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Prechlorination of algae-laden water: The effects of transportation time on cell integrity, algal organic matter release, and chlorinated disinfection byproduct formation

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ABSTRACT

The prechlorination-induced algal organic matter (AOM) released from *Microcystis aeruginosa* (*M. aeruginosa*) cells has been reported to serve as a source of precursors for chlorinated disinfection byproducts (DBPs). However, previous studies have mainly focused on the precursors either extracted directly from the cell suspension or derived immediately after algal suspension prechlorination. This study aims to investigate the impacts of water transportation time after algal suspension prechlorination on cell integrity, AOM release, and DBP formation during the dissolved phase chlorination. The damage to cell integrity after prechlorination was indicated to depend not only on chlorine dose but also on transportation time. The highest dissolved organic carbon (DOC) and dissolved organic nitrogen (DON) values were observed at 2 mg/L chlorine preoxidation before transportation, but were obtained at 0.4 mg/L chlorine after 480-min simulated transportation. The variation of DON with transportation time was indicated to be mainly influenced by the small molecular weight nitrogenous organic compounds, such as amino acids. Additionally, formation of the corresponding chlorinated carbonaceous disinfection byproducts (C-DBPs) and nitrogenous disinfection byproducts (N-DBPs) during the dissolved phase chlorination showed the same variation tendency as DOC and DON respectively. The highest C-DBP (98.4 μg/L) and N-DBP (5.5 μg/L) values were obtained at 0.4 mg/L chlorine preoxidation after 480-min simulated transportation. Therefore, when prechlorination is applied for algae-laden water pretreatment, not only chlorine dose but also transportation time needs to be considered with regard to their effects on cell integrity, AOM release, and chlorinated DBP formation.

1. Introduction

Algae blooms worldwide have arisen increasing interest because of their negative effects on drinking water production. The traditional water treatment process cannot effectively remove algae due to their negatively-charged surface, diverse morphology, low specific density, and high motility (Pieterse and Cloot, 1997; Ma et al., 2007; Takaara et al., 2010). Chlorine, as a commonly used oxidant in algae-laden water preoxidation, has been applied at the intake points of water sources to improve algae removal (Shen et al., 2011). However, some studies have indicated that overdosed chlorine pretreatment may destroy cyanobacterial cells and result in the release of algal organic matter (AOM) to the water sources (Daly et al., 2007; Lin et al., 2009; Ma et al., 2012a).

The AOM released from *Microcystis aeruginosa* (*M. aeruginosa*) cells has been reported to serve as a source of precursors for disinfection byproducts (DBPs), not only carbonaceous disinfection byproducts (C-DBPs) such as trihalomethanes (THMs), halogen acetaldehyde (HAs), haloketone (HKs), and haloacetic acids (HAAs), but also nitrogenous disinfection byproducts (N-DBPs) such as haloacetonitriles (HANs), haloacetamides (HAcAms), and halogenated nitromethane (HNMs) (Plummer and Edzwald, 2001; Huang

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et al., 2009; Zhou et al., 2014a, 2015; Zhu et al., 2015). The formation potential of various C-DBPs and N-DBPs has been studied in detail for the chlorination of AOM extracted from algal cells (Lui et al., 2011; Yang et al., 2011). The prechlorination of algae-laden water has drawn great attention due to induced AOM release and DBP formation problems (Chiu and Wang, 2007). The release of numerous carbohydrates, proteinaceous compounds, and amino acids in AOM can eventually contribute to the chlorinated DBP formation because of their dissolved organic carbon (DOC) and dissolved organic nitrogen (DON) contents (Fang et al., 2010a, 2010b; Wert and Rosario-Ortiz, 2013). Additionally, AOM is rich in organic nitrogen (org-N), and can produce higher quantities of N-DBPs than the natural organic matter (NOM), i.e., humic acid, in chlorination (Fang et al., 2010b). The genotoxicity and carcinogenicity of N-DBPs are higher than those of C-DBPs, such as THMs and HAAs, resulting in the increasing interest in studying N-DBPs (Muellner et al., 2007; Richardson et al., 2007).

However, previous studies on AOM-induced DBP formation have mainly focused on precursors either extracted directly from the cell suspension or derived immediately by the filtration of preoxidized algal suspension (Zamyadi et al., 2012; Wert and Rosario-Ortiz, 2013; Zhou et al., 2014a), and cannot directly reflect or give guidance for practical water treatment scenarios. It should be noted that most highly algae-laden waters, i.e., those in reservoirs and lakes, are far away from drinking water treatment plants (DWTPs). It takes several to dozens of hours for the transportation of preoxidized raw water to DWTPs. The ratios of damaged cells after preoxidation can be increased by the extended transportation time (Qi et al., 2016). This would further influence the AOM release and chlorinated DBP formation process. Therefore, it is meaningful to investigate the impacts of transportation time after algal suspension prechlorination on AOM release and DBP formation during the dissolved phase chlorination.

Based on the aforementioned concerns, this study aims to: 1) investigate the effects of transportation time on algal cell integrity after prechlorination; 2) detect the prechlorination-induced variation of released AOM during simulated transportation; 3) evaluate chlorinated DBP formation from the prechlorination dose and transportation time aspects; 4) clarify the relationship between released AOM and DBP formation.

2. Materials and methods

2.1. Materials and reagents

The algae species used in this study was *M. aeruginosa* because of its prevalence in algae blooms and relevance to water quality and treatment challenges in waterworks (Kemp and John, 2006; Sano et al., 2011). *M. aeruginosa* (strain FACHB-905), previously described by Shen et al. (Shen and Song, 2007), was obtained from Wuhan Institute of Hydrobiology, Chinese Academy of Sciences, and cultured in BG-11 medium (Rippka et al., 1979). The detailed algae growth conditions are presented in Text S1. SYTOX green nucleic acid stain was purchased from Invitrogen, USA. Sodium hypochlorite (NaOCl, Sigma-Aldrich) stock solution and phosphate buffer solution (PBS; 10 mM, pH = 7.5) were prepared just before the experiments. Sodium thiosulfate ($Na_2S_2O_3$) stock solution of 0.5 g/L was prepared every week and stored in darkness. Nineteen amino acids (tryptophan, tyrosine, arginine, phenylalanine, histidine, methionine, glutamate, lysine, glutamine, aspartic acid, asparagine, leucine, isoleucine, threonine, valine, proline, serine, alanine, and glycine) were purchased from Sigma-Aldrich. Standard solutions of the studied DBPs were purchased from AccuStandard (USA).

2.2. Experimental methods

M. aeruginosa cultures were harvested at the exponential growth phase and then diluted with PBS after centrifugal cleaning (4500 rpm, 10 min; three cycles of centrifugation and supernatant removal) to obtain the cell density of 1.0×10^6 cells/mL for all experiments. In order to study the effects of prechlorination dose and simulated transportation time on the damage to cell integrity, release of AOM and formation of chlorinated DBPs, algal suspensions were rapidly mixed at 250 rpm for 5 min after the addition of chlorine (0, 0.2, 0.4, 0.8, 2 mg/L); $Na_2S_2O_3$ was then added to quench the preoxidation, followed by slowly mixing at 40 rpm for 0–480 min to simulate long-term transportation. All the experiments were conducted in the dark according to the practical transportation condition of raw water to drinking water treatment plants. In addition, the mixing speed of 80 rpm was also conducted to check the influence of flow velocity on algal cell integrity after 0.2 mg/L chlorine preoxidation. Samples were siphoned after different mixing time (0, 30, 60, 120, 240, 480 min) and divided in two subsamples: the first sample was evaluated for cell integrity detection. The remaining sample was immediately filtered through a 0.45 μm glass fiber filter for the concentrations determination of DOC, DON, protein, and amino acids, and the subsequent experiments on chlorinated DBP formation.

The experiments assessing the chlorinated DBPs formed during the chlorination of the dissolved phase in preoxidized algal suspensions were carried out in amber glass bottles capped with Teflon-faced septa. The mass ratio of chlorine dosage (as Cl_2) to DOC was 3:1. The chlorinated samples were maintained at 25 ± 1 °C in the dark for 72 h and then quenched with ascorbic acid (Sigma-Aldrich) for the chlorinated DBP analyses.

2.3. Analytical methods

2.3.1. Cell integrity detection

Cell integrity was determined for individual cells using a flow cytometer (FACSCalibur 4CLR, BD Biosciences, San Jose, USA) equipped with an argon ion laser emitting at a fixed wavelength of 488 nm for fluorescence measurement. Full details of the cell integrity analysis are presented in Text S2. Scanning electron microscopy (SEM; SU-8020, Hitachi, Japan) was used to observe the morphologies of the cyanobacterial cells.

2.3.2. Analysis of DOC and DON

The DOC concentration in the dissolved phase of algal suspensions was measured with a Shimadzu TOC-V_{CPH} analyzer. A Flow-Access continuous flow analyzer (SAN^{++}, SKALAR, Netherlands) was used to determine the nitrite, nitrate, and ammonia concentrations. DON concentrations were determined by subtracting the measured nitrite, nitrate, and ammonia concentrations from total nitrogen. The total nitrogen was analyzed as nitrate after potassium persulfate oxidation (Delia et al., 1977).

2.3.3. Measurement of protein and amino acids

Soluble protein was measured with a Micro BCA™ Protein Assay Kit (Thermo Scientific) (Smith et al., 1985). Identification and quantification of amino acids were carried out using an Agilent 1290 liquid chromatography system (Agilent, USA) equipped with a QQQ (Agilent6460, USA) tandem mass spectrometer. An ACQUITY UPLC® HSS T3 column (2.1 mm × 100 mm, 1.8 μm) (Waters, USA) was used for separation. The total run time was 50 min for each sample. Other details of conditions can be found in Text S3.

2.3.4. DBPs analysis

Chloroform (TCM), chloral hydrate (CH), dichloroacetone (DCP),