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Fouling of extracellular algal organic matter during ultrafiltration: The influence of iron and the fouling mechanism

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ABSTRACT

In this study, membrane fouling and the mechanism of algal extracellular organic matter (EOM) due to various trace heavy metals (iron) during ultrafiltration (UF) was investigated in detail. In both early and late exponential growth phases, the results indicated that the membrane fouling caused by EOM at low iron concentrations in this study was more severe than that at high and normal iron concentrations. Low iron concentrations produced the highest total (R) and reversible fouling resistance (R_{re}), of which R_{re} was higher, followed by membrane resistance (R_m), and irreversible fouling resistance (R_{ir}). The analysis of EOM characteristics indicated that low iron in this study stimulated the growth of algae beyond high and normal iron concentrations, including increases in chlorophyll *a*; protein (tryptophan-like and tyrosine-like organic matter) content; and macro, medium and small molecular organic matters. Humic-like organics were more synthesized under high iron concentrations. Analyses of membrane fouling behavior illustrated that cake formation was the major fouling mechanism for the three iron concentrations, and it accounted for a greater proportion of fouling in the low iron concentration than in the other two iron concentrations; cake resistance played a more critical role in the late exponential growth phase than in the primary exponential phase.

1. Introduction

Water resources are an important part of earth's life system and are a human resource. However, many rivers and lakes are subjected to land-sourced pollutants and farming pollution that result in eutrophication. Microalgae, commonly found in algae blooms, has become a worldwide problem for the treatment of drinking water. They not only release an undesirable taste and odor but also toxins and organics, which cause the formation of precursors of disinfection by-products during chlorination and require high coagulant dosages during water treatment and disinfection [1,2].

Traditional water treatment has limited effects in treating algae-rich waters [3]. Membrane filtration technology is an attractive technology for microalgae removal. This method offers the absolute removal of algal cells and is less affected by changes in raw water quality [4]. Even in algae biomass harvesting, which usually includes centrifugation, flocculation, gravity sedimentation, and air flotation, membrane technology has drawn increasing attention [5]. However, membrane fouling remains the main disadvantage that leads to a loss of flux and performance efficiency. Membrane fouling caused by algae has been widely investigated in recent years [6]. It has been reported that the accumulation of algal cells on membranes can result in a rapid increase of transmembrane pressure, whereas extracellular algal organic matter (EOM) was considered to be the main membrane foulant for both polymeric and ceramic membranes [7,8]. Qu et al. investigated ultrafiltration (UF) membrane fouling by *Microcystis aeruginosa* EOM and found that pore clogging and cake layer formation were the key factors in membrane fouling [9]. A macro molecular biopolymer was demonstrated to be the major component in membrane fouling [10]. Moreover, the irreversible fouling by EOM was found to be mainly caused by polysaccharides under ambient solution chemistry, and fouling by tryptophan-like substances turned out to be more irreversible with the presence of calcium [11].

These studies were conducted under normal algal growth conditions (BG11 medium); nevertheless, the formation of algal blooms or red tides is caused by complex interactions of various factors in the natural environment. Abundant nutrients, light, and temperature, as well as other factors, all could influence the growth of algae and water blooms [12]. da Silva et al. investigated the photosynthetic physiology of *Rhodomonas* sp. and found that the total carbohydrate content increased 2.5 times more in a nitrogen sufficient medium than in starvation conditions [13]. Huang et al. found that the characteristics

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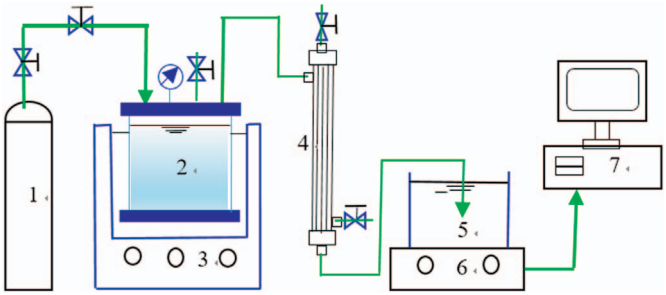

1) Nitrogen tank 2) 4 L water vessel 3) Low temperature storage tank 4) Hollow fiber membrane 5) Effluent 6) Electronic balance 7) Data record.

Fig. 1. Schematics of the membrane filtration set-up.

of algogenic organic matter (AOM) changed in different ways under various N/P ratios, and the membrane fouling by AOM can also be affected by N/P changes [14]. The impact of trace metals also had a great influence on algal growth. Many heavy metals such as copper, zinc, manganese, etc., are necessary for algal metabolism at low concentrations; however, they were toxic at high concentrations [15].

Iron is one of the trace metals that limit the growth of algae, and it not only plays a large role in eutrophic water bodies but also in the outbreak of algae blooms [16]. However, the role of iron has been a longstanding puzzle before the work of John Martin, who proposed that iron in certain areas of the ocean might be a limiting factor that controls phytoplankton abundance and productivity [17]. Lukae and Aeterger studied the influence of trace metals on algal growth and toxin production and found that *M. aeruginosa* cells grew much more slowly at low iron concentrations or without iron but produced 20–40% more toxin at high iron concentrations [18]. The growth of *M. aeruginosa* as well as the photosynthetic capacity and chlorophyll *a* content were also stimulated by ferric chloride [19]. Zhou found that both iron morphology and concentrations had significant effects on *Anabaena flos-aquae*, and a low iron environment was more conductive to the growth of *A. flos-aquae* [20], whereas high iron concentrations had inhibitory effects on algal growth in Dianchi Lake [21]. Furthermore, many freshwater cyanobacteria, such as *Anabaena* and *Microcystis*, were reported to release siderophores to chelate iron for their physiological metabolisms in the absence of iron [22]. Electron transmission, nitrogen absorption and utilization, and chlorophyll photosynthesis and respiration were also affected by iron during the growth of phytoplankton, which may have a promotional effect on algal blooms in water [23]. Despite these important findings from previous studies, as iron concentrations in lakes or oceans change dramatically [20,24], it remains unclear whether the changes in algal growth that originate from the variation of iron could lead to changes in algal organic components as well as changes in membrane fouling in water treatment. These studies would undoubtedly have important meaning for algal growth and reproduction as well as important guidance for membrane fouling control and prediction; however, there were few studies conducted on these problems.

Therefore, the purpose of this study was to investigate the effects of iron on EOM characteristics, while the associated membrane fouling and the mechanism of UF were also studied. Iron was investigated in this research because iron is the trace element that was discovered first, has an irreplaceable function in the life activities of prokaryotes and eukaryotes, ranks first in plant essential trace elements [16], and was one of the chemical limit indicators in drinking water health standards [25].

2. Materials and methods

2.1. Algal cultivation and EOM extraction

The cultivation method of microalgae was similar to that of our previous study [13]. Briefly, *M. aeruginosa* was cultured under controlled ambient conditions of 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. *M. aeruginosa* was selected as the test organism because the species represents classical bloom algae in the aquatic environment. After the exponential growth phases, the microalgae were centrifuged (6000*g*) for 15 min and washed twice with deionized water, and microalgae were cultivated in a BG-11 medium without iron for a 5-d starvation period before the experiment. The initial cell densities of the experiment were 1.6×10^6 cell/mL. The iron concentration was prepared by 1 mmol/L ferric citrate solution based on the BG11 medium, and the ferric citrate concentrations were 0.0012 g/L, 0.006 g/L, and 0.03 g/L, with iron concentrations of 0.274 mg/L, 1.37 mg/L, and 6.86 mg/L, respectively. The iron concentrations were selected according to previous research and because a low iron concentration is a common phenomenon during algae reproduction in summer [26].

Algal EOM was obtained by centrifuging the algal cells at the primary and late exponential phases at 6000*g* for 15 min and then filtering through a Millipore 0.45 μm filter [13].

2.2. Fouling experiment protocol

A hollow fiber ultrafiltration (UF) membrane protocol was employed to conduct the bench-scale filtration and backwash experiments with the widely used PVDF UF membrane in the water treatment. The pore size of the membrane was 0.03 μm, and 3 cords of this hollow fiber membrane with lengths of 24 cm were assembled into a module, of which the total surface area was 24.5 cm^2. A stream of 0.1 MPa N_2 was utilized to feed the water sample into the membrane tank and draw out the permeate (Fig. 1). The permeate was collected in a beaker laid on an electronic balance (VW2200H, accuracy ± 0.1 g, Shimadzu) that measured the weight at timed intervals with a computer. Prior to filtration, all virgin membranes were presoaked in Milli-Q water (18.25 MΩ cm) for at least 24 h at 4 °C.

For each performance, the EOM solution at a dissolved organic carbon level of 5 mg/L (pH 7.0) was used to feed the UF system. After each EOM was filtrated, backwashing was conducted using Milli-Q water, and then the membrane was positive flushed to detect the membrane flux recovery. The backwashing time was 2 min, the pure water flux after backwash was named J_b, the ending flux of each test was named Je, and the EOM solution after filtration was named J.

The reversible fouling resistance and irreversible fouling resistance were calculated based on Darcy's law.