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Algae-laden water treatment using ultrafiltration: Individual and combined fouling effects of cells, debris, extracellular and intracellular organic matter

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ABSTRACT

Membrane fouling is a major obstacle for applying Ultrafiltration (UF) in algae-laden water treatments. Both membrane permeability and energy consumption may be negatively influenced by the accumulation of algal bodies (i.e., algal cells and debris) and algae-derived organic matter, including extracellular organic matter (EOM) and intracellular organic matter (IOM), on the membrane surface. This study was aimed to investigate individual and combined UF membrane fouling by algae-derived foulants including cells, debris, EOM and IOM to identify the main foulants and to gain an increased understanding of fouling mechanisms involved in algae-laden water treatments using UF. The characteristics of the algal foulants were determined with respect to particle distribution, zeta potential, interfacial free energy, and fluorescence excitation-emission matrix (FEEM) spectrum. The results indicated that algal cells resulted in the fastest flux decline during filtration, but that algal organics (i.e., EOM and IOM) caused more adsorptive and irreversible fouling than did algal cells. For the combined fouling, the flux decline was considerably aggravated because the algal organics filled the voids in the cake layer formed by the cells and debris, but the fouling reversibility was not substantially aggravated due to the retention of EOM and IOM in the aforementioned cake layer. A synergistic effect was not observed in UF membrane fouling caused by the combined foulants in this study. Furthermore, both algal debris and IOM caused severe flux decline and irreversible fouling, suggesting that cell breakage should be strictly controlled for real algae-laden water treatments that employ UF.

1. Introduction

Algae blooms commonly occur in rivers and reservoirs, and *Microcystis aeruginosa* is one of the dominant algae species [1,2]. The algae bloom usually occurs alongside eutrophication, and it becomes a critical threat to human health and make drinking water treatment difficult. Even worse is that algal cell breakage, which could release a high concentration of dissolved organic carbon (DOC), has been observed in traditional treatment plants using coagulation, sedimentation and sand filtration [3]. Although pre-oxidation proves to be a highly efficient method for improving algae removal, the inevitable problem of cell breakage and intracellular organics release are cumbersome [4,5]. Moreover, cell breakage and the release of organics make water treatment processes much more complicated (e.g., increases in assimilable organic carbon and toxic organics such as microcystins) [6,7].

Ultrafiltration (UF), which utilizes a thin membrane with an approximately 10 nm pore size, may completely retain algal cells via physical size exclusion. Therefore, UF is increasingly applied in algae-laden water treatment. However, the membrane fouling caused by *Microcystis* cells and by organic matter excreted from or released by the cells will boost energy consumption and shorten the lifetime of the membrane [8,9]. Thus, membrane fouling significantly hinders the practical application of UF technology for algae-laden water treatment. To overcome fouling problems, a variety of pretreatments, including peroxidation, coagulation, sand filtration and dissolved air flotation (DAF) were adopted to treat the raw water and thus reduce the amount of algal pollutant's access to the membrane system [2]. Though some pretreatments can remove over 95% of algae cells, a large number of algae cells still have access to the membrane system due to the large amount of algal cells (exceeding 1×10^7 cells mL^{-1}) in source water when an algae bloom occurs. Although fewer algal cells enter the UF system, algal pollutants accumulate during filtration and resulting increased concentrations of algal pollutants. Moreover, some extra-

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cellular dissolved organic matter in algae-laden water cannot be removed efficiently in pretreatment because the targeted pollutants of coagulation and sand filtration involve particles and colloids rather than dissolved organics [2]. Hence, algal foulants cannot be eliminated in pretreatment, and it is crucial to gain a better understanding of the membrane fouling by algal cells and their metabolites.

Some studies have focused on the fouling mechanism of algal foulants and have concluded that organic matter was the major foulant during algae-laden water membrane treatments. Qu et al. [10] investigated the difference in fouling potential between dissolved extracellular organic matter (EOM) and bound EOM, and found that bound EOM led to more irreversible fouling, while dissolved EOM led to more reversible fouling. Li et al. [11] compared the UF membrane fouling by EOM and intracellular organic matter (IOM), and concluded that IOM caused a more severe flux decline than EOM. Furthermore, it was demonstrated that algal cells, which could be totally retained by the UF membrane, also induced a severe flux decline [12,13]. However, the individual fouling performance of algal debris is rarely reported. Moreover, algal debris may appear in water plants due to interference factors such as oxidant dosing and pump shear stress [13,14]. In drinking water plants with natural algae-laden water as source water, algae bodies (i.e., intact cells and debris) and algae derived organic matter (i.e., EOM andIOM) always coexist. It was reported that organic matter and inorganic particles could exert a combined effect on fouling during filtration [15–18]. Compared to inorganic particles, algal cells possess some special characteristics such as compressibility, which may make their interaction with organic matter much more complicated. The interplay between algal cells and their metabolites (e.g., EOM and IOM) is rarely investigated. Thus, a study focused on the individual and combined fouling by algal foulants is of great importance.

This study investigated the individual and combined fouling effects of algal-derived foulants including cells, debris, EOM and IOM to identify the main foulants and to gain an increased understanding of the fouling mechanisms involved in the UF of algae-laden water. Towards this end, the cells, debris, EOM, and IOM were extracted from lab cultured *Microcystis aeruginosa* and characterized in terms of FEEM components, molecular weight (MW) distribution and particle size distribution. UF tests of each individual foulant and their mixture were conducted. Moreover, the interfacial interaction between algae-derived foulants and membrane surface was analysed via calculating the free energy of cohesion.

2. Materials and methods

2.1. Algae culture, organic extraction and feed water preparation

Microcystis aeruginosa (PCC7820) was purchased from the Institute of Hydrobiology, Chinese Academy of Sciences. The algae were axenically cultivated in an incubator at 25 °C with illumination of 5000lx provided for 14 h per day [19]. The BG-11 medium was used to provide sufficient nutrients for algal growth. *Microcystis aeruginosa* in stationary phase (harvested at 35d) was used in this study.

To extract the EOM and cells, the harvested algae suspension was centrifuged at 10000g and 4 °C for 30 min. Subsequently, the EOM was obtained via filtering the supernatant using a 0.45 μm mixed cellulose filter (Taoyuan Co. Ltd, China). The algal cells remaining in the centrifuge tubes and on the filters were collected and re-suspended using simulated water composed of 0.5 mM $CaCl_2$, 1.0 mM $NaHCO_3$, and 15.0 mM $NaClO_4$ in Milli-Q water. To extract IOM, the freezing/thawing method, which was a successive process of freezing at −70 °C for 2 h and thawing at 40 °C for 30 min, was applied to the re-suspended cell solution [11]. Finally, the sample was separated into debris and IOM by centrifugation and microfiltration as described above. The fouling characteristics of the extracted cells and organics were not identical but approximated to that of raw cells due to the possible denaturing of algal cells and organics resulting from the extreme conditions used. To extract the AOM (EOM+IOM) from algae solutions, the untreated algae suspension was first subjected to the three freezing/thawing cycles as described above. Then the supernatant was filtered. Because the initial cell debris was prone to self-aggregation (As shown in Fig. S1 in the Supplementary Material) due to the autoflocculation induced by the released IOM [20], there were debris aggregates in the feed water denoted as debris.

2.2. Ultrafiltration setup

Flat UF membranes made of polyvinylidene fluoride (PVDF) (Tianchuang, Hangzhou, China) were used in this study. The MWCO of the membrane was 60 kDa and the effective membrane area was 45.3 cm^2. The membranes were negatively charged, with a zeta potential of −11.2 mV (pH 7.5, 1 mmol/L KCl). The contact angle of the membrane was determined as 85.4 ± 2.1° by the standard sessile drop method with de-ionized water serving as the probe liquid. The roughness of the membrane was 58.3 ± 3.3 nm, obtained by analysing atomic force micro-scopy (AFM) images of the membrane. To remove preservative materials prior to filtration, new membranes were soaked in Milli-Q water for 2 h with the water changed at least three times, and then cleaned and rinsed for 5 times [21].

The UF system consisted of an UF cell (Amicon 8400, Millipore, MA, USA), a nitrogen gas cylinder to provide a constant pressure (100 kPa), an electronic balance connected to a computer, and several accessories. The rinsed membrane was placed in the bottom of the UF cell with its skin (glossy) side towards the solution [22]. The electronic balance connected to a computer automatically logged the weight data of the filtered solution every 5 s. Before the filtration test, Milli-Q water was filtered through the membrane until there was no interference for the measurement of organic material.

2.3. Membrane fouling assessment

In this study, a series of feed waters with different foulants were prepared with the detailed compositions shown in Table 1. The concentration of algal cell was chosen as 2.0×10^6 cells mL^{-1} as reported by Chiou et al. [23] and Qu et al. [24], so that the obtained results could be compared with the reported results. The concentrations of algal cell debris were described by the cell concentration of the algae suspension, which was used to extract the cell debris. The loss of cell debris during the extraction process was strictly controlled. Regarding algal organics, the DOC concentrations were adopted as 5.0 mg/L according to the DOC concentration (2.9–5.6 mg/L) of real algae-laden water [25] and concentrations (4.3–10.5 mg/L) used in similar studies [26–29].

To determine the adsorptive fouling, the PVDF membrane was placed into the UF cell with the glossy side exposed to the solution. A stirrer was employed to provide a constant stirring velocity (300 rpm). Pressure was not applied during this process and the outlet was sealed so that no water was filtered through the membrane. The adsorptive fouling was evaluated through the flux of Milli-Q water before and after the adsorptive fouling test. Eq. (1) shows the determination of relative

Table 1
Detailed information of feed water.

No.	Foulants	DOC (mg/L)	Cell concentration (cells/mL)	UV_{254} (cm^{-1})	Zeta potential (mV)
1	EOM	≈5.0	0	0.089	–
2	IOM	≈5.0	0	0.021	–
3	Cells	< 0.3	2×10^6	< 0.005	−34.4
4	Debris	< 0.3	2×10^6	< 0.005	−20.8
5	Cells+EOM	≈5.0	2×10^6	0.091	−38.1
6	Debris+IOM	≈5.0	2×10^6	0.026	−21.9
7	Debris+EOM +IOM	≈5.0	2×10^6	0.056	−25.4