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Evaluation of different algogenic organic matters on the fouling of microfiltration membranes

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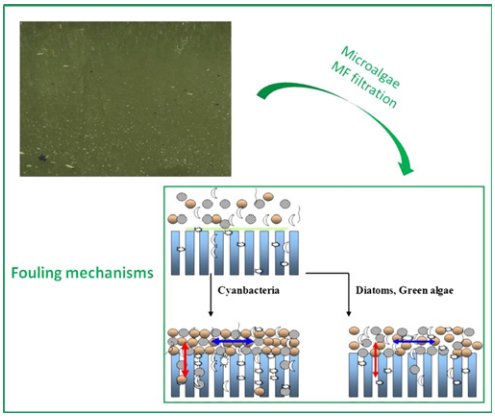
HIGHLIGHTS

- Membrane fouling caused by different algogenic organic matters varied significantly.
- Two sets of membrane fouling mechanisms were proposed in AOM MF.
- Surface free energy of membranes and foulants was used to analyze membrane fouling.

GRAPHICAL ABSTRACT



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ABSTRACT

This paper systematically investigated the microfiltration membrane fouling behavior of various algogenic organic matters (AOMs) that were extracted from five classical bloom algae (cyanobacteria, green algae and diatoms). The results indicated that membrane fouling by different algae varied significantly by algal species and AOM chemical compositions. Cyanobacteria of the species *Aphanizomenon flos-aquae* (APF)-AOM caused the strongest flux decline, followed by *Anabaena flos-aquae* (ANF)- and *Microcystis aeruginosa* (MA)-AOMs. Analysis of AOM characteristics indicated that the membrane fouling depended on the synergies that arose from specific combinations of fluorescence excitation–emission matrix (EEM), molar sizes and/or membrane material properties. By applying the extended version of Derjaguin Landau Verwey Overbeek (XDLVO) theory, it was found that the cohesion free energies and the adhesion free energies between APF-, ANF-, and MA-AOMs and each of the membranes were more negative than those between membranes and the green algae and the diatoms of *Scenedesmus obliquus* (SO)- and *Cyclotella* (Cy)-AOMs; more negative energies indicate that the attraction forces are much stronger and can cause heavier membrane fouling. SO-AOM and Cy-AOM have less negative cohesion free energies and adhesion free energies with the membranes, and there was less membrane fouling with those AOMs. The surface free energy of membranes and foulants is a useful parameter for membrane fouling analysis.

1. Introduction

Lakes and freshwater reservoirs are two of the most important drinking water resources. However, because they often suffer from eutrophic conditions or environmental influence, algal blooms frequently

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occur in lakes and reservoirs. Some of the bloom-forming species may cause water safety problems. MF membranes can remove turbidity, pathogens and some natural organic matter (NOM); algae can also be rejected by microfiltration (MF) and can cause heavy membrane fouling [1].

Membrane fouling is a formidable challenge for the application of membrane separation technologies for drinking water treatment. Many studies have been conducted on this problem. The fouling of MF membranes is complex; it is influenced by membrane characteristics, membrane pore size, operation conditions, and the water characteristics [2,3]. The presence of inorganic matter and NOM in water can also induce colloidal fouling, which results in a decline in the transmembrane flux [3]. Many investigators have reported that the fouling NOM layer, which increases hydraulic resistance to the permeate flux, is mainly composed of the hydrophobic fraction of the NOM [4]. However, Lee et al. have shown that the hydrophilic fraction of NOM might actually be a major foulant of the membrane [5]. Compared with the focused studies that have been performed on the fouling of membranes by inorganic particles and NOM, the knowledge of algal fouling on MF membrane is inadequate. Membrane fouling by algae during water treatment might be significant because algae are reported to impact a number of water treatment processes, including coagulation, filtration, oxidation and disinfection by-product formation [6,7]; algogenic organic matters (AOMs) released by algae represent a considerable proportion of the organic carbon in surface waters during algal blooms [7]; AOMs are a significant contaminant in the membrane filtration process.

Qu et al. studied the fouling of ultrafiltration (UF) membranes by extracellular organic matter released from *Microcystis aeruginosa* and reported that the algal extracellular organic matter could cause substantial membrane fouling during UF; the rapid flux decline was attributed to hydrophilic organics [8]. In a further study, they found that the dissolved AOM could cause greater flux decline but less irreversible membrane fouling compared with bound AOM, because the bound AOM contained larger and hydrophobic molecules, which could result in the foulant layer being more porous but having a higher affinity to the membrane surface than dissolved AOM [9]. Moreover, AOM was found to be responsible for the severe fouling of a ceramic MF membrane with high MW biopolymers be the dominant foulants [10]. Her et al. also observed that algal organic matter showed a low rejection rate by a nanofiltration membrane and that it caused substantial membrane fouling [11]. These studies were conducted on membrane fouling by AOM (mainly *M. aeruginosa*); however, membrane fouling caused by AOM still has not been systemically studied, particularly with the goal of assessing the extent of membrane fouling by different algae and their metabolites. This information is important for membrane filtration of surface water that is rich in nutrients and is characterized by seasonal algal blooms. Although algae have been classified according to pigmentation and cell complexity from a biologist's perspective [12], they are not grouped in natural water bodies according to their characteristics; dominant species may emerge when algal blooms occur, and the AOM released by dominant species should be further considered. Even in waters where algal blooms are rarely seen, the right water quality and weather conditions can lead to algal bloom. Algal blooms caused by different algae have their own unique characteristics. It is anticipated that these AOM differences might have appreciable effects on membrane fouling. Each AOM might cause a unique membrane fouling mechanism. Therefore, the knowledge of the relations between membrane fouling and AOM during the bloom occurrence will provide useful information for prediction of membrane fouling or pretreatment of the water prior to filtration.

This study investigated the potential impact of different AOMs on the fouling of MF membranes. Five algae were selected to represent three classical seasonal algal blooms, i.e., cyanobacteria, green algae and diatoms. An extended version of the Derjaguin Landau Verwey Overbeek (i.e., the extended DLVO or XDLVO) theory [13] was applied for the analysis of the membrane fouling effects.

2. Materials and methods

2.1. Algae cultivation and AOM extraction

Freshwater algae, including *M. aeruginosa*, *Aphanizomenon flos-aquae*, *Anabaena flos-aquae*, *Scenedesmus obliquus* and *Cyclotella*, were obtained from the Institute of Hydrobiology, Chinese Academy of Sciences, China. *M. aeruginosa*, *A. flos-aquae* and *A. flos-aquae* were grown at 20 °C using BG-11 medium under controlled ambient conditions with 12 h of fluorescent light and 12 h of darkness and an irradiance of approximately 90 μmol/m^2·s, which was provided by a cool-white fluorescent light [14]. *S. obliquus* was grown using SE medium (soil extract, also known as Brostol's solution) at 25 °C and a 12–12 h light–dark cycle with an irradiance of approximately 120 μmol/m^2·s [15]. *Cyclotella* was grown using D1 medium (diatom medium) at 20 °C and a 12–12 h light–dark cycle with an irradiance of approximately 90 μmol/m^2·s [16].

AOM was extracted from algal solutions in the stationary growth phase by centrifuging at 10,000 *g* for 15 min and then filtering through a 0.45 μm filter (mixed cellulose) [8]. *M. aeruginosa*, *S. obliquus* and *Cyclotella* solutions with cell densities of approximately 7.5×10^7, 1.4×10^7 and 1.1×10^6 cells/mL, respectively, were used for AOM extraction in this study. Because *A. flos-aquae* and *A. flos-aquae* have special cellular morphologies, optical density (OD) monitoring at 680 nm was selected to identify their cell density [17,18]; the corresponding OD_{680} used for *A. flos-aquae* and *A. flos-aquae* were 1.737 and 1.403, respectively. The concentrations used above were identical in magnitude with the concentrations typical of algal-blooms in China [19]. AOMs extracted from *M. aeruginosa*, *A. flos-aquae*, *A. flos-aquae*, *S. obliquus* and *Cyclotella* are henceforth abbreviated as MA-AOM, APF-AOM, ANF-AOM, SO-AOM and Cy-AOM, respectively.

2.2. Membrane and filtration unit

The MF membrane used was a 0.1 μm Millipore hydrophilic mixed cellulose flat sheet membrane (VCWP, 80%–100% of nitrate cellulose and 0%–20% of acetate cellulose) (Millipore Corporation, US). Prior to filtration, all virgin membranes were pre-soaked in Milli-Q water for 24 h to remove impurities.

A dead-end filtration unit was used for the MF experiment (Fig. 1). The membrane filtration vessel was a cup-type filtration vessel; its effective volume was 300 mL and the effective filtration area was 3.32×10^{-3} m^2. The applied pressure was maintained at 0.1 MPa using a nitrogen cylinder, and the operation temperature was maintained at 25 ± 0.5 °C under the low temperature storage tank. The clean water flux was established by filtering Milli-Q water for 2 h before permeating the samples. The mass of permeate was measured using an electronic balance (Shimadzu, UW2200H, accuracy ± 0.01 g), and the results were recorded simultaneously by an on-line computer. For each experiment, a fresh membrane disk was used, and the DOC concentrations of all AOM solutions were adjusted to 5 ± 0.05 mg/L before filtration. To minimize the effect of ionic strength and pH during the comparison of membrane performances, all AOM solutions were adjusted to identical ionic strengths and were neutralized to pH 7.0 before each experiment. The relative flux (J/J0), which is defined as the ratio of permeate flux (J) to the initial flux (J0), was adopted for the comparison of membrane foulings.

2.3. Analytical methods

2.3.1. DOC and SUVA analyses

Dissolved organic carbon (DOC) and ultraviolet absorbance at a wavelength of 254 nm (UV_{254}) were measured by a total organic carbon analyzer (TOC-V_{CPH}, Shimadzu) and a UV spectrophotometer (Hach-5000), respectively. Specific ultraviolet absorbance (SUVA) was calculated using the ratio of UV_{254} to DOC.