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Investigation of the mechanisms of membrane fouling by intracellular organic matter under different iron treatments during ultrafiltration

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HIGHLIGHTS

- UF fouling mechanism by IOM under different iron treatments was investigated.
- UF membrane is more seriously fouled by IOM at low iron concentration.
- Cake formation combined with intermediate blocking was the main UF fouling mechanism of IOM filtration.

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ABSTRACT

Iron is an important trace element in algal growth and water eutrophication. This study focused on the ultrafiltration (UF) membrane fouling mechanism by the intracellular organic matter (IOM) of *Microcystis aeruginosa* under different iron treatments. The results indicated that the membranes experienced faster flux decline and worse fouling reversibility when the IOM formed under low iron concentrations. In contrast, less IOM membrane fouling was found under normal and high iron concentrations. The mass balances of the dissolved organic carbon (DOC) content implied that the IOM in the low-iron treatment was associated with higher IOM retention and a higher capacity of reversibly deposited organics, whereas more IOM in the high-iron treatment passed through the UF membrane. The IOM in the low-iron treatment was composed of more biopolymer macromolecules, whereas the IOM in the high-iron treatment contained more UV-absorbing hydrophobic organics. The fluorescence excitation-emission matrix (EEM) spectra coupled with peak-fitting analysis implied that the fouling associated with protein-like components was more irreversible in the low-iron treatment than those in the normal- and high-iron treatments. Cake formation combined with intermediate blocking was identified as the main membrane fouling mechanism responsible for the flux decline caused by IOM solutions in the three iron treatments in this study.

1. Introduction

Water eutrophication is a phenomenon in natural lakes and reservoirs that leads to the frequent occurrence of algal blooms, usually resulting in serious water treatment problems. Nutrients, such as nitrogen and phosphorus, light and/or other environmental factors are generally considered the main factors causing water eutrophication (Wang et al., 2010; Anderson et al., 2002). Compared with traditional treatments, ultrafiltration (UF) is an attractive technology for drinking water and wastewater treatment because it completely removes particles, including microorganisms such as protozoa (e.g., Giardia and Cryptosporidium) (Wang et al., 2017; Yang et al., 2018). UF has also gained increasing attention as a technique in algae biomass harvesting (Zhang et al., 2010). Unfortunately, an inherent problem of UF is membrane fouling, which has limited its usage. Natural organic matter (NOM), soluble microbial products (SMP), and extracellular polymeric substances (EPS) have been identified as important membrane foulants during UF (Shi et al., 2017). Previous studies have described the membrane fouling mechanisms using pore clogging, gel layer formation and/or cake layer formation (Polyakov and Zydeny, 2013), and to prevent

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membrane fouling, several strategies have been proposed, including periodic backwashing, chemical cleaning, membrane surface modification, and biological control (Lipp et al., 2005; Huang et al., 2016).

Algae fouling in membrane systems is a topic that has come to the forefront of discussion in recent years in the field of membrane filtration. Previous research indicated that the charged hydrophilic (CHPI) and neutral hydrophilic (NHPI) fractions of extracellular organic matter (EOM) released by algae caused greater flux declines than the hydrophobic (HPO) and transphilic (TPI) fractions. Additionally, protein-like, polysaccharide-like, and humic-like substances were demonstrated to be the major components responsible for membrane fouling (Zhou et al., 2014). Intracellular organic matter (IOM) is also released into natural waters following cell death in aquatic ecosystems and/or during peroxidation processes, hydraulic sheering and other external stresses (Huang et al., 2009). Compared with the widely investigated membrane fouling by EOM solutions, the role of IOM in fouling has seldom been explored. Although IOM was reported to account for 77–86% of total algal organic matter (AOM) according to previous researches (Li et al., 2012) and although various major differences exist between EOM and IOM, such as the molecular weight (MW) distribution and fluorescence excitation-emission matrix (EEM), the investigation of membrane fouling by IOM remains limited. Han et al. (2016) investigated the effects of nitrogen and phosphorus concentrations on AOM generated from the diatom *Nitzschia palea* and concluded that aromatic proteins and soluble microbial products were the main components in both EOM and IOM. The presence of algal cells resulted in fast flux decline during filtration, but the algal organics (i.e., EOM and IOM) caused more adsorptive and irreversible fouling than the algal cells, and both the algal debris and IOM caused a severe flux decline and irreversible fouling (Liu et al., 2017).

Several assessment methods, including those that use a fluorescence excitation-emission matrix (EEM), molecular weight distribution, Fourier transform infrared (FTIR) spectrophotometer, and chemical cleaning, were developed to determine the level of membrane fouling (Henderson et al., 2009). Although many efforts that have been made to investigate the membrane fouling mechanisms and fouling reversibility (Li et al., 2013; Zheng et al., 2009), a clear understanding of the fouling behavior and fouling mechanisms of IOM has not yet been achieved. Recently, an improvement in analytical methods made NOM fouling analysis more efficient. High-performance size-exclusion chromatography (HPSEC) combined with a peak-fitting prediction is a promising technique for separating chromatographic peaks into isolated fractions and provides qualitative information on dissolved organic carbon (DOC) removal based on a comparison between raw water and different treatments (Chow et al., 2008; Lai et al., 2015). In addition, the proposed EEM fluorescence spectroscopy coupled with parallel factor analysis (PARAFAC) was determined to be suitable for major foulant identification and mechanism determination (Yu et al., 2014).

However, algal growth in natural water is influenced by many factors, including the abundance of nutrients and light and the variations in temperature, all of which can cause changes in the organic matter released by the algae (Yeesang and Cheirsilp, 2011). Previous research suggested that, in addition to the algal species and growth phase, considerable attention should be paid to the relation between membrane fouling and the characteristics of AOM (Qu et al., 2012). Notwithstanding the many studies that have been conducted on the impact of environmental factors on algae growth (Wang et al., 2010; Anderson et al., 2002), the pattern of IOM released under different environmental factors remains unclear but likely exerts different effects on membrane fouling. Iron was one of the first trace elements to be discovered and has an irreplaceable function in algal growth. Iron also plays a substantial role in the outbreak of algal blooms. However, the role of iron was a long-standing puzzle before the work of Martin and Fitzwater (1988), who proposed that iron was the limiting factor controlling phytoplankton abundance and productivity in a certain area of the ocean. Zhou (2016) studied the effects of iron on the population density of fresh algae and found that both the iron morphology and concentrations had significant effects on *Anabaena flos-aquae*. Furthermore, in Dianchi Lake, a low iron environment was more conductive to the growth of *A. flos-aquae*, whereas a high-iron environment had inhibitory effects on algal growth (Liu et al., 2006). Photosynthetic capacity, nitrogenase activity and chlorophyll a content can also be stimulated by iron, which may have a promotional effect on algal blooms in water bodies (Knauer et al., 1997). The amount of IOM released under the various iron concentrations and the consequent effects on membrane fouling remain unclear because few studies have investigated these issues.

The objective of this study was, therefore, to investigate the membrane fouling characteristics and mechanisms associated with IOM under different iron treatments. Iron was investigated in this research because algal electron transmission, nitrogen absorption and utilization, chlorophyll photosynthesis and respiration are affected by the availability of iron, and the iron concentration was varied to correspond to the concentrations observed in various lakes and oceans (Lv et al., 2006). HPSEC combined with peak fitting and EEM-PARAFAC was utilized in this study to analyze the fouling behaviors of the IOM solutions with different iron concentrations. The membrane fouling characteristics and mechanisms of IOM under various iron treatments were evaluated by classical filtration models. This research will undoubtedly have important implications for algae bloom and water eutrophication control and will provide important guidance for membrane fouling control and prediction during UF.

2. Materials and methods

2.1. Algal cultivation and IOM extraction

Microcystis aeruginosa was cultivated under the following controlled ambient conditions: 12 h of fluorescent light and 12 h of darkness at a temperature of 25 °C and an irradiance of approximately 90 μmol/m^2•s of the BG11 medium. *M. aeruginosa* was selected in this research because it is a dominant algae species in lakes and reservoirs. The *M. aeruginosa* in an exponential growth phase was centrifuged (6000×*g*) for 15 min and washed twice with deionized water; the algal cells were cultivated in BG11 medium without iron for a 5 d starvation period. Then, the algae were transferred to batches of BG11 medium with different iron concentrations. These iron concentrations, which were consistent with our previous research (Huang et al., 2017), were 0.274, 1.37, and 6.86 mg/L, which were prepared by adding ferric citrate concentrations of 0.0012, 0.006, and 0.03 g/L, respectively, to the BG11 medium. The iron concentrations were denoted as low iron, normal iron, and high iron, respectively. The initial cell density was 1.6×10^6 cell/mL. The iron concentrations were selected according to previous studies (Wang and Dou, 1998). For example, a low iron concentration is a common phenomenon during algae reproduction in summer. The normal iron concentration of 1.37 mg/L was used in this research because most laboratory experiments involving *M. aeruginosa* cultivation are performed on BG11 medium with a ferric citrate concentration of 0.006 g/L.

IOM was extracted by centrifuging an algal cell suspension of the stationary phase at 6000 r/min for 15 min. When the supernatant was removed, the same volume of ultrapure water was