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Interactions of specific extracellular organic matter and polyaluminum chloride and their roles in the algae-polluted water treatment

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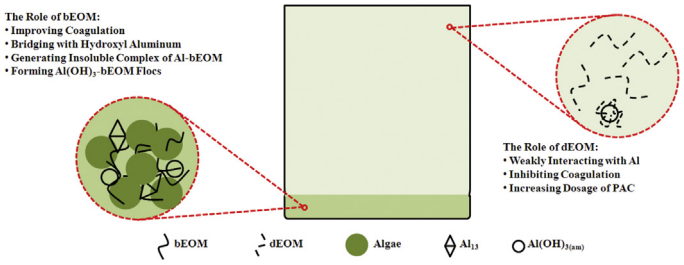
HIGHLIGHTS

- bEOM as a bond between algae cells and PAC improved the algae treatment.
- dEOM weakly reacted with PAC or inhibited coagulation.
- Al_{13} and $Al(OH)_{3(am)}$ played an essential role in the dEOM and bEOM treatment.
- It was recommended to treat the algae at its initial growth stage.

GRAPHICAL ABSTRACT



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ABSTRACT

Extracellular organic matter (EOM) is ubiquitous in the algae-polluted water and has a significant impact on the human health and drinking water treatment. We investigate the different characteristics of dissolved extracellular organic matter (dEOM) and bound extracellular organic matter (bEOM) recovered from the various growth period of *Microcystis aeruginosa* and the interactions of them and polyaluminum chloride (PACl). The roles of the different EOM in the algae-polluted water treatment are also discussed. The functional groups of aromatic, O—H, N—H, C—N and N—O in bEOM possessing the stronger interaction with hydroxyl aluminum compared with dEOM is responsible for bEOM and algae removal. Some low molecular weight (MW) organic components and protein-like substances in bEOM are most easily removed. And dEOM weakly reacts with PACl or inhibits coagulation, especially dEOM with the high MW organic components. The main coagulation mechanisms of bEOM are the generation of insoluble Al-bEOM through complexation, the bridge of $AlO_4Al_{12}(OH)_{24}(H_2O)_{12}^{7+}$ (Al_{13}), the adsorption of $Al(OH)_{3(am)}$

Abbreviations: PACl, polyaluminum chloride; AOM, algae organic matter; IOM, intracellular organic matter; EOM, extracellular organic matter; dEOM, dissolved extracellular organic matter; MW, molecular weight; Al_{13}, $AlO_4Al_{12}(OH)_{24}(H_2O)_{12}^{7+}$; XPS, X-ray photoelectron spectroscopy; TOC, total organic carbon; DOC, dissolved organic carbon; SUVA, specific ultraviolet absorbance; FEEM, fluorescence excitation-emission matrix; GPC, gel permeation chromatography; FTIR, Fourier transform infrared spectroscopy; UV_{254}, ultraviolet absorbance at 254 nm; EP, exponential phase; SP, stationary phase; DP, decline phase; T_1, tryptophan-like substances (in the FEEM spectra); T_2, aromatic-like substances; A, humic-like substances; C, fulvic-like substances; S, soluble microbial product-like substances; Al^{IV}, tetrahedral Al; Al^{VI}, octahedral Al.

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and the entrapment of flocs. The adsorption of Al_{13} and $Al(OH)_{3(am)}$ mainly contribute to dEOM removal. It is also recommended to treat the algae with dEOM and bEOM at the initial stage.

1. Introduction

Algae blooms have become a serious environmental issue and made a challenge to the water treatment in the countries all over the world [1,2]. Aside from the problems caused by the excessive reproduction of algae, algae organic matter (AOM) yielded by them also threaten human health and increase the cost of water treatment plant [3]. AOM has been discovered in most algae, such as *Microcystis aeruginosa, Scenedesmus quadricauda, Anabaena flos-aquae, Fragilaria crotonensis, Chlamydomonas geitleri* and so on [4–6]. It can be generally classified into two groups, intracellular organic matter (IOM) and extracellular organic matter (EOM). And EOM originated from metabolic activity of algae and cell lysis is suggested to reduce the coagulation efficiency [7], accelerate the membrane fouling [8,9] and to be transformed into disinfection by-products (DBPs) in the chlorination [3]. However, little information is available on the specific EOM which is responsible for the adverse effects in the water purification. Dissolved extracellular organic matter (dEOM) and bound extracellular organic matter (bEOM) are two essential part of EOM. dEOM exists in the culture medium and bEOM adheres to the cell surface respectively [10,11]. In the membrane treatment, EOM has a critical influence on membrane fouling [12]. The membrane flux is reduced sharply when dEOM is dominant due to forming the denser cake layer while the small molecules in bEOM results in the more serious irreversible fouling [10]. Besides, dEOM and bEOM might play the critical roles in the water treatment, especially in the coagulation.

Coagulation as an important water treatment technology is widely applied in the algae removal and harvesting [13]. The effects of EOM on the coagulation are still controversial. Although EOM as the flocculation aid improves the coagulation efficiency [14], some EOM easily form the chelate complexes with coagulant, which significantly increases the amount of coagulant dosage and reduces the treatment efficiency [7,15,16]. The specific EOM might make this difference. Thus, it is interesting to further investigate the roles of specific EOM in the coagulation. Besides, no attention yet focused on the interactions of specific EOM and coagulant, but a better understanding of their relationship is an important step towards revealing the coagulation mechanism in algae treatment.

M. aeruginosa was one of the most popular algae species in the algal bloom. In this study, the specific EOM, dEOM and bEOM, were collected at its different growth phase. And the removal performances of dEOM and bEOM were detected according to the analysis of dissolved organic carbon (DOC), specific ultraviolet absorbance (SUVA), ultraviolet spectroscopy, molecular weight (MW) and fluorescence excitation-emission matrix (FEEM) spectroscopy before and after coagulation. And the interactions of EOM and polyaluminum chloride (PACl) were further investigated via fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS). The implications of coagulation mechanism in algae, dEOM and bEOM removal were discussed.

2. Materials and methods

2.1. Cultivation of M. aeruginosa

M. aeruginosa supplied by the Freshwater Algae Culture Collection at the Institute of Hydrobiology (China) was cultivated in BG11 medium at 25 °C with continuous mixing by a shaking apparatus. And the cultures of *M. aeruginosa* were illuminated at a 12 h-light/12 h-dark cycle [4,17]. The growth of *M. aeruginosa* was monitored by measuring cell count and absorbance at 680 nm [5]. Cell count was performed using a light microscope (Olympus Corporation, Japan) and hemocytometer. Absorbance was determined by a TU-1900 ultraviolet/visible (UV/VIS) spectrophotometer (Purkinje General Instrument Co., Ltd., China). The inoculation concentration of *M. aeruginosa* is about 6×10^6 cells/ml in the experiment. The concentration of *M. aeruginosa* in the culture after inoculating is about 1.50×10^5 cells/ml, and the algae are in the lag phase.

2.2. dEOM and bEOM extraction

Culture and algae cells were respectively separated and harvested at different growth periods. The culture was centrifuged at 4000 round/min for 15 min in a high-speed versatile refrigerated centrifuge (Eppendorf, Germany). The supernatant was filtered through 0.45 μm membrane filter to remove the residual cells, and the filtrate was referred to as dEOM solution [10,18]. The collected algae cells via centrifugation and filtration were re-suspended by the same volume of 0.6% NaCl solution. The solution was centrifuged at 10,000 round/min for 15 min. And bEOM solution was obtained after the supernatant was filtered through 0.45 μm membrane filter [10,18].

2.3. Characterization of dEOM and bEOM

2.3.1. DOC, ultraviolet spectroscopy and SUVA

Dissolved organic carbon of dEOM and bEOM was measured by a Liqui TDC II total organic carbon (TOC) analyzer (Elementar, Germany). It was calculated via subtracting inorganic carbon from total carbon. The standard samples of inorganic carbon and total carbon with the concentration of 10 and 50 mg/L were used as the control. The UV/Vis spectrophotometer was used to scan a range of absorbance values from 190 to 400 nm with a 1 cm quartz cell. The ultraviolet absorbance at 254 nm (UV_{254}) was also obtained, and the specific UV absorbance (SUVA) was calculated as Eq. (1) [5,19]:

$$SUVA = UV_{254}(cm^{-1})/DOC(mg/L) \times 100 \quad (1)$$

2.3.2. Fluorescence excitation-emission matrix spectroscopy

FEEM spectra were recorded on a F-7000 fluorescence spectrometer (Hitachi High Technologies, Tokyo). Emission spectra were scanned from 200 nm to 550 nm with 1 nm increment and excitation spectra were scanned from 200 nm to 450 nm with 5 nm increments. The slits of emission and excitation were 5 nm and PMT voltage was set at 725 V [6,20]. Deionised water blanks were run every 4 analyses and the intensity of the Raman line of water was measured to monitor instrument stability [6].

2.3.3. Gel permeation chromatography analysis

Molecular weight (MW) distributions of dEOM and bEOM were assayed using gel permeation chromatography (GPC) (Waters, USA) which mainly consisted of Waters™ 2487 dual λ absorbance detector, Waters™ 515 HPLC pump, and WAT011545 Ultrahydrogel™ linear column (7.8 × 300 mm, effective molecular