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Use of fluorescence excitation–emission matrices coupled with parallel factor analysis to monitor C- and N-DBPs formation in drinking water recovered from cyanobacteria-laden sludge dewatering

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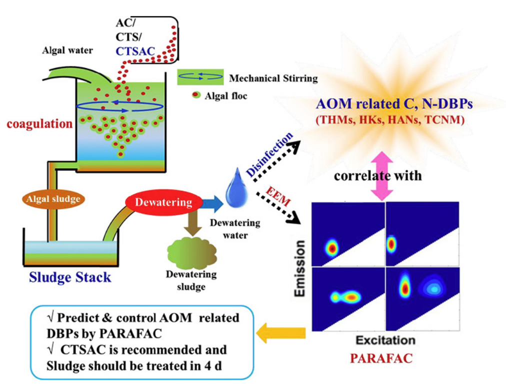
HIGHLIGHTS

- AOM and cyanobacteria-related C-, N-DBP formation was first studied by EEM-PARAFAC.
- THMs and HANs have strong linear relationship with tryptophan-like substance.
- TCNM formation was correlated strongly with amino acid-like substance.
- The optimal coagulant specie and sludge storage time were obtained.

GRAPHICAL ABSTRACT



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ABSTRACT

This is the first time that correlations between the spectroscopic properties of algal organic matter (AOM) and cyanobacteria-related C- and N-disinfection byproduct (DBP) formation have been presented. Three types of coagulants, aluminium chloride (AC), chitosan (CTS) and a composite chitosan-aluminium chloride (CTSAC), were selected to assess and compare the performance of coagulation to control DBPs formation in dewatering water (DW). Fluorescence excitation–emission matrices (EEMs) coupled with parallel factor analysis (PARAFAC) indicated that four components dominated the EEM of the DW samples. Examination of C-, N-DPBs formation and attendant changes in the AOM parameters allows the establishment of strong linear relationships between yields of the trihalomethanes, haloacetonitriles and trichloronitromethane and the relative changes in the fluorescence compounds. Stronger linear correlations were found between trihalomethanes and tryptophan-like substance C1 ($r = 0.918$), between haloacetonitriles and C1 ($r = 0.934$), and between trichloronitromethane and amino acid-like substance C2 ($r = 0.915$) than other AOM parameters, suggesting that tryptophan-like substance and amino acid-like substance in AOM play major roles in generating cyanobacteria-related DBPs upon chlorination. Furthermore, because the CTSAC composite was effective in removing fluorophores and caused little cell lysis during the first 4 days of sludge storage, the production of C-, N-DBPs in the DW was lower than those in the AC or CTS systems for the same storage period. This indicates the feasibility of surrogate monitoring of the production of cyanobacteria-related C-, N-DBPs via online measurements of water EEM fluorescence. CTSAC composite

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coagulant is thus recommended, and the sludge should be disposed of within 4 days to obtain DW with lower DBPs formation potentials.

1. Introduction

Frequent cyanobacterial blooms in lakes or reservoirs are a great challenge of drinking water treatment process. Specific algal species that cause cyanobacterial blooms (e.g. *Microcystis aeruginosa*) release undesirable algal organic matter, which can cause a variety of problems in drinking water treatment processes (Li et al., 2012). In particular, algal organic matter (AOM) leads to production of carbonaceous disinfection byproducts (C-DBPs) and nitrogenous disinfection byproducts (N-DBPs) during the disinfection process which was resulted from the high dissolved organic carbon (DOC) and dissolved organic nitrogen (DON) content (Fang et al., 2010a; Li et al., 2012). Most of the AOM contained within algal cells is intracellular organic matters (IOM), whereas the metabolites released into surrounding environment during growth phases are extracellular organic matters (EOM). It was identified that the chlorination of IOM produced greater quantities of C-, N-DBPs than was the case for EOM (Fang et al., 2010b).

It should be noted that the IOM can be released into the surrounding environment when cell lysis occurs, and to remove EOM is more difficult than IOM which is contained within cells (Li et al., 2012). Therefore, effective removal of intact cyanobacteria cells should be a significant part of drinking water treatment process to control cyanobacteria related DBPs production. Coagulation treatment which is a key unit in conventional drinking water treatment plants (DWTPs) to remove algae, has been reported as an effective method to remove algal cells (Zamyadi et al., 2013).

Our previous studies confirmed the application of several inorganic and organic coagulants (e.g. aluminium chloride and chitosan) could effectively remove intact cyanobacterial cells which could remove IOM simultaneously, but they were ineffective at the removal of extracellular EOM (Pei et al., 2014; Sun et al., 2012). To improve the coagulation efficiency, we have proposed a novel chitosan–aluminium chloride composite, which is not only able to remove intact cyanobacterial cells, but can also adsorb large amount of EOM (Ma et al., 2016a). Therefore, the risk posed by toxic cyanobacteria-related DBPs could be largely alleviated due to the effective intact cyanobacterial cells removal, which would remove IOM, while reducing EOM.

The flocs containing intact cyanobacterial cells form the solid phase and accumulate in the drinking water sludge after coagulation and sedimentation processes. It should be noted that large volumes of drinking water sludge are generated from coagulation process: about 7% of the plant throughput (Razali et al., 2007). Due to population growth and increasing water demand, much more drinking water treatment sludge is generated and dewatered, and then the collected water was recycled to the head of drinking water treatment plants (DWTPs) to minimize the discharge to sewage from the DWTPs (Zhou, 2011).

However, during the treatment process of cyanobacteria contained drinking water sludge, there is still a risk of damage occurring to the cyanobacteria resulting in the release of undesirable IOM into the recycled water, thus exacerbating DBPs formation in the following disinfection process. Previous studies reported that cyanobacterial cells coagulated by the conventional AC coagulant, organic CTS coagulant and the novel CTSAC composite coagulant lysed on different days during sludge storage (Ma et al., 2016a; Pei et al., 2014; Sun et al., 2012). Thus, even though the CTSAC composite is able to largely reduce the risk of DBPs after coagulation compared to conventional or organic coagulant, it may promote the production of cyanobacteria-related DBPs after storage of cyanobacteria-containing sludge.

To minimize risk of cyanobacteria-related DBPs, and reduce the formation of DBPs by application of optimal coagulant along with processing of coagulated sludge before DBPs increase in DW. To date, there is still little available information on C- and N-DBPs formation from AOM in DW generated from cyanobacteria-containing drinking water sludge.

Fluorescence spectroscopy, which could rapidly and efficiently examining the quality and quantity of dissolved organic matter (DOM), has become increasingly popular to predict DBPs formation (Wei et al., 2016a; Wei et al., 2015; Yang et al., 2015). In particular, fluorescence excitation–emission matrices (EEM) coupled with parallel factor analysis (PARAFAC) has been valuable tool for sensitively recognizing different fluorescing compounds and tracking their variations (Baghoth et al., 2011; Murphy et al., 2008; Stedmon and Markager, 2005; Wei et al., 2016b). PARAFAC is an analytical technique to extract the information contained in an EEM dataset, identify individual components, and decompose them into component concentration (Stedmon and Bro, 2008; Wei et al., 2016b).

EEM–PARAFAC has been remarkably successful in characterizing DOM and establishing relationships between derived components and DBPs in several applications, such as: indicating that a humic-like component related with higher aromaticity has a higher tendency to form THMs and haloacetic acid (HAA) upon chlorination during storm events (Nguyen et al., 2013); and determining that protein-like and humic-like compounds correlated with chloral hydrate and trichloronitromethane (TCNM) yields in disinfection of leachates from different aged leaf litter (Jian et al., 2016). However, the utilization of EEM–PARAFAC for predicting a number of emerging cyanobacteria-related C- and N-DBPs has not been tested yet. It is significant to assess whether relationships between spectroscopic properties and cyanobacteria-related DBPs can be built, due to the increasing interest in performing on-line monitoring of drinking water treatment processes.

The aims were as follows: (1) test the effects of different coagulants on the formation of cyanobacteria-related C-,N-DPBs in DW following storage of the cyanobacteria-containing sludge as in DWTPs; (2) find a coagulant which improves the water quality in DW; and (3) examine the correlations between cyanobacteria-related C- and N-DBPs and PARAFAC components, so as to determine whether fluorescence spectroscopy could be used to monitor cyanobacteria-related C-, N-DBPs in treatment process of drinking water. A composite coagulant (CTSAC), an organic coagulant (CTS) and an inorganic coagulant (AC) were used to comparatively study coagulant effects on DBP formation in the DW. The C-DBPs, including THMs and haloketones (HKs), and N-DBPs, including haloacetonitriles (HANs) and TCNM, were measured in this study. To the best of our knowledge, the relationships between PARAFAC components and cyanobacteria-related C-,N-DBPs, as well as the production of C-,N-DPBs in the DW collected from cyanobacteria-laden sludge generated with different kinds of coagulant (inorganic, organic, and composite) has not been reported. This study will provide valuable information for real-time monitoring of DBPs and optimization of the drinking water treatment process.

2. Materials and methods

2.1. Algae cultivation

The cyanobacterial strain of *Microcystis aeruginosa* (FACHB-905) was provided by the Institute of Hydrobiology, Chinese Academy of Sciences. It was cultured in BG11 under a light–dark regime of 14 h/10 h with