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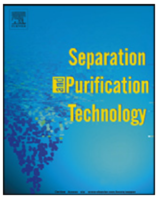

Hydrophobicity and molecular weight of humic substances on ultrafiltration fouling and resistance

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ABSTRACT

Humic substances are the major foulant during ultrafiltration (UF) of wastewater. This study evaluates the effects of hydrophobicity and fractionated humic substances on UF fouling and permeation resistance. A commercial humic acid (HA) obtained from Aldrich was subjected to DAX-8 resin for fractionation of hydrophobic and hydrophilic fractions. These fractions were fractionated further into different molecular weight groups using gel filtration chromatography. The hydrophilic fraction exhibited the greatest flux decline, revealing that hydrophobicity decreases fouling. Since the size of particle fractions was significantly smaller than the pore size of membranes, fouling was greatest for the largest fraction with a 100-kDa membrane and the smallest fraction with a 10-kDa membrane. Severe fouling was due to adsorption and pore blocking. For the first 300 min of filtration, the fouling rate was high in all fractions and is more for 100-kDa than 10-kDa membrane due to greater hydraulic resistance of the HA deposit on the membrane surface. The effect of resistances was also investigated. Each operationally defined resistance depended on membrane pore size, pressure, and HA characteristics. For hydrophobicity and the molecular weight effect, the hydrophilic fraction has the strongest resistance. This study suggested that strong resistance is responsible for irreversible fouling and that is primarily due to pore adsorption and pore blocking.

1. Introduction

Membrane technology is widely utilized for water and wastewater treatment, and in food, chemical, and pharmaceutical industries because of the technology's high removal capability and ability to meet multiple treatment objectives. The use of membranes in wastewater treatment technology has received considerable attention due to modified membrane characteristics, reduced membrane cost and their ability to remove different contaminants. For instance, different membrane systems have been applied for byproduct disinfection by removing organic precursors [1,2], and include the use of ultrafiltration (UF) for removing natural organic matter (NOM) [3–6]. However, one primary barrier to increased use of membrane technology is membrane fouling.

Generally, the fouling and the resultant flux decline are affected by membrane type, feed characteristics and operating conditions. Among membrane characteristics, pore size [7], pore size distribution [8], charge [9], hydrophobicity [10] and roughness [11] all affect the degree of membrane fouling. Wastewater characteristics, which interact with a membrane, also play a key role in membrane fouling. These characteristics include ionic strength [12], pH [1], presence of divalent ions [5], hydrophobicity of a particular compound [3] and size of solutes [13]. For operating conditions, temperature, pressure, pH [14], feed rate and influent contaminant concentration all influence permeate flux [15].

Humic substances (HSs) are a major part of NOM. Membrane fouling by HSs is a primary factor limiting pressure-driven membrane processes such as UF. Fouling caused by humic acid (HA) is influenced mainly by characteristics of the HSs and membrane, hydrodynamic conditions and the chemical composition of feed water [16].

Ultrafiltration membranes have been widely examined in removing NOM from drinking water sources. Previous studies have indicated that electrostatic interactions and solute transport properties, such as mass transfer coefficient, influence membrane performance [17,18]. Cho et al. [3] revealed that even a loose negatively charged UF membrane with a molecular weight cutoff (MWCO) value of approximately 8000 could be applied to remove low-weight (ca. 2000) macromolecular NOM. The concept of an effective MWCO has been introduced in several studies to account for enhanced NOM removal behavior of a negatively charged membrane under the same hydrodynamic operational conditions.

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Considerable disagreement exists about fouling mechanisms and the extent of the effects of hydrophobicity of a substrate on membrane fouling [14]. Is the flux decline proportional to membrane pore size? Is the hydrophilic portion of a substrate responsible for membrane fouling? What is the effect of membrane pressure on permeate flux? To what extent is fouling reversible? Clearly, a systematic study is required to address these questions. Consequently, this study quantifies the fouling phenomenon as a function of HA characteristics, with respect to HA hydrophobicity and molecular size on UF performance. A commercial humic substance was fractionated into hydrophobic and hydrophilic fractions, as well as fractions with different molecular weights. Specifically, factors associated with UF pore size (10 and 100 kDa) and operating transmembrane pressures (100–240 kPa) were varied to determine their effects on the permeate flux of these fractions. An operationally defined flux resistance was then utilized to provide a flux decline percentage (final flux divided by initial flux) and to calculate the following parameters: intrinsic resistance (R_m); weak resistance (R_{wa}); strong resistance (R_{sa}); and, reversible resistance (R_r).

2. Materials and methods

2.1. Samples

Approximately 1 g of commercial HA (Aldrich, sodium salt) was initially dissolved in Milli-Q water, filtered through a 0.45-μm filter and stored at 4 °C. The stock solution was further diluted to dissolved organic carbon (DOC) of 2 mg/L, the pH adjusted to 7 (10^{-3} M Na_2HPO_4 buffer) and conductivity of 1 mS/cm (with NaCl added) prior to use. Additionally, the concentrated HA sample (1 g/L) was fractionated into hydrophobic and hydrophilic fractions using DAX-8 resin (Supelite), based on the procedures described by Thurman and Malcolm [19]. The detailed procedures are outlined elsewhere [12]. Briefly, the hydrophilic fraction was collected with acidified HA (pH 2) and the hydrophobic fraction was obtained with 0.1 N NaOH eluent. Overall recovery factor was approximately 92%.

As explained in Lin et al. [20], the HA solution was fractionated into four groups – G1, G2, G3 and G4 – each with different apparent molecular weights (AMWs) using gel filtration chromatography (GFC). Briefly, Sephadex G-75 (Pharmacia) was used as a column packing material; polyethylene glycol was used for calibration of AMWs of 0.4, 1.5, 6, 12 and 20 kDa; blue dextrans (Pharmacia) was employed as an eluent to determine column bulk void volume. The recovery for the fraction by GFC was roughly 95%. The AMW fraction of G1 (8.6–33.4 kDa), G2 (2.2–8.6 kDa), G3 (0.56–2.2 kDa) and G4 (0.14–0.56 kDa) was 37%, 24%, 27% and 12%, respectively.

2.2. UF system

The negatively charged polysulfone hollow fiber membrane (inner diameter, 1.0 mm; thickness, 0.25 mm; length, 25 cm; surface area, 7.8 cm^2) (A/G Technology Co.) was operated in a cross-flow mode. The N_2 cylinder was employed to provide feed pressure; pressure gauges were placed at the inlet and retentate exit points (Fig. 1). The membrane was initially washed with alcohol at 70 kPa inlet pressure for 5 min and then rinsed with distilled water for 8 h prior to use.

The DOC rejection (R, %) is defined as [1]:

$$R = \left(1 - \frac{C_p}{C_f}\right) \times 100 \tag{1}$$

where C_p and C_f are permeate and feed DOC concentrations, respectively.

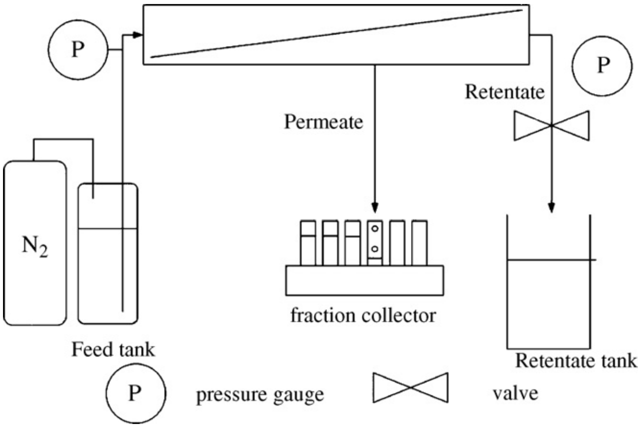

Fig. 1. Schematic of UF operation.

2.3. Experiments

Two membrane pore sizes (10 and 100 kDa) and three transmembrane pressures (100, 170 and 240 kPa) were evaluated at a constant pH (7.0 ± 0.1), influent DOC concentration (2 mg/L) and ionic strength (1 mS/cm) for three samples (unfractionated, hydrophobic and hydrophilic fractions). In total, 18 experiments were conducted. For the AMW study, only two pressures (100 and 170 kPa) at a constant ionic strength (300 μS/cm) and pH 7 were employed. During the 24-h UF operational period, the permeate was collected periodically for DOC analyses. Influent and retentate rates were measured to determine the permeate rate.

2.4. Resistance

The operationally defined resistances include R_m; R_{wa}; R_{sa} and R_r. The premise of resistance is based on the assumption that R_r, which forms via a polarization layer and gel formation, can be eliminated by water washing alone. The R_{wa}, which formed due to weak adsorption of the component present in the feed on the membrane, can be reduced with chemical cleaning, whereas R_{sa} remains after chemical cleaning. A similar approach was used by Cho et al. [21].

The R_m of the membrane was first determined by determining the membrane permeate flux (J, m/s) with deionized water.

$$J = \frac{P_T}{R_m} \tag{2}$$

where P_T is transmembrane pressure (Pa) and R_m in N s/m^3.

The flux after UF operation at a constant rate (5 mL/min or velocity of 0.12 m/s) can be expressed as

$$J = \frac{P_T}{R_m + R_r + R_{wa} + R_{sa}} \tag{3}$$

By rinsing the membrane with deionized water at constant flow rate of 5 mL/min for 30 min after UF operation, this study assumed R_r can be eliminated, resulting in a new flux:

$$J' = \frac{P_T}{R_m + R_{wa} + R_{sa}} \tag{4}$$

Another new flux was obtained by first rinsing the membrane with 0.1 N NaOH solution for 10 min and then deionized water for 30 min.

$$J'' = \frac{P_T}{R_m + R_{sa}} \tag{5}$$

Consequently, Eqs. (2)–(5) were used to derive the fractions of these different resistances.