Identification of key factors affecting the organic fouling on low-pressure ultrafiltration membranes

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ABSTRACT

The fouling behavior of the hollow fiber ultrafiltration (UF) membrane by the mixtures of dissolved organic matters (DOMs) has been systematically investigated. The organic foulants included humic acid (HA), bovine serum albumin (BSA) and sodium alginate (SA), which represented humic substances, proteins and polysaccharides, respectively. According to the experimental results, the filtration process of organic mixtures could be divided into a fast fouling stage and a slow fouling stage no matter what mixture was used. Scanning electronic microscopy (SEM) and the attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR) analysis of the surface of the fouled membranes revealed a significant difference in the structure of fouling layer, which may be attributed to the different deposition rates of the organics. More importantly, the molecular weight of DOMs, solution zeta potential (ZP) and particle size were examined in order to identify the key factors contributing to the fouling behavior. A strong correlation was found between fouling resistance and the content of small molecules in DOMs and solution zeta potential based on statistical analysis. Both factors played significant roles in membrane fouling. A more serious fouling could be observed with a higher proportion of small molecules or a more negative charge density of solution. Furthermore, the normalization data indicated that the effect of small molecule on membrane fouling was more important compared to the ZP of the solution.

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1. Introduction

Membrane filtration has been extensively used for water treatment in the past decades [1]. However, a major challenge to the applications of membrane technology at different scales is fouling, which causes a great reduction in the productivity, leading to a severe filtration flux decline [2]. Membrane fouling is a complex issue [3]. Generally, dissolved organic matters (DOMs) including humic substances, proteins and polysaccharides are recognized as the major foulants that block the membrane pore and reduce permeate flux. Many studies have been conducted to investigate the organic matters responsible for membrane fouling and subsequently to understand the fouling mechanisms.

Using model organic foulants to investigate the fouling behavior is a common method employed in microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) [4,5]. Humic acid (HA), bovine serum albumin (BSA) and sodium alginate (SA) are used as representative compounds of DOMs. A complete understanding of the mechanisms governing HA fouling has been unraveled, including the effects of adsorption (foulant–foulant, foulant–membrane), concentration polarization and aggregate desorption during UF and NF filtration [6,7]. Huisman et al. reported that the initial stage of filtration was mainly controlled by protein–membrane interactions (hydrophobic interactions, electrostatic interactions, aggregation behavior), but in the later stages of filtration, protein–protein interactions (cake layer) dominated the fouling behavior [8]. Because of a broad size distribution, SA has both small molecules with high diffusivities and large molecules with low diffusivities. Therefore, they would be fractionated in the deposited cake with larger molecules closer to the membrane and smaller ones in the bulk [9].

However, compared to an individual foulant, membrane fouling caused by the mixtures of different organic foulants is more complicated. Hence, a new approach to investigate the membrane fouling behavior of combined foulants becomes more important [10,11]. A few studies investigated the combined fouling effect by using both inorganic/organic colloids and NOMs. It was found that flux decline rate in combined fouling experiments was higher than what was expected based on the sum of colloidal and organic fouling alone during silica colloids and HA in NF membrane [11]. This aggravated membrane fouling referred to a significant synergistic effect, which is attributed to a mechanism of hindered back diffusion of colloidal and organic foulants. In addition, Contreras et al. reported

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three mechanisms, increased hydraulic resistance of the mixed cake layer structure, hindered foulant diffusion and changed colloid surface properties due to organic adsorption, which played a role in combined fouling to various degrees [12]. These studies focused on the interactions between different organic matters, but ignored the interaction between organics. Tomaszewski et al. demonstrated that electrostatic attraction of humic substances–protein drove encapsulation of positively charged protein by HA, which could alter the surface properties of the complexes [13]. A number of literatures have shown that protein and polysaccharide molecules could link together with chemical and physical interactions [14,15]. These interactions result in modification of molecular structure, and affect interfacial characteristics. Therefore, the interactions between NOMs might also lead to the change in membrane fouling behavior.

Recently, a few of studies investigated the effect of combined organic mixtures on the fouling of UF and RO membranes. Jermann et al. [16] revealed the impact of molecular interactions between HA and SA on UF fouling mechanisms. This effort led to the conclusion that a mutual influence could affect each other due to steric effects and chemical interactions. HA can function as a bridge between alginate and membrane, causing a more stable and less reversible fouling layer than the individual alginate cake. However, Katsoufidou et al. [17] studied the effect of HA/SA mixtures during UF hollow fibers in dead-end mode in the presence and absence of calcium ions. The experimental results manifested that no significant synergistic effects occurred. The fouling behavior of the mixtures was quite similar to that of polysaccharides alone. Research efforts on organic fouling have also been made on RO membranes [18,19], which discovered that there was an inverse correlation between the size of the foulants aggregates and the intermolecular adhesion force. Foulant aggregate size generally decreases with the increase in intermolecular adhesion force.

Although researchers have made their efforts to understand the role of organics on membrane fouling, their results however are often insufficient and/or contradictory. The present study systematically investigated the fouling characteristics of UF membrane by using HA, BSA and SA as model compounds. The objective is to reveal the key factors governing the fouling behavior in combined foulants. Emphasis is placed on finding the relationship between fouling resistance and solution properties. The distribution of solution molecular weight and electrostatic interaction between foulant–foulant and foulant–membrane are used to explain the fouling behavior.

2. Materials and methods

2.1. Organic foulants

Polysaccharide, protein and HA were chosen to represent typical NOMs in drinking water. The HA stock solution was prepared by dissolving 1 g of HA (Sigma-Aldrich, USA) into 500 mL 0.01 mol/L NaOH solution. BSA and SA (from brown algae) solutions were purchased from Genview (0BS10440, purity > 99%) and Sigma-Aldrich (A2158), respectively. The two solutions were dissolved in 500 mL deionized (DI) water with 1 g of BSA or SA. All solutions were stirred for 24 h, and then filtered through a 0.45 μm glassfiber membrane to remove residual non-dissolved matters. The filtered solutions were stored in a sterilized glass bottle (1000 mL) at 4 °C. Dissolved organic carbon (DOC) was measured by a TOC analyzer (TOC-Vcph, Shimadzu, Japan). The distribution of the apparent molecular weight (AMW) of the organics in solution was analyzed by high pressure size exclusion chromatography (HPSEC) (Fig. S1).

Table 1
The characteristics of the synthetic water.

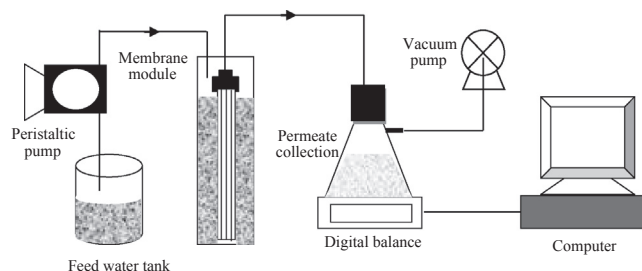|	Ratio	HA (mg/L)	BSA (mg/L)	SA (mg/L)	pH
HA:BSA	21	6.75 ± 0.1	3.35 ± 0.1	–	6.98 ± 0.04
	11	5.01 ± 0.3	5 ± 0.3	–	7.17 ± 0.05
	12	3.33 ± 0.1	6.67 ± 0.2	–	7.14 ± 0.01
HA:SA	21	6.6 ± 0.05	–	3.4 ± 0.03	7.12 ± 0.02
	11	5 ± 0.2	–	5 ± 0.2	6.97 ± 0.05
	12	3.29 ± 0.03	–	6.71 ± 0.06	6.91 ± 0.05
BSA:SA	21	–	6.7 ± 0.1	3.2 ± 0.2	7.25 ± 0.05
	11	–	5 ± 0.2	5 ± 0.2	7.27 ± 0.04
	12	–	3.45 ± 0.05	6.55 ± 0.04	7.22 ± 0.05

Fig. 1. The schematic of ultrafiltration hollow fibers in dead-end mode.

Two model organics could be mixed together in order to investigate the combined effects. Similarly, 0.001 mol/L NaOH and 0.001 mol/L HCl were used to regulate the pH value at 7. A summary of the synthetic water characteristics is shown in Table 1.

2.2. The hollow-fiber polyvinyl chloride membrane module

The hollow-fiber UF membrane module is made of Polyvinyl Chloride (PVC) (Litree Co., Hainan, China). It has a filtration area of 0.01 m², with the inner and outer diameters of 0.85 mm and 1.45 mm, respectively. The nominal pore size is 0.01 μm and molecular weight cutoff (MWCO) is 50 kDa. Each module contains 10 fibers, with an effective length of 23.0 ± 1 cm. The contact angle of the PVC membrane is measured as 33.67° ± 0.46, indicating a hydrophilic property [20].

2.3. Experimental procedures

A schematic diagram of the UF system is shown in Fig. 1. Feed solution was pumped into a membrane module (dead-end mode, outside-in) at a transmembrane pressure of 30 kPa. The permeate production was measured by a balance connected to a computer. A virgin membrane was used in each experiment in order to compare the results under the same condition. Prior to ultrafiltration test, the virgin membrane was soaked in deionized (DI) water for 24 h. DI water was initially permeated and pure water flux was measured until a constant flux was achieved (30 min was shown to be enough). It is well known that membrane flux imposes significant influence on membrane fouling [21]. So the initial flux (pure water flux) was set at 60 ± 3 L/(m² h). The organic solution (3 L) was then filtered and the flux was measured for 4 h. Every experiment was repeated three times.

The degree of membrane fouling is evaluated by membrane filtration resistance calculated by Darcy's law:

$$J = \frac{\Delta P}{\mu(R_m + R_f)} \tag{1}$$