ammonia concentrations from TN. UV absorbance at 254 nm (UV_{254}) was measured using UV spectrophotometry (HACH DR 2000). Then specific UV absorbance (SUVA) was calculated by dividing UV_{254} values by TOC values. Ozone dose was measured by UV spectrophotometry at 600 nm by the decolorization of indigo trisulfonate (Bader and Hoigné, 1981). Excitation–emission matrix (EEM) measurements were conducted using a Hitachi F-4500 fluorescence spectrophotometer. Excitation wavelengths were incremented from 220 to 500 nm; for each excitation wavelength, the emission was detected from 250 to 550 nm,both with 5 nm increments. Data corrected by ignoring the signals from a blank sample (Chen et al., 2003; Fang et al., 2010b) were analyzed using Surfer Software (Golden Software, Inc. 2002, USA.).

After 3 days incubation, water samples were extracted and then analyzed immediately. THMs, HANs, HKs, and TCNM were determined by liquid/liquid extraction with methyltertiary-butyl-ether (MTBE) and quantified by gas chromatography and triple quadrupole MS (Thermo Fisher Scientific, USA) with a TG-5Ms column ($30\ m \times 0.25\ mm \times 0.5\ \mu m$), based on USEPA Method 551.1. HAAs were determined by liquid/liquid extraction with methyltertiary-butyl-ether (MTBE) followed by derivatization with acidic methanol and quantified by GC–MS-MS, based on USEPA Method 552.2. The temperature programs for DBPs detection were modified as follows: (1) THMs: held at 30 °C for 10 min, ramped to 72 °C at 7 °C/min and held for 1 min, ramped to 220 °C at 40 °C/min and held for 1 min; (2) HANs,HKs and TCNM: held at 30 °C for 10 min, ramped to 72 °C at 7.0 °C/min and held for 1 min, ramped to 220 °C at 40 °C/min and held for 1 min, ramped to 250 °C at 50 °C/min and held for 2 min; (3) HAAs: held at 35 °C for 10 min, ramped to 72 °C at 7.0 °C/min and held for 1 min, ramped to 220 °C at 40 °C/min and held for 1 min, ramped to 250 °C at 50 °C/min and held for 2 min.