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

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ARTICLE INFO

Article history:

Received 12 March 2008

Received in revised form 6 September 2008

Accepted 4 October 2008

Keywords:

Hydrophobicity

Molecular size

Ultrafiltration

Humic substances

Fouling

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.

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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 0.1N 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 cm²) (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]:

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

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 $\mu\text{S}/\text{cm}$) 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.

$$J = \frac{P_T}{R_m} \quad (2)$$

where P_T is transmembrane pressure (Pa) and R_m in Ns/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

$$J = \frac{P_T}{R_m + R_r + R_{wa} + R_{sa}} \quad (3)$$

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:

$$J' = \frac{P_T}{R_m + R_{wa} + R_{sa}} \quad (4)$$

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

$$J'' = \frac{P_T}{R_m + R_{sa}} \quad (5)$$

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

2.5. Analysis

The DOC (samples filtering through 0.45- μm paper) was measured using a TOC analyzer (O.I. 1010 model). The Fourier transform infrared spectroscopy (FTIR) spectrum of 4000–400 cm^{-1} was obtained via the KBr pellet technique on a Nicolet Magna II 550 FT-IR spectrometer. The KBr pellet had a weight ratio of approximately 1:200 (sample/Harshaw Stabilized KBr) and was prepared on a Harshaw Model 15 Quick Press. These values appeared to provide good results without noticeable over deconvolution.

3. Results and discussion

3.1. Fraction of hydrophobic/hydrophilic components

The recovery of commercial HA into hydrophobic and hydrophilic fractions using XAD-8 resin was roughly 92% with the majority being the hydrophilic fraction (91%). Fig. 2 presents the FTIR spectra of different transmittances among three samples of unfractionated HA (Fig. 2a), hydrophobic (Fig. 2b) and hydrophilic fractions (Fig. 2c). Clearly, the peaks of the hydrophobic and hydrophilic fractions differ from those of unfractionated HA. All three forms of HA (Fig. 2a–c) had characteristic peaks in the range of 3000–3500 cm^{-1} corresponding to OH stretching vibra-

Fig. 2. FTIR profiles (a) humic acid (b) hydrophobic fraction and (c) hydrophilic fraction.

Fig. 3. Absolute flux decline as a function of ionic strength at 170 kPa transmembrane pressure for the 100 kDa membrane size.

tions. These OH stretching vibrations varied slightly (Fig. 2a–c). The loss of the hydrogen bond in the hydrophobic fraction of HA causes weak OH stretching vibration. More intensive peak of hydroxyl is formed in hydrophilic fraction may be due to intermolecular hydrogen bonding. The prominent peaks at 1580 and 1387 cm^{-1} (Fig. 2a), correspond to COO^- [22,23], 1646 cm^{-1} (Fig. 2c) for $\text{C}=\text{O}$ stretching of COOH and the absence of these corresponding peaks in Fig. 2b. Similarly, the prominent peak at 1459 cm^{-1} is primarily due to aromatic part, and clearly indicates fractionation of HA. Moreover, the peak at 1142 cm^{-1} for the hydrophilic fraction may be due to $\text{C}-\text{O}$ stretching of esters or ether [24], the hydrophilic fraction has a higher intensive peak than unfractionated HA and hydrophobic fraction, and may be due to esters or ethers.

The UF experiments were performed at a constant DOC of 2 mg/L, conductivity of 1 mS/cm and pH of 7 (with 10^{-3} M phosphate buffer). Since NaOH and HCl were used in fractionating HA, a relatively high conductivity (1 mS/cm) was employed. Such high conductivity significantly affects permeate flux. As a blank, this study calculated the flux and flux ratio of water with electrical conductivities of 0, 1 and 2 mS/cm for up to 24 h. The flux decline for 1 mS/cm conductivity was approximately 25% after 24 h (Fig. 3).

As expected, initial flux increased as transmembrane pressure increased (Table 1). Membrane pore size of 100 kDa was larger than some molecules in HA. The initial fluxes for the 100 kDa membrane were markedly higher than those of the 10 kDa membrane. For example, at 240 kPa, the initial flux for the hydrophobic fraction for the 100 kDa membrane was $136 \mu\text{m}^3/\text{m}^2 \text{ s}$, and only $95 \mu\text{m}^3/\text{m}^2 \text{ s}$ for the 10 kDa membrane.

Figs. 4 and 5 present the effects of transmembrane pressure on flux decline for hydrophobic and hydrophilic fractions of HA and unfractionated HA for membrane pore sizes of 100 and 10 kDa, respectively. Experimental data clearly demonstrate that in all cases, the hydrophilic fraction has the greatest flux decline due to increased fouling. Notably, the hydrophobic fraction and unfractionated HA exhibit a similar flux decline at the highest pressure of 240 kPa. As membrane pressure and pore size increase, fouling

Table 1
Initial fluxes of humic acid fractions at different pressures.

Pressure (kPa)	Pore size (kDa)	Initial flux ($\mu\text{m}^3/\text{m}^2 \text{ s}$)
100	100	67–79
	10	40–42
170	100	104–107
	10	59–60
240	100	125–136
	10	88–95

Fig. 4. Absolute flux decline for 100 kDa pore size at different transmembrane pressures. (a) 100 kPa (b) 170 kPa and (c) 240 kPa (DOC = 2 mg/L, pH 7, and conductivity = 1 mS/cm).

increases, resulting in increased flux decline. With increased pressure, the rate of flux decline increases (Fig. 4a–c and 5a–c). Similarly, for the hydrophilic fraction, the rates of flux decline and fouling increased for the 100-kDa membrane. For hydrophobic and hydrophilic fractions and unfractionated HA, the hydrophilic fraction exhibits severe fouling and accounts for greatest flux decline even through the membrane used was hydrophobic and the reason is mainly attributed by a combination of adsorption and electrostatic attractions. Experimental data clearly suggests that hydrophobicity affects fouling to certain extent only; this finding is consistent with that obtained by Namakura and Matsumoto [25].

Fig. 6 presents the DOC rejection profiles for two different membrane pore sizes at a constant pressure of 100 kPa. The DOC rejection pattern for the two sizes was completely different from each other. For a large pore size UF, data are scattered and no trend exists regarding which fraction is removed best by UF (Fig. 6a). However, DOC rejection efficiency increased over time (feed volume). The small molecules of HSs initially passed through the large pores in UF; hence, DOC rejection was reduced. However, over operation for up to 24 h, DOC was eventually rejected due to closed pores, resulting in a rejection rate of about 55% (Fig. 6a).

For the small pore size (Fig. 6b), the unfractionated HA yielded the highest DOC rejection rate, which was relatively constant

Fig. 5. Absolute flux decline for 10 kDa pore size at different transmembrane pressures. (a) 100 kPa (b) 170 kPa and (c) 240 kPa (DOC = 2 mg/L, pH 7, and conductivity = 1 mS/cm).

(around 80%) throughout the experimental run. Such a high DOC rejection rate, however, did not correlate with the flux decline; which, in fact, yielded the smallest flux decline (Fig. 5a). Conversely, DOC rejection of hydrophilic fraction was only about 50%, which exhibited the worst flux decline (Fig. 5a). This experimental finding is same as that obtained by Zularisam et al., [26], who determined that hydrophilic NOM exhibited increased flux decline and less NOM removed due to pore adsorption. The interactions between the hydrophobic membrane and each fraction of HA account for the inability of the membrane to remove DOC.

3.2. Fraction of apparent molecular weight components

Fig. 7 shows the absolute membrane fluxes as a function of AMWs of HAs at a transmembrane pressure of 170 kPa. Again, the initial fluxes for the small pores were significantly less than those of the large pores (50 versus $183 \mu\text{m}^3/\text{m}^2 \text{ s}$) (Fig. 7 legend). For the 10-kDa membrane, the smallest AMW fraction (G4) exhibited the greatest flux decline (Fig. 7a), the small solute may enter into pores resulting in interior pore fouling. This experimental finding was supported by the fact that adsorption increased as solute size decrease [27]. As time progressed, the flux for the largest fraction (G1) declined further, possibly due to exterior pore blockage.

Fig. 6. DOC rejection as a function of membrane pore size at a constant transmembrane pressure 100 kPa. (a) 100 kDa and (b) 10 kDa.

Notably, unfractionated HA had the smallest flux decline. Conversely, the largest fraction (G1) had the largest flux decline for the 100-kDa membrane (Fig. 7b), whereas the G4 fraction (smallest) had the smallest flux decline. Apparently, the smallest solutes could pass through the large pores. For comparison, the DOC rejection efficiencies for the G4 fraction were approximately 60% and 80% for the 100 and 10-kDa membranes, respectively. Notably, the

Fig. 7. Absolute flux decline for different membrane sizes at a constant transmembrane pressure 170 kPa. The initial fluxes for 100 kDa ranged from 174 to 183 $\mu\text{m}^3/\text{m}^2\text{ s}$ and 46 to 50 $\mu\text{m}^3/\text{m}^2\text{ s}$ for 10 kDa membrane. (a) 10 kDa and (b) 100 kDa (DOC = 2 mg/L, pH 7 and conductivity = 300 $\mu\text{S}/\text{cm}$).

G4 fraction had a 60% DOC rejection for the 100-kDa membrane, which is likely due to the aggregation of small particles, thereby resulting in pore adsorption and pore blocking.

As pore size increased, flux decline increased. Only 25% of the original flux existed after 24 h for G1 and G2 fractions, whereas about 40% of the flux remained for G4 fraction (Fig. 7b). Clearly, the interactions between the AMW of HAs and MWCO of the membrane

Table 2

UF resistances of different fractions of humic substances (operation time = 1440 min).

Membrane pressure	Feed	R_{total} (Ns/m ³)	R_{m} (%)	R_{r} (%)	R_{wa} (%)	R_{sa} (%)
100 kDa membrane size						
100 kPa	Hydrophobic	5.06E+09	25	33	4	38
	Humic acid	4.56E+09	33	47	8	12
	Hydrophilic	1.14E+10	13	25	17	45
170 kPa	Hydrophobic	1.12E+10	15	31	9	45
	Humic acid	6.38E+09	26	34	14	26
	Hydrophilic	1.74E+10	10	21	20	49
240 kPa	Hydrophobic	1.17E+10	15	45	11	29
	Humic acid	1.16E+10	17	35	11	37
	Hydrophilic	2.42E+10	8	23	9	60
10 kDa membrane size						
100 kPa	Hydrophobic	5.86E+09	40	25	2	33
	Humic acid	4.37E+09	57	16	2	25
	Hydrophilic	7.97E+09	31	27	2	40
170 kPa	Hydrophobic	8.5E+09	34	26	8	32
	Humic acid	7.32E+09	39	32	1	28
	Hydrophilic	1.07E+10	27	27	4	42
240 kPa	Hydrophobic	7.01E+09	25	28	3	44
	Humic acid	5.8E+09	30	14	4	52
	Hydrophilic	1.95E+10	10	44	22	24

Fig. 8. Absolute flux decline for G1 fraction as function of membrane size and transmembrane pressures. The initial fluxes for 100 kDa ranged from 91 (100 kPa) to 188 $\mu\text{m}^3/\text{m}^2 \text{ s}$ (170 kPa) and those for 10 kDa from 34 (100 kPa) to 48 $\mu\text{m}^3/\text{m}^2 \text{ s}$ (170 kPa) (DOC = 2 mg/L, pH 7 and conductivity = 300 $\mu\text{S}/\text{cm}$).

have an important role in membrane fouling. The size of the G1 fraction is smaller than the 100-kDa membrane pore size; hence, fouling was due to pore blockage, gel layer formation and concentration polarization. However, the size of the G1 fraction is equal or greater than the 10-kDa membrane pore size; thus, the fouling mechanism can be explained primarily by gel layer formation and concentration polarization. As Li and Chen [28] stated, severe fouling is caused only by pore blockage and adsorption when compared to fouling by gel layer formations and concentration polarization.

Experimental results were essentially the same for a pressure of 100 kPa (data not shown), with the exception that flux decline was small. Fig. 8 presents the effect of pressure and membrane size for the largest G1 fraction. A large membrane pore size combined with a high pressure resulted in the highest flux decline and rate of flux decline. The flux decline was negligible for a small pore size combined with a low pressure.

3.3. Resistances

The resistances for all conditions were calculated. Table 2 shows the distribution of each fraction for the effect of hydrophobicity. Although, data appear scattered at first glance, a general trend existed in that the hydrophilic fraction accounts for the largest R_{sa} ; the hydrophilic fraction also had the highest flux decline (Figs. 4 and 5). Furthermore, pressure significantly affected the distribution of each operationally defined resistance. Pore size also affected each distribution. For instance, at a constant pressure of 100 kPa, the distribution for R_r for HA increased from 16% for 10 kDa to 47% for a loose membrane (100 kDa).

For a small membrane size (10 kDa), R_m was highest for the two low-pressure cases; as pressure decreased, R_m increased. The high ionic strength used (1 mS/cm) contributes to this high resistance. The R_{sa} and R_r accounted for most of the remaining fraction with an insignificant contribution from R_{wa} . As the membrane pore size increased, the distribution of the R_{sa} fraction always exceeded that of R_m ; the molecules of the ionic strength solution passed through the membrane with large pores, reducing R_m . A high R_{sa} fraction indicated that the membrane must be replaced frequently. In short, the membrane resistance of each operationally defined resistance depends on membrane pore size, pressure and the characteristics of HAs.

Fig. 9a and c presents the effects of AMWs on resistance for 10 and 100 kDa membranes at a pressure of 100 kPa, respectively. As membrane pore size decreased, membrane resistance R_m increased. Fig. 9b and d plots the resistance of the 10 and 100 kDa membranes, respectively, at a pressure of 170 kPa. The total resis-

Fig. 9. Resistance distributions as a function of apparent molecular weight. (a) 10 kDa 100 kPa (b) 10 kDa 170 kPa (c) 100 kDa 100 kPa and (d) 100 kDa 170 kPa (DOC = 2 mg/L, pH 7 and conductivity = 300 $\mu\text{S}/\text{cm}$).

tance of the 10 kDa membrane increased with the pressure, (Fig. 9a versus b), whereas that of the 100 kDa membrane remained roughly constant (Fig. 9c versus d). For the 10-kDa membrane, R_{sa} was dominant in the G4 fraction. These experimental results are important as strong membrane resistance is probably due to pore adsorption and/or pore blockage. The G1 fraction is responsible for the strong resistance of the 100-kDa membrane. The strong resistance of the 10-kDa membrane is due to the G4 fraction.

4. Conclusions

Humic acid was successfully fractionated into hydrophobic and hydrophilic parts. In both 10 and 100 kDa membranes and at all pressures, the hydrophilic fraction had highest fouling and unfractionated HA was the least, even when the membrane used was hydrophobic. Flux decline is mainly due to the combination of adsorption and electrostatic attractions, suggesting that hydrophobicity affects the fouling only to certain extent. The G4 fraction in the case of the 10-kDa membrane and the G1 fraction in the case of the 100-kDa membrane had the highest fouling. These fractions are comparatively smaller than respective membranes pore and, hence, severe fouling was caused only by adsorption and pore blockage when compared to fouling by gel layer formations and concentration polarization. The G4 fraction, for which the size is very small compared with the 100-kDa membrane, exhibits some flux decline, which may be due to the formation of aggregates. A large membrane pore size combined with a large pressure generates the highest flux decline and rate of flux decline, and fouling is increased. For a small pore size combined with a low pressure, the flux decline and fouling are negligible. The highest R_{sa} for the hydrophilic fraction and smallest molecular size fraction in the case of the 10-kDa membrane or largest molecular size fraction in the case of the 100-kDa membrane reveals strong resistance, which is responsible for irreversible fouling due to pore adsorption and pore blocking.

Acknowledgement

The authors would like to thank the National Science Council of the Republic of China for financially supporting this research under contract no. NSC 95-2221-E-212-022.

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