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Understanding ultrafiltration membrane fouling by extracellular organic matter of *Microcystis aeruginosa* using fluorescence excitation–emission matrix coupled with parallel factor analysis

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HIGHLIGHTS

- EEM–PARAFAC based approach was proposed for EOM fouling analysis.
- Tryptophan-like and polysaccharides in EOM proved the major foulants.
- Major irreversible foulants changed according to interaction between foulants.
- Hydrophobic adhesion was drastically enhanced under acid solution condition.

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ABSTRACT

This study presents a novel approach evaluating the foulant properties of extracellular organic matter (EOM) on ultrafiltration (UF) by examining the organic matter properties of the feed, permeate, reversible and irreversible foulant layers using excitation–emission matrix coupled with parallel factor analysis (EEM–PARAFAC) together with dissolved organic carbon (DOC) and polysaccharide analysis. Fate of each EOM component as well as total carbon mass balance under various solution chemistries were illustrated, and major foulants and fouling mechanisms involved were identified. Component 1 (i.e. tryptophan-like substances) and polysaccharides were identified as the major foulants under all solution chemistries, but major irreversible foulants changed under different solution chemistries. Under the ambient solution chemistry, polysaccharides contributed more to irreversible fouling, while Component 1 fouling turned out to be more irreversible with the presence of calcium. Calcium bridging effect, pore blocking and initial pore-competition resulted in the changes above. The significant increase of irreversible fouling observed under acid condition was attributed to the extremely enhanced hydrophobic adhesion between hydrophobic foulants (Component 1 and Component 3) and polyethersulfone (PES) membrane. The proposed EEM–PARAFAC based approach proved suitable for major foulant identification and mechanism implication, suggesting its potential for analyzing membrane fouling caused by complex matrix.

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1. Introduction

Low-pressure membrane processes, which include microfiltration (MF) and ultrafiltration (UF), are receiving increased attention in drinking water treatment due to their high cost-effectiveness [1,2]. However, efficient application of low-pressure membrane processes is significantly reduced by membrane fouling. Membrane fouling contributes to increased operational costs and need for frequent chemical cleaning, as well as shortened membrane service life. The frequent occurrence of algal blooms in water sources poses a serious challenge to the membrane filtration process [3]. Algae-rich water can cause serious membrane fouling, and extracellular organic matter (EOM) secreted by algae is widely regarded as major foulants [3–5]. Therefore, understanding of fouling mechanisms involved in low-pressure membrane fouling with EOM is of practical importance for sustainable application of low-pressure membrane processes.

Membrane fouling caused by EOM has been widely investigated [3–7]. With foulant fractionation techniques (i.e. size fractionation and hydrophobicity fractionation), sub-fractions of EOM with different characteristics were obtained, and then fouling contribution of each part could be examined individually. It was found that the high-molecular weight (MW) fraction of EOM contributed to a significant portion of fouling, while hydrophobic and hydrophilic components in EOM were respectively responsible for irreversible fouling and flux decline during membrane filtration [5,7,8]. Moreover, it was demonstrated that most of high-MW EOM was proteins and polysaccharides, while hydrophobic part of EOM was dominated by proteins and hydrophilic part was dominated by polysaccharides [5,9]. Therefore, proteins and polysaccharides

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in EOM proved the major foulants in membrane fouling [10]. However, these results still seem limited and incomplete because interactions between different components and other complex matrix effects of EOM during fouling were not considered in the fractionation approach [11].

In order to avoid this problem, filtering the integral solution (without pre-fractionation) and characterizing the fates of sub-fractional components during the membrane filtration will provide relevant information on the fouling contribution of each component, but not interfere with the intact of the feed solution. This approach will incorporate the matrix effects of EOM into the fouling analysis. However, in the approach proposed above, an expeditious and informative characterization technique for dissolved organic matter (DOM) and its sub-fractional components is necessary. Three-dimensional excitation and emission matrix (EEM) fluorescence spectroscopy has proved such an eligible technique. Without any preparation of a sample, it can promptly and sensitively (at least an order of magnitude more sensitive than ultraviolet absorbance, UVA) characterize the sub-fractional components of DOM [12]. EEM has been widely employed in EOM studies, and protein-like and humic-like compositions in the EOM were identified [5,6,8,9]. However, it is hard for previous works to present accurately quantitative information because they only examined the major peaks, i.e. a limited number of excitation–emission coordinated pairs of EEM [5,6,9]. The rather qualitative data obtained by this visual inspection cannot be used to calculate the fates of organic components.

In order to present EEM data more quantitatively, multi-way data analysis was used to process the three-dimensional EEM fluorescence data. Multi-way data analysis using parallel factor (PARAFAC) analysis was found to be able to decompose the complex EEMs into independent fluorescent components [13,14]. The term multi-way is used to describe data with more than two dimensions. Fluorescence EEM data are multi-way (three-way) as the fluorescence of a sample varies depending on the wavelength of light absorbed (excitation) and the wavelength at which fluorescence is observed (emission). Combining the data from a series of samples results in a three-way data. PARAFAC models three-way data using Eq. (1), fitting the equation by minimizing the sum of squares of the residuals (ε_{ijk}) [13].

$$x_{ijk}=\sum_{f=1}^{F} a_{if} b_{jf} c_{kf}+\varepsilon_{ijk}, i=1,2,..,I; j=1,2,..,J; k=1,2,..,K; \quad (1)$$

x_{ijk} is one element of the three-way data array with dimensions I, J and K. In the analysis of EEMs, the number x_{ijk} is the fluorescence intensity of sample i measured at emission wavelength j and excitation wavelength k. The final term ε_{ijk} represents the unexplained signal (residuals containing noise and other un-modeled variation). The outcome of the model is the parameters a, b and c. Ideally, these respectively represent the concentration, emission spectra, and excitation spectra of the underlying fluorophore groups (components). The fluorescent components can be identified according to their emission spectra and excitation spectra obtained, and their relative concentrations can be determined by fluorescence intensities (sample scores) generated from PARAFAC model [15]. Therefore, this fluorescence excitation–emission matrix spectroscopy coupled with parallel factor analysis (EEM–PARAFAC analysis) can provide quantitative information associated to the concentration of respective component. When examining the samples of feed, permeate, retentate and backwash solution during filtration by this approach, the fate of each component during the UF procedures can be achieved. Furthermore, fouling contribution of each component and major foulants can be directly analyzed. However, it should be noted that this fluorescence-based approach cannot characterize polysaccharides, which were proved to play a significant role in membrane fouling. To remedy this defect, the polysaccharide concentration of each sample can be measured in addition to EEM–PARAFAC analysis, and then the fouling fate of polysaccharides can be illustrated as well.

On the other hand, solution chemistry was found to exert a significant effect on the membrane fouling by EOM. More serious fouling was also found at lower pH and with the presence of calcium [5,8,16]. But the effect of pH on irreversible fouling of EOM during low-pressure membrane filtration is still unclear, and the effect of calcium on irreversible fouling was still controversial [5,8]. Additionally, the effect of solution chemistry on detailed fouling behavior of each sub-fractional component of EOM still remains to be investigated.

In this study, EEM coupled with PARAFAC and polysaccharide analysis were adopted for characterizing the feed, permeate, and reversible and irreversible foulant layers in ultrafiltration of EOM. By this approach, fouling fate of each component of EOM was illustrated and compared with total carbon mass balance measured. With these results, major foulants as well as dominative mechanisms involved were discussed. Effects of solution chemistries (i.e. pH, and the presence of calcium) on EOM fouling were investigated using this approach. *Microcystis aeruginosa* was used for EOM extraction in this research because of its prevalence in algae blooms in China [17].

2. Materials and methods

Algae cultivation and EOM extraction were similar to our former study described by Qu et al. [5]. Briefly, *M. aeruginosa* was cultured in batch mode with BG11 medium at temperature of 25 °C with illumination of 5000 lx provided for 14 h every day. Cultures were harvested at the stationary phase with culture time of 25–28 days. Algal EOM was extracted by centrifuging the cell suspension at 10,000 rpm (11,179 *g*) and at 4 °C for 15 min and subsequently filtering the supernatant with a 0.45 μm mixed cellulose filter (Taoyuan Co. Ltd., China). The dissolved organic carbon (DOC) concentration of the extracted EOM was first measured, and then the EOM solution was diluted to 5 ± 0.2 mg/L as DOC [8].

2.1. Feed solution of UF

To investigate the effects of various pH values, solution pH was adjusted to 3.0 ± 0.1, 7.0 ± 0.1, and 11.0 ± 0.1 by sodium hydroxide solution (0.1 N) and hydrochloric acid (0.1 N). It should be noted that although the extreme acid and based conditions are unlikely to be encountered in real UF process, it still can shed light on the trend of the effect of pH on fouling. Moreover, effect of these pH values on organic fouling has been widely studied, thus it is convenient to make a comparison between current and previous studies [18–20].

To investigate the effect of calcium ion on EOM fouling, calcium chloride stock solution (1 g/L) was prepared and used to adjust calcium concentration (i.e. 0 mM, 2 mM, 5 mM, and 10 mM). After dosing calcium ion, the solution pH was fixed at 7.0 ± 0.1. The ionic strengths of the feed solutions with different calcium concentrations were kept constant by changing the background sodium chloride concentrations. The ionic strength was controlled by measuring the conductivity using conductivity meter (FE30, Mettler Toledo, Switzerland). The relatively high dosage of calcium in current study compared with others (i.e. 0 mM–2 mM) is attributed to the comparatively high ionic strength in EOM solution (i.e. 536 ± 14 μS/cm), which will mitigate the effect of calcium on fouling [21,22]. Notably, calcium chloride is an ingredient of BG11 medium (0.25 mM Ca^{2+} in fresh BG11), thus the remaining calcium in extracted EOM was first measured to be 0.03 ± 0.01 mM. Both of the calcium concentrations in BG11 and in fresh extracted EOM were far lower than those examined.

All chemical reagents used in the experiment were analytical grade and were used without further purification. Prior to filtration, all prepared feed solutions were stirred for stabilization for 1 h.

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