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Fouling of nanofiltration membrane by effluent organic matter: Characterization using different organic fractions in wastewater

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Abstract

The UF membrane with molecular weight cutoff (MWCO) ranging from 2 to 100 kDa and XAD-8 resin were employed to identify the characteristic of molecular weight (MW) distribution of wastewater effluent organic matter (EfOM) in terms of TOC and UV_{254}, as well as the amounts of the hydrophilic/hydrophobic organic fractions in different MW ranges. Then, the nanofiltration (NF) membrane fouling experiments were carried out using the above fractionated water to investigate the effect of MW distribution and hydrophilic/hydrophobic characteristics of EfOM on the membrane flux decline using the fractionated water samples. The experimental results have shown that 45.61% of the total organics belongs to the low MW one, among which the percentage of the hydrophilic organics with low MW (less than 2 kDa) was up to 28.07%, while that of the hydrophobic organics was 17.54%. In particular, the hydrophilic fraction was found to be the most abundant fraction in the effluents. MW distribution has a significant effect on the membrane fouling. When the MW was less than 30 kDa, the lower the MW, the larger was the specific flux decline, while in the case of MW higher than 30 kDa, the higher the MW, the larger was the specific flux decline, and the decline degree of low MW organics was larger than the high MW one. With the same MW distribution range, specific flux decline of the hydrophilic organic was considerably slower than that of the hydrophobic organic, which indicated that the hydrophobic organic fractions dominantly contribute to the flux decline.

Key words: molecular weight (MW) distribution; hydrophilic/hydrophobic; nanofiltration; specific flux

Introduction

Membrane process is becoming widespread because of its higher permeate flux but lower pressure. However, the wide use of membrane technology has been hampered greatly by membrane fouling, such as the declining of permeate flux, the increasing of membrane pressure, and the shortening of membrane life. It was reported that fouling was more severe for the larger pore size nanofiltration (NF) membranes compared to the smaller pore size membrane because of the greater effect of adsorption and pore restriction (or pore plugging) on the larger pore (Nghiem and Hawkes, 2007; Tang *et al*., 2007). NF membrane has a molecular weight cutoff (MWCO) in the range of 200–1000 Da intermediate between conventional reverse osmosis and ultrafiltration; the pore size is less than ultrafiltration (UF) membrane but the operation pressure is less than the reverse osmosis (RO) membrane. Therefore, research of NF gained considerable interest over the last years. Membrane fouling has been extensively investigated. The possible causes of NF membrane fouling depend on various factors, for example, membrane properties (i.e., membrane morphology, charge, and hydrophobicity, etc.), types of solutes (molecular weight (MW), $\log K_{ow}$, pK_a, etc.), feed water characteristics (concentration, ion strength, pH, etc.), and operating conditions (pressure, temperature, crossflow rate, etc.) as well as the interaction among membrane-solute-solvent.

For organic fouling, it was reported that the membrane surface tended to adsorb more hydrophobic fraction of nature organic matter (NOM) than hydrophilic fraction and the former was the major foulant (Yuan and Zydney, 2000; Tu *et al*., 2005). However, Mänttäri *et al*. (2000) found the improvement of pure water flux after filtration of humic acid possibly owing to the hydrophobic parts of humic acid binding onto the hydrophobic parts of the membrane, and the hydrophilic parts of humic acid directed towards the solution, which increased the membrane hydrophilicity. Other studies demonstrated that the high MW hydrophilic organic such as the protein or polysaccharids tended to deposit or scale on the membrane surface to decline the permeate flux significantly (Park *et al*., 2006; Li *et al*., 2007). High MW fraction contributed to the layer formation to foul the membrane. However, the flux may be severely reduced when treating low

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MW hydrophobic solutes even though the MWCO of the membrane was orders of magnitude greater than the size of the solute molecules (Hahn and O'melia, 2004; Lindau *et al*., 1998). In addition, Braeken *et al*. (2005) reported that hydrophobic molecules generally had a low retention, while hydrophilic molecules with a similar MW below the membrane MWCO showed a high retention, which could be explained by hydration of the molecules. There were several conflicting results between different researchers about the fouling mechanism. The fouling cause material probably owing to the different wastewater characterization, treatment technology, and operation conditions, as well as NF membrane properties etc. However, it is difinite that the MW distribution and hydrophobicity of dissolved organic compounds had a significant influence on NF membrane fouling.

During the reclamation of wastewater, organic constituents contained in wastewater effluent, designated as effluent organic matter (EfOM), are found to play an important role as membrane foulants. However, the EfOM were complex and represented a wide range of soluble organic compounds, not only the macromolecular hydrophilic/hydrophobic organisms as polysaccharides, proteins collids (Rosenberger *et al*., 2006; Jarusutthirak and Amy, 2007), and humic and fulvic acids etc., but also the low MW hydrophilic/hydrophobic organisms as amino sugars, nucleic acids etc. (Barker *et al*., 2000). According to origins, organic constituents can be classified as NOM derived from drinking water sources and synthetic organic compounds (SOC) produced during domestic use and disinfection byproducts (DBPs) generated during disinfection processes of water and wastewater treatment as well as soluble microbial products (SMP) derived during biological processes of wastewater treatment (Drewes *et al*., 1999). The complexity and heterogeneity of the EfOM contribute to varying physical and chemical behaviors in membrane fouling, making the membrane fouling mechanisms difficult to be explained. In this study, the MW distribution of wastewater EfOM, as well as the amount of the hydrophilic/hydrophobic organic fraction in different MW ranges were identified, and the NF membrane fouling characteristics were discussed.

1 Materials and methods

1.1 Source water

Wastewater effluents utilized in fractionation campaigns were collected from Xi'an Wastewater Treatment Plant, which employs the Carrousel Oxidation Ditch process. The characteristics of wastewater samples were as follows: DOC 4.25–9.43 mg/L, UV_{254} 0.106–0.163 cm^{-1}, Specific UVA (SUVA), a ratio of UVA to DOC, 1.72–2.49 L/(m·mg). SUVA represents an index of aromaticity.

1.2 Bench-scale flat sheet experiments

The bench-scale experiments were performed using a crossflow filtration unit, which included a plexiglass flat-sheet membrane test cell. The effective membrane area was 0.96×10^{-2} m^2. The commercially available NF70 was applied as thin film composite (TFC) membranes with the polyacrylonitrile (PAN) as selective layer and polysulfone (PSF) as support layer. The NF membranes were stored in a 1 wt.% $NaHSO_3$ solution in DI water.

Nanofiltration membrane sheets were rinsed with effective methods to remove the preservation liquids and the preconditioning agents and/or additives used in the manufacturing processes (Zhao and Yuan, 2006) and then transferred to the bench-scale test cell. The membrane sheets were then compacted at a pressure 1.2 times higher than the operation pressure until the steady pure water flux was reached. The crossflow velocity and feed pressure were controlled by means of back pressure regulator and bypass valve.

1.3 Experimental section

1.3.1 Isolation protocol

The ultrafiltration membrane with MWCO ranged from 2 to 100 kDa, and XAD-8 resin was employed to identify the characteristic of MW distribution of EfOM and the hydrophilic/hydrophobic organic fractions. The effluent of wastewater collected was filtered with a 0.45-μm filter to remove the particulate materials to insure that the dissolved organic carbon (DOC) was approximately equal to the total organic carbon (TOC). Then, part of the wastewater effluent was subjected to SCM UF system for MW distribution measurement, and the other part was first pH adjusted to 2, then, adsorbed by XAD-8 resins. The XAD-8 resins (Rohm and Haas, USA) were used to fractionate EfOM into hydrophobic (XAD-8 adsorbable) and hydrophilic constituents (the remaining fractionation escaping the XAD-8 resins). The hydrophilic fraction was adjusted to pH 7 again and isolated with the MWCO UF membrane. The samples were stored in sealed containers at a temperature of 4°C until use.

1.3.2 Membrane resistances

By analyzing the various resistances, the type of NF membrane fouling could be evaluated indirectly. With reference to classification methods (Shon *et al*., 2007), nanofiltration membrane resistances (m^{-1}) were divided into groups: R_m, the membrane resistance; R_{cp}, the resistance owing to concentration polarization; R_c, the resistance owing to the cake layer, and R_p, the resistance owing to pore blocking. The resistances could be calculated by Darcy's Law.

1.3.3 Experiments of flux decline

Experiments of flux decline were performed in the same range of initial fluxes for each pretreated membrane. The pH was adjusted to 7 with HCl or NaOH solution. For each experiment, the reflux ratio (Q_f/Q_p) was operated at 8:1 and concentrate flow streams were continuously recirculated to the feed tank. Prior to filtration experiments, a 300-mL measured wastewater sample was initially pumped to the crossflow bench-scale system for pre-adsorption. The transmembrane pressure was kept at 0.5 MPa during the experiments. Permeate and retentate as well as feed samples were periodically collected to determine TOC and UV_{254}. Permeate was continuously measured using digital balance (BS210S, Sartorius, Germany), which was connected to the computer to monitor the cumulative volumetric flux throughout the experiments.

2 Results

2.1 Characterization of MW distribution of EfOM fractions

The hydrophilic components were measured directly, whereas, the hydrophobic isolations were calculated by subtraction with mass conservation. The MW distributions of EfOM and each isolate were determined.

According to the classification methods (Edzwald, 1993), when SUVA values ranged from 4 to 6.5, organic matter was mainly composed by humic acid and fulvic acid. This dissolved organic matter was usually characterized by more aromaticity and stronger hydrophobicity with larger molecular weight. When SUVA value was less than 3, the organic compounds had less aromaticity and relative hydrophilicity with a lower molecular weight. In this study, the SUVA was lower than 3 L/(m·mg) in the range of 1.72 to 2.49 L/(m·mg), which demonstrated that EfOM was mainly constituted of low MW hydrophilic organisms. The distribution of each EfOM fraction is illustrated in Fig. 1. The EfOM was comprised of 74.56% dissolved organism with the hydrophilic organism as the highest portion (50.79%). This result was in agreement with the study of Shon *et al*. (2006) and Imai *et al*. (2002). In this study, among the different MW distribution organisms, 45.61% of the organic MW was lower than 2 kDa, which particularly represents the highest MW distribution interval, among which the hydrophilic matter shared 28.07% and the hydrophobic matter shared 17.54%.

The feed temperature was measured to calibrate the flux decline trends.

2.2 Specific flux decline of EfOM and hydrophilic fractions with different MW distribution

The initial concentration of each fraction was adjusted to a TOC value of approximately 6 mg/L (which was the DOC value of the EfOM) to investigate the hydrophilicity/hydrophobicity and MW on membrane

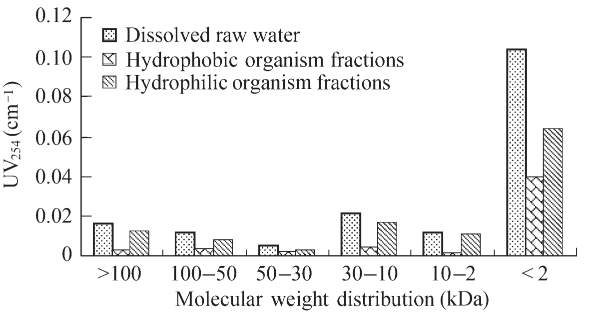

Fig. 1 Molecular weight (MW) distribution of effluent organic matter (EfOM) in terms of UV_{254} absorbance.

fouling character. The performance of NF70 membrane in treating different fractions was studied in terms of normalized permeate flux (J/J_0) (Fig. 2), where J_0 was pure water permeate flux.

Generally speaking, the evolution of membrane fouling decline experienced three steps: first, the permeate flux declined quickly because of the formation of concentration polarization; secondly, the flux continued decreasing because of the adsorption and deposition, but the rate of decline was down slowly; lastly, the flux decline tended to a critical flux until a cake layer or gel layer was formed. During NF process, the forces of the interaction between the membrane surface and particles are important in understanding the fouling phenomena. Therefore, the flux decline rate and extent were different because of the different operation conditions (operation pressure, flux recovery, velocity), water qualities, and membrane types (Kilduff *et al*., 2004; Koyuncu *et al*., 2004).

Figure 2a shows that MW exhibited a significant effect on NF membrane specific flux decline. The specific flux decline according to the MW degression sequence was 38.58%, 31.68%, 26.58%, 50.31%, and 60.42% in about 180 min.

Figure 2b depicts that the specific flux decline according to the MW degression sequence of hydrophilic organic fraction was 19.32%, 22.38%, 6.7%, 4.7%, and 56.84% in about 360 min.

3 Discussion

3.1 Effect of MW on NF membrane flux decline

Wang and Fukushi (2003) observed that the membrane foulants were connected with the flux recovery. With the decreasing of the flux recovery, MW of membrane pollutants increased and formed a porosity layer; when the recovery was 50%, high MW organisms ranging from 30 to 100 kDa were the main surface deposition. In this study, the recovery was only 12.5%. The permeate flux decline is illustrated in Fig. 2a; when the MW was less than 30, the lower the MW, the larger was the specific flux decline. In the condition of MW higher than 30 kDa, the higher MW was according to the more rapid flux decline. This was possibly because high MW organisms ranging from 30 to 100 kDa were deposited on the membrane surface to increase cake layer resistance, whereas, organisms with MW lower than 30 kDa were difficult to deposit and formed concentration polarization resistance. As illustrated in Fig. 3, low MW organics mainly formed concentration polarization resistance in NF membrane, and for high MW organics, the main resistances formed on the membrane were cake layer resistance and concentration polarization resistance. Therefore, both low and high MW organics can cause significant flux decline.

In addition, specific flux decline of low MW fractions was higher than the high MW fractions (Fig. 2a). It was possibly owing to the adsorption between the hydrophobic fractions and the membrane surface, which increased the fouling. Correspondingly, as illustrated in Fig. 1, the small-

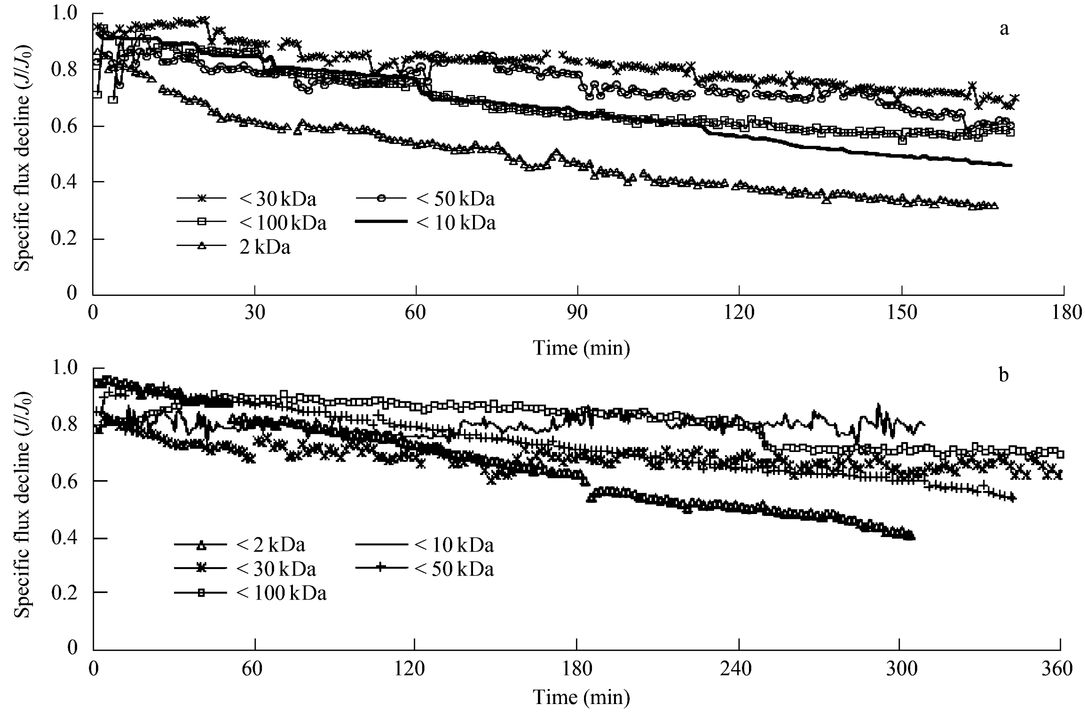

Fig. 2 Specific flux decline with different MW distribution of EfOM (a) and of hydrophilic organic fraction (b).

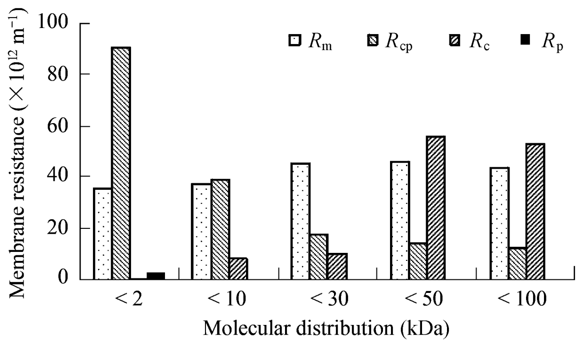

Fig. 3 Membrane resistance with different MW distribution of EfOM.

er the MW, the more the hydrophobic organic contained. In addition, according to the membrane fouling model, it may also because of that low MW organics can cause pore blocking/pore constriction and lead to the decrease of the effective membrane filtration area; while cake layer formed by high MW existed porosity, which may have some permeability and slow down the membrane flux decline.

3.2 Effect of hydrophobicity/hydrophilicity on NF membrane flux decline

In contrast with Fig. 2a, with the same MW distribution range, the specific flux of hydrophilic organic declined lesser and slower than that of the raw wastewater, which indicated that the hydrophobic fraction was the major factor causing permeate flux decline while the hydrophilic fraction had relatively small effect. However, when the hydrophilic fraction of MW was smaller than 2 kDa, the permeate flux declined more. The selectivity of NF membranes mainly depend on the following effects: steric effects, Donnan rejection and dielectric exclusion with the combination of hydrodynamic force, adsorption and permeation dragging force, etc. Thus, different conditions share different dominant interact forces. As noted above, the low MW hydrophilic fraction had the tendency to accumulate and foul owing to lack of back-transport. In addition, it can penetrate the membrane and block in the pores. As a result, the flux will be reduced severly.

4 Conclusions

A detailed investigation on membrane fouling with different fractions of EfOM was conducted and obtained the following results.

The Low MW and hydrophilic fraction was found to be the most abundant fraction in the EfOM of Xi'an Wastewater Treatment Plant.

MW of organic fractions exhibited a significant effect on NF membrane specific flux decline. When the MW was less than 30 kDa, the lower the MW, the larger was the specific flux decline, and in the condition of MW higher than 30 kDa, the higher MW was according to the more rapid flux decline. In addition, specific flux decline of low MW fractions was higher than the high MW fractions.

With the same MW distribution range, hydrophobic fraction was the major factor causing permeate flux decline while the hydrophilic fraction had relatively small effect.

Acknowledgments

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