



Mechanism of humic acid fouling in a photocatalytic membrane system

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ABSTRACT

Photocatalytic membrane filtration has emerged as a promising technology for water purification because it integrates both physical rejection and chemical destruction of contaminants in a single unit, and also largely mitigates membrane fouling by natural organic matter (NOM). In this study, we evaluated the performance of a photocatalytic membrane system for mitigating fouling by a humic acid, which is representative NOM, and identified critical properties of the humic acid that determined membrane fouling. We prepared a partially oxidized humic acid (OHA) through the photocatalysis of a purified humic acid (PHA), and the OHA showed reduced fouling for polyvinylidene fluoride (PVDF) ultrafiltration membranes compared to PHA. Molecular-level characterizations indicated that OHA had a reduced molecular size, an increased oxygen content, and increased hydrophilicity. OHA also formed smaller aggregates on the fouled membrane surfaces than PHA. The introduction of oxygen-containing, hydrophilic functional groups, e.g., -OH and -COOH, to the humic acid and the depolymerization or mineralization of the humic acid in photocatalysis could result in the reduction of the foulant-membrane and foulant-foulant interactions, as characterized by atomic force microscopy (AFM), thereby mitigating membrane fouling. Foulant-membrane adhesion forces were always larger than foulant-foulant adhesion forces in our study, irrespective of the humic acid before or after photocatalytic oxidation, which may suggest that the reduction of foulant-membrane interactions is critical for membrane fouling control. In summary, this study sheds light into humic acid fouling in a photocatalytic membrane system through a systematic and comprehensive research approach, and provides insights for the design of novel membrane materials and processes with improved performance for water purification.

1. Introduction

Pressure-driven membrane filtration, including microfiltration, ultrafiltration, nanofiltration, and reverse osmosis, is becoming a promising physical process for the removal of a broad range of contaminants in water and wastewater [1–4]. Despite the effectiveness of membrane filtration for water and wastewater treatment, this developing technology still faces great challenges of membrane fouling, intensive chemicals and energy consumption for operation and maintenance, and further treatment or disposal of concentrated waste. Specifically, membrane fouling compromises the yield of purified water (i.e., flux), and also impairs membrane selectivity for contaminant removal [5–7]. Natural organic matter (NOM), such as humic acids, fulvic acids, and tannic acids, is ubiquitously present in various waters and

results in significant membrane fouling [8]. NOM not only accumulates on membrane surfaces or inside membrane pores to foul the membranes but also leads to the formation of disinfection byproducts (e.g., trihalomethanes, haloacetic acids) [9], and thus requires removal in water and wastewater treatment.

Many previous studies have been conducted to understand membrane fouling with NOM, by evaluating the topography of foulants on membrane surfaces, and by exploring the effect of water matrices (e.g., pH, cations), molecular sizes of the foulants, and interactions between the foulants and the membrane surfaces (e.g., electrostatic forces, hydrophobic attraction) on fouling [10–16]. To mitigate membrane fouling, different strategies have been used in engineering practices, including pre-treatment of water prior to membrane filtration (e.g., coagulation, activated carbon adsorption, oxidation), regular

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maintenance and cleaning of membranes (e.g., physical vibration and backwashing, chemical treatment) [17], surface modification of conventional membranes (e.g., grafting of hydrophilic and zwitterionic functional groups) [18–20]), and the development of new membranes [20]. Notably, the pre-treatment of oxidation has been demonstrated to achieve significant improvement for the removal of humic substances and to mitigate membrane fouling [21]. Taking ozonation as an example, ozone decomposes foulants into small molecules and remarkably prevents membrane fouling, due to the formation of highly reactive hydroxyl radicals ($\cdot\text{OH}$) and other radicals [22,23]. However, chemical corrosion, potential toxicity, and the relatively high cost and energy consumption of the operation have prevented ozone from broad application in water purification [24,25].

Photocatalytic membrane filtration has recently emerged as a promising technology for water and wastewater treatment, and the synergy between physical separation and chemical oxidation promotes contaminant removal and mitigates membrane fouling. Photocatalysts, either suspended in water or immobilized on the membrane surfaces, produce a series of reactive oxygen species (ROS) under light illumination. The ROS can destroy small-molecule contaminants, decompose large-molecule NOM, and inactive microorganisms in water, and the process can minimize further treatment or disposal of the brine and largely mitigate membrane fouling from NOM and biofilms [26]. In addition, photocatalysts can potentially harvest sunlight and activate O_2 and H_2O in ambient conditions, and thus photocatalysis can reduce the energetic and chemical footprint for water and wastewater treatment [27–29].

Our study aims to provide a molecular-level understanding of how photocatalytic membranes prevent NOM fouling in water and wastewater treatment. In this study, photocatalysts containing titanium dioxide (TiO_2) were suspended in water containing a humic acid, which is typical NOM, to simulate the tandem photocatalytic membrane system of a photocatalytic slurry reactor with a downstream ultrafiltration membrane separation unit. This tandem photocatalytic membrane system was selected, in contrast to an integrated system with the photocatalyst loaded on the membrane, because the system (i) avoids polymeric membrane oxidation and deterioration in photocatalysis, (ii) improves the mass transfer rate and photoreactivity for oxidation; and (iii) allows easy illumination for photocatalysis [30–32]. TiO_2 was selected because it is an inexpensive, stable, and efficient photocatalyst for water purification, and it mainly produces the most powerful oxidant $\cdot\text{OH}$ that reacts with most organics near diffusion-limited rates in water for NOM decomposition [33–35]. TiO_2 has been demonstrated to facilitate the photocatalytic oxidation of humic acids in recent years [36–39]. Uyguner *et al.* studied the molecular weight distribution of a humic acid after TiO_2 -based photocatalysis under UVA irradiation, whereby lower molecular size (less than 10 kDa) and higher UV absorbing compounds were formed [40]. Liu *et al.* also investigated the photocatalytic oxidation of a humic acid on TiO_2 , and the very hydrophobic acid fraction in the humic acid decayed rapidly to form hydrophilic charged species, whereas the hydrophilic neutral fraction was the most persistent [41]. However, due to the complex structure of humic acids and varying experimental conditions, the mechanism of photocatalytic oxidation for humic acid decomposition and consequent impacts on membrane fouling are still not well understood. How photocatalysis changes the molecular structure of the humic acids and the corresponding mechanical interactions with the membranes, which is critical for fouling mitigation, remains elusive. Moreover, previous research that compared membrane fouling mitigation before and after foulant oxidation could be misleading. Oxidation may not only tailor the molecular structure but also reduce the mass of the foulants (e.g., through mineralization), and foulant mass reduction could lead to artifacts in evaluating the effect of humic acid structural changes on membrane fouling.

Our study uses a thorough and systematic approach to understand the molecular structure of the humic acid before and after

photocatalysis, and to identify key foulant properties that determine membrane fouling. First, a commercially available humic acid was purified via acid precipitation and dialysis to obtain the purified humic acid (PHA). The PHA was then subjected to photodegradation in the presence of TiO_2 to produce the oxidized humic acid (OHA) with half decay of the chemical oxygen demand (COD) as a representative photo-oxidized product of PHA. Next, both PHA and OHA, of the same concentration, were used to understand their fouling behaviors on an ultrafiltration membrane. The membrane flux was recorded, and physical and chemical properties of the foulants and fouled membranes were characterized by X-ray photoelectron spectroscopy (XPS), size-exclusion chromatography (SEC), fluorescence excitation-emission matrix (EEM) spectroscopy, and contact angle analysis. Atomic force microscopy (AFM) was also applied to investigate membrane fouling by the foulants at the microscale or nanoscale in an aqueous environment. AFM not only provides details of foulant topography on membrane surfaces, but also interrogates foulant and membrane mechanical properties and interactions (e.g., foulant-foulant and foulant-membrane forces, elasticity, viscosity) [42–45]. We are the first to report molecular features of the humic acid before and after photocatalytic oxidation, and the results shed light on fouling mitigation in a photocatalytic membrane system. The PHA decomposed into smaller and more hydrophilic fragments after photocatalytic oxidation, and the OHA became softer, and less adhesive to the membrane surfaces as well as to the foulant itself. This discovery can also be translated into deeper understanding of other strategies for mitigating membrane fouling (e.g., ozonation, which is currently used in industrial practices for water and wastewater treatment), and can help achieve efficient, robust, and energy- and cost-effective membrane filtration.

2. Materials and methods

2.1. Chemicals and materials

2.1.1. Chemicals

Unless otherwise specified, all chemicals were reagent grade. Milli-Q deionized water was supplied from a DIRECT-Q 3 ultrapure water purification system with a resistivity of $18.2 \text{ M}\Omega\cdot\text{cm}$ at 25°C . Sodium hydroxide (NaOH), hydrochloric acid (HCl), isopropyl alcohol, ethanol, sodium phosphate monobasic ($\text{NaH}_2\text{PO}_4\cdot 2\text{H}_2\text{O}$), sodium phosphate dibasic ($\text{Na}_2\text{HPO}_4\cdot 12\text{H}_2\text{O}$), sodium sulfate (Na_2SO_4), and TiO_2 nanopowder (Aeroxide® P25, with a reported average particle size of 21 nm) were purchased from Sigma-Aldrich. A humic acid sodium salt was also purchased from Sigma-Aldrich (H16752, technical grade). Ultrafiltration membranes (YMBY3001, supplied by Synder Filtration, polyvinylidene fluoride (PVDF), molecular weight cutoff (MWCO) of 100 kDa) were purchased from Sterlitech.

2.1.2. Production of purified humic acid (PHA)

The humic acid from Sigma-Aldrich was treated to remove impurities, including fulvic acids, metals, and ash, based on a modified acid and base washing method [46,47]. HCl was first added to the humic acid to produce a final concentration of 0.1 g of the humic acid per mL of the solution (ca. pH 1). The suspension was mixed for 2 h, and centrifuged at 3000 rpm for 30 min. Following the centrifugation, the supernatant was discarded, and the precipitate was re-suspended in a HCl solution (1 mol L^{-1}). This centrifugation and resuspension procedure was repeated five times. Next, the precipitate from centrifugation was dissolved in a NaOH solution, with ca. pH 13, and the solution was mixed for 2 h and centrifuged at 3000 rpm for 30 min. The supernatant was filtered twice through $0.45 \mu\text{m}$ PVDF filters, and the filtrate was acidified to ca. pH 1.0 with HCl. After settlement over 12 h, the solution was centrifuged again at 3000 rpm for 30 min, and the precipitate was dialyzed with Spurr 7 dialysis membranes (VWR 25223–050, MWCO of 1000 Da) and freeze-dried. A stock PHA solution of 250 mg L^{-1} was prepared from the freeze-dried PHA (pH 7) and stored in the dark at

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