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Characteristics of C-, N-DBPs formation from algal organic matter: Role of molecular weight fractions and impacts of pre-ozonation

Shiqing Zhou [a], Shumin Zhu [a], Yisheng Shao [a,b,*], Naiyun Gao [a]

[a] State Key Laboratory of Pollution Control and Resource Reuse, Tongji University, Shanghai 200092, China
[b] China Academy of Urban Planning & Design, Beijing 100037, China

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ABSTRACT

Extracellular organic matter (EOM) and intracellular organic matter (IOM) of *Microcystis aeruginosa* have been reported to contribute to the formation of carbonaceous disinfection by-products (C-DBPs) and nitrogenous disinfection by-products (N-DBPs). Little is known about DBPs formation from different molecular weight (MW) fractions, especially for N-nitrosodimethylamine (NDMA). This study fractionated EOM and IOM into several MW fractions using a series of ultrafiltration membranes and is the first to report on the C-DBPs and N-DBPs formation from chlorination and chloramination of different MW fractions. Results showed that EOM and IOM were mainly distributed in low-MW (<1 KDa) and high-MW (>100 KDa) fractions. Additionally, the low-MW and high-MW fractions of EOM and IOM generally took an important part in forming C-DBPs and N-DBPs, either in chlorination or in chloramination. Furthermore, the effects of pre-ozonation on the formation of DBPs in subsequent chlorination and chloramination were also investigated. It was found that ozone shifted the high-MW fractions of EOM and IOM into lower MW fractions and increased the C-DBPs and N-DBPs yields to different degrees. As low-MW fractions are more difficult to remove than high-MW fractions by conventional treatment processes, therefore, activated carbon adsorption, nanofiltration (NF) and biological treatment processes can be ideal to remove the low-MW fractions and minimize the formation potential of C-DBPs and N-DBPs. Moreover, the use of ozone should be carefully considered in the treatment of algal-rich water.

1. Introduction

Blooms of cyanobacteria are ubiquitous in lakes and reservoirs and pose a great challenge for drinking water supplies (Xie et al., 2013; Yang et al., 2008; Zamyadi et al., 2013). Specific cyanobacteria species (e.g., *Microcystis aeruginosa*) generate a variety of algal organic matter (AOM), including extracellular organic matter (EOM) and intracellular organic matter (IOM). EOM are the excreted metabolities of algal cells during exponential and stationary growth phases, whereas IOM result from cell lysis by aging of algae population and pre-oxidation

* *Corresponding author*. State Key Laboratory of Pollution Control and Resource Reuse, Tongji University, Shanghai 200092, China. Tel./fax: +86 21 65982691.
E-mail address: yishengshao2011@163.com (Y. Shao).
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in water treatment process (Coral et al., 2013; Henderson et al., 2008; Pivokonsky et al., 2006). These organic substances are poorly removed by coagulation or pre-oxidation enhanced coagulation, and contribute to carbonaceous disinfection by-products (C-DBPs) or nitrogenous disinfection by-products (N-DBPs) formation during chlor(am)ination due to the dissolved organic carbon (DOC) and dissolved organic nitrogen (DON) content (Fang et al., 2010a, 2010b; Li et al., 2012; Wert and Rosario-Ortiz, 2013).

The characterization of EOM and IOM has been reported in the literature, with respect to aromaticity (SUVA), fluorescence, hydrophobicity, proteins, carbohydrates, and molecular weight (MW) distribution (Henderson et al., 2008; Her et al., 2004; Li et al., 2012; Nguyen et al., 2005). In general, EOM and IOM are considered to contain more organic nitrogen (low DOC/DON), more hydrophilic content, and less aromatic content (low SUVA) (Fang et al., 2010b; Henderson et al., 2008; Li et al., 2012). Henderson et al. (2008) found that the AOM of *Microcystis aeruginosa* was dominated by proteins and polysaccharides, and had bimodal MW distribution with 55% greater than 30 KDa and 38% less than 1 KDa. In another study, Li et al. (2012) observed that IOM's MW fractions in <1 KDa, 40–800 KDa, and >800 KDa were ~27%, 42%, and 31%, respectively, while MW of the primary EOM molecules ranged within 1–100 KDa. Furthermore, size fractionation results of Qu et al. (2012) showed that the DOC fractions of high-MW (>100 KDa) and low-MW (<1 KDa) in the EOM of *Microcystis aeruginosa* accounted for 42.91% and 24.9% of total DOC. Meanwhile, 27.70% and 31.79% of total proteins, and 27.73% and 40.44% of total polysaccharides were distributed in the high-MW and low-MW fractions, respectively.

Cyanobacteria-derived organic matter have been identified for decades as potential precursors for various C-DBPs and N-DBPs (e.g., trihalomethanes (THMs), haloacetic acids (HAAs), haloacetonitriles (HANs), trichloronitromethane (TCNM), and *N*-nitrosamines) (Bond et al., 2011, 2012; Hoehn, 1980; Hong et al., 2008; Huang et al., 2009). Fang et al. (2010b) reported that the EOM of *Microcystis aeruginosa* formed smaller quantities of C-DBPs and N-DBPs than did IOM and algal cell, in chlorination and chloramination. Li et al. (2012) showed that the specific yields of chloroform and chloroacetic acid were 21.46 and 68.29 μg/mg C for IOM, and 32.44 and 54.58 μg/mg C for EOM, respectively. Moreover, *N*-nitrosodimethylamine (NDMA) formation has also been reported from cyanobacteria-derived organic matter after chlorination and chloramination (Fang et al., 2010b; Li et al., 2012; Zamyadi et al., 2012). While there have been several studies investigating the DBPs formation of EOM and IOM, little is known about the DBPs formation potential (DBPFP) from different molecular weight fractions, especially for the formation of NDMA.

Pre-ozonation prior to disinfection has often been used as a pre-treatment ahead of the conventional process in drinking water treatment (Coral et al., 2013; Hua and Reckhow, 2013). Previous studies showed that ozone can react with some DBP precursors and affect the formation of DBPs depending on the water qualities and DBP species. For example, Plummer and Edzwald (2001) reported that pre-ozonation increased the chloroform formation to different degrees during chlorination of two algae species. Hua and Reckhow (2007) showed that pre-ozonation decreased THMs, HAAs and total organic halogen (TOX) for most natural waters, while increased these DBPs for a water of low humic content. Wert and Rosario-Ortiz (2011) exhibited that pre-ozonation reduced the formation of THMs by up to 10 μg/L and the sum of five HAAs by up to 5 μg/L at two full-scale drinking water facilities. Therefore, a sequential ozone-chlorination (O_3–Cl_2) or ozone-chloramination (O_3–NH_2Cl) process would be necessary to investigate the impact of pre-ozonation on C-DBPs and N-DBPs formation from EOM and IOM.

The objective of this study were: (1) to compare different molecular weight characteristics of EOM and IOM from *Microcystis aeruginosa*; (2) to evaluate the contributions of different molecular weight fractions on the formation of C-DBPs and N-DBPs; (3) to investigate the effects of pre-ozonation on the formation of DBPs during subsequent chlorination and chloramination.

2. Materials and methods

2.1. Algae cultivation and AOM extraction

Microcystis aeruginosa (FACHB-912) was obtained from the Institute of Hydrobiology, Chinese Academy of Sciences, and cultured in BG11 media. The cultures were incubated at 25 °C in 1 L conical flasks, under a 12-h diurnal cycle every day. *M. aeruginosa* cells in late exponential growth phase were harvested and centrifuged at 10,000 *g* for 10 min. The supernatants were subsequently filtered through 0.7 μm GF/F glass-fiber filters (Whatman), and the filtrates were referred as EOM. Thereafter, the remaining cell pellets in glass-fiber filters together with centrifugal sediments were washed three times and then re-suspended in ultrapure water (Milli-Q, USA). The cells were then exposed to three freeze/thawing cycles to release the intracellular materials, followed by centrifuging and filtration. The filtrates were used as IOM.

2.2. MW fractionation of EOM and IOM

EOM and IOM were fractionated into different fractions using a series of ultrafiltration (UF) membranes (polyethersulfone; Sartorius, Germany) with MW cut-offs of 100, 30, 10, 5, and 1 KDa, respectively. The fractionation experiment was conducted in a 400 mL stirring cell (Amicon 8400, Millipore Corp., USA) under a constant nitrogen gas pressure of 0.1 MPa. Prior to the operation, ultrapure water was filtered through the membranes to remove any possible leached organics until the DOC of the effluent was less than 0.1 mg-C/L. After UF separation, the filtrates were analyzed for their organic contents and tested for DBP formation potentials (DBPFP). Finally, the DOC, DON, UV_{254} and DBPFP of EOM and IOM fractions within the MW ranges of <1, 1–5, 5–10, 10–30, 30–100 and >100 KDa were determined.

2.3. DBP formation potential experiments

The C- and N-DBPFP experiments during chlorination and chloramination were carried out using sealed 300 mL amber bottles at 25 °C in the dark for 3 days. The doses of chlorine