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Natural organic matter fouling of low-pressure, hollow-fiber membranes: Effects of NOM source and hydrodynamic conditions

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ABSTRACT

Effects of natural organic matter (NOM) source and hydrodynamic conditions on both hydraulically reversible and irreversible fouling of low-pressure, hollow-fiber (LPHF) membranes were systematically investigated using representative sources of natural waters and wastewater effluents. It was found that NOM source plays a primary role in determining the fouling of these membranes. Increase in permeate flux promoted membrane fouling, but to a lesser extent than NOM source. Permeate backwash flux appeared to restore permeability more effectively for the polyether sulfone (PES) membranes than to the polyvinylidene fluoride (PVDF) membranes used. NOM characterization revealed that organic colloids contributed predominantly to the hydraulically reversible fouling, and potentially to the irreversible fouling. Overall, this study demonstrated the importance of NOM source and the presence of organic colloids in the fouling of LPHF membranes, as well as the relevance of hydrodynamic operating conditions on the hydraulic reversibility of the fouling.

1. Introduction

The 21st century has embarked on the large-scale application of low-pressure, hollow-fiber membranes (LPHF) in water and wastewater treatment, in terms of both a wider geography and a larger treatment capacity (US-EPA, 2001). Nevertheless, one important issue that presents a major impediment to the progress of this technology is membrane fouling. The term membrane fouling is usually employed to describe the loss of membrane hydraulic permeability due to the accumulation of aquatic materials on the membrane surface during the filtration process; this results in the reduction of the productivity of membrane and ultimately increases the cost of operation. Membrane fouling is a universal phenomenon observed with membrane systems used in water treatment. This study was undertaken with three specific objectives: (1) to develop experimental data with regard to the fouling of LPHF membranes by representative sources/types of natural

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organic matter (NOM) under controlled hydrodynamic conditions, (2) to demonstrate the effects of NOM source and hydrodynamic operating conditions on the reversibility of NOM fouling, and (3) to elucidate the potential role of colloidal and/or high molecular weight (HMW) components of NOM in the fouling of LPHF membranes.

The mechanism for the fouling of low-pressure membrane systems used in water treatment is poorly understood, in part as a result of the complex and unstable nature of organic materials present in natural waters. Field testing of LPHF membranes usually indicates a relationship between the magnitude of membrane fouling and seasonal or temporal variation of the NOM content and/or character in source waters. Characterization of foulant samples collected from membranes used in pilot and large-scale systems has shown the predominant presence of HMW macromolecules such as polysaccharides (Kimura et al., 2004). Meanwhile, much bench-scale testing of membrane fouling has been conducted using laboratory-use flat sheet membranes and natural waters or synthetic model waters containing isolated and/or fractionated NOM. The results have implied that colloidal NOM and/or HMW macromolecules may be the most problematic component in fouling of low-pressure membranes (Fan et al., 2001; Lee et al., 2004). Using hollow-fiber membranes, Carroll et al. compared the fouling of a polypropylene (PP) LPHF membrane by fractionated NOM samples. Their results indicated that the "hydrophilic neutral" fraction of NOM has the highest fouling potential (Carroll et al., 2000, 2002). Because the colloidal fraction of NOM was not isolated in their study, the "hydrophilic neutral" fraction determined likely includes both colloidal NOM and uncharged macromolecules in the original samples. Another study using size-fractionated humic acid (HA) samples demonstrated that the fouling of a polysulfone (PS) LPHF membrane increased as the molecular weight (MW) of HA fractions increased (Lin et al., 1999). In contrast to membranes used in above-mentioned studies, low-pressure membranes currently used in large-scale water treatment facilities are predominantly hollow-fiber membranes often made of polyvinylidene fluoride (PVDF) or polyether sulfone (PES) because of their superb chlorine and acid resistance. Structural modification of these membranes has also been a common practice for manufacturers to reduce membrane fouling. Therefore, the role of colloidal NOM in the fouling of these types of membranes is assessed in this study. For the convenience of discussion, colloidal NOM is used herein as a term for both colloidal NOM and HMW (macromolecular) NOM noted in the aforementioned studies. It is noteworthy that other colloidal materials in natural waters, such as fine aluminosilicate (Howe and Clark, 2002) and iron oxide particles (Schafer et al., 2000), can to a certain extent play a role in the fouling of low-pressure membranes. However, these colloidal materials either exist at a lower concentration in natural waters than organic materials (Roberts et al., 2004) or are associated with NOM due to adsorption of NOM on their surfaces (Schafer et al., 2000).

Little information is available in the literature on the specific chemical and physical factors that govern the fouling of LPHF membranes. In comparison, many interesting studies have been reported on the fouling of "high-pressure" membranes, including nanofiltration (Hong and Elimelech, 1997; Seidel and Elimelech, 2002) and some tight ultrafiltration membranes (Cho et al., 2000, 2002). These studies have demonstrated that membrane fouling is affected not only by the chemical properties of NOM and the membrane, but also by physical, especially hydrodynamic, operating conditions. It was generally found that both favorable surface interactions and increase in permeation drag force (or enhancement of convective transport of NOM to membrane surface) results in increase of NOM fouling. It was also found that, as a result of the competition between hydrodynamic forces and surface interactions, critical permeate fluxes may exist above which NOM fouling will substantially increase. This leads to possible pathways for fouling control either by modifying the membrane surface to reduce its affinity for organic foulants (Hester and Mayes, 2002; Taniguchi et al., 2003; Mosqueda-Jimenez et al., 2004) or by optimizing hydraulic conditions (Field et al., 1995). Although the structural properties of high- and low-pressure membranes may differ from each other, it is still expected that coupling effects between chemical and physical conditions do exist during the fouling of LPHF membranes by different types of NOM.

Lastly, membrane fouling is detrimental to both short-term and long-term productivity of LPHF membrane systems. Therefore, chemical and physical aspects of membrane fouling are relevant not only to the total amount of fouling obtained at the end of a filtration run (as have been focused on in the majority of previous studies), but also to the efficiency of subsequent hydraulic backwash or chemical cleaning in the restoration of membrane permeability. Most commercial LPHF systems operate in dead-end mode. Modifying hydraulic conditions during filtration is not practical, but variations in backwashing fluxes are oftentimes employed to reduce long-term fouling. Chellam and Jacangelo, 1998 found in a pilot-scale study that the effectiveness of hydraulic backwash was strongly dependent upon the existence of a critical recovery, i.e., percentage of permeate remaining after being used for backwash. The outside-in hollow-fiber membranes used in their study showed a dramatic decrease of backwash effectiveness once the recovery was below this critical value. Since this study was conducted using only one natural water source, evaluation of feedwater quality on fouling was difficult to assess. Likewise, another study using riverine water samples also demonstrated that irreversible fouling of hollow-fiber membranes can be controlled by varying operating conditions, such as transmembrane pressure (TMP) (Crozes et al., 1997). Despite these findings, the correlation between chemical properties of feedwater and backwash conditions remains to be determined.

2. Materials and methods

2.1. *Natural water samples*

Natural water samples were chosen based on preliminary characterization to represent typical organic materials present in various water sources, i.e., autochthonous (microbially

derived) NOM, allochthonous (terrestrially derived) NOM, and wastewater effluent organic matter (EfOM), as listed below:

- *White River raw water*: sampled from Indianapolis, Indiana, representing autochthonous NOM
- *Twente Canal raw water*: sampled from The Netherlands, representing autochthonous NOM
- *Tampa Bay raw water*: sampled from Tampa Bay Regional Water Treatment Plant, Florida, representing allochthonous NOM
- *Scottsdale secondary effluent*: sampled from City of Scottsdale Water Campus, Arizona, representing EfOM.

The water samples were prefiltered using 1.2 μm glass fiber filters (Whatman, Model GF/C) to remove coarse materials, including most bacteria and other macrobiota, and then stored at 4 °C in an environmental chamber. Prior to each fouling experiment, water samples were removed from the chamber and warmed to room temperature (18.5–19.0 °C). Some characteristics of the feedwaters are summarized in Table 1.

2.2. Low-pressure, hollow-fiber membranes

Four types of LPHF membranes were evaluated in the study. These membranes have all been used in full-scale facilities, and encompass the typical range of pore size and major materials. Selected characteristics of these membranes were obtained from the respective manufacturers and are presented as follows:

- *PVDF1*: a submerged, outside-in ultrafiltration (UF) membrane made of PVDF and possessing a nominal pore size of 0.02 μm
- *PVDF2*: a submerged, outside-in microfiltration (MF) membrane made of PVDF and having a nominal pore size of 0.1 μm
- *PES1*: an inside-out UF membrane made of PES and having a nominal pore size of 150–200 kDa
- *PES2*: an inside-out UF membrane made of PES and having a nominal pore size of 0.016 μm or 100 kDa.

The fibers supplied by the manufacturers were potted into mini modules with effective lengths of 0.24–0.28 m and membrane surface areas between 0.0055 and 0.0060 m^2. The PES2 fibers were provided by the manufacturer as potted mini modules with a surface area of approximately 0.0060 m^2, comparable to the others built in the laboratory. All new modules were cleaned by filtering at least 2 L of ultrapure water prior to the onset of fouling experiments. No pre-wetting of the modules was undertaken in this study because of the hydrophilic surface properties of the membrane fibers used.

2.3. Bench-scale filtration unit

The bench-scale testing unit used in the study was comprised of two parallel channels that allowed two membranes to be tested simultaneously. Both channels were operated under constant flux and either in an inside-out or submerged outside-in flow configuration. Each channel (cf. Fig. 1), consisting of a clear polycarbonate shell with a length of 300 mm, a disposable membrane module, and a digital compound pressure gauge (Cecomp Electronics, DGP100B ± 15PSIG-5), shared a dual channel digital peristalic pump (Cole Parmer, Masterflex digital standard pump) with the other channel. The pump was used as both the filtration and the backwash pump. In the case of the submerged membrane configuration, another dual channel peristalic pump (Cole Parmer, Masterflex precision pump) was used to feed raw water into the the polycarbonate shell that was employed as the feedwater column with the top open to the atmosphere. The water level in each shell was maintained constant by overflowing the excessive feedwater to a separate glass vessel.

Table 1 – Characteristics of the feedwaters used in the study

NOM source	White River	Twente Canal	Tampa Bay	Scottsdale
DOC (mg C/L)	3.9	9.5	17.2	6.0
UVA_{254} (cm^{-1})	0.091	0.236	0.743	0.102
SUVA (L/mg m)	2.32	2.49	4.32	1.70
PS-DOC (mg C/L)[a]	0.21	0.51	0.44	0.39
Percentage of PS-DOC	5.4	5.4	2.6	6.5
XAD-8/-4 resin fractionation				
Hydrophobic (HPO)	39%	45%	60%	32%
Transphilic (TPI)	25%	23%	22%	28%
Hydrophilic (HPI)	36%	32%	17%	40%
HPI DOC (mg C/L)	1.4	3.0	2.9	2.4
Ca (mg/L)	79.2	48.5	47.0	81.8
pH	8.0	7.7	7.0	6.9

[a] PS-DOC is a measure of the colloidal/HMW fraction in the source water, consisting of primarily polysaccharide and protein. It was derived from the HMW peak of the SEC-DOC spectrum.

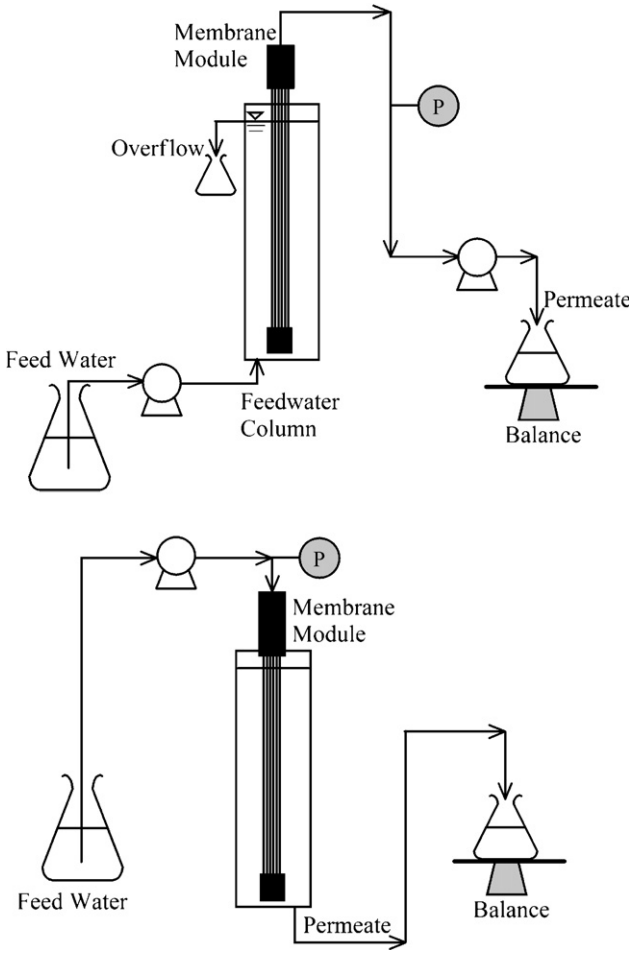

Fig. 1 – Schematic diagrams of the bench-scale testing unit in submerged, outside-in (upper) and inside-out (lower) configurations. Backwash is not shown, but was conducted by reversing the flow direction of the permeate pump, and therefore, the configurations are the same as in filtration mode.

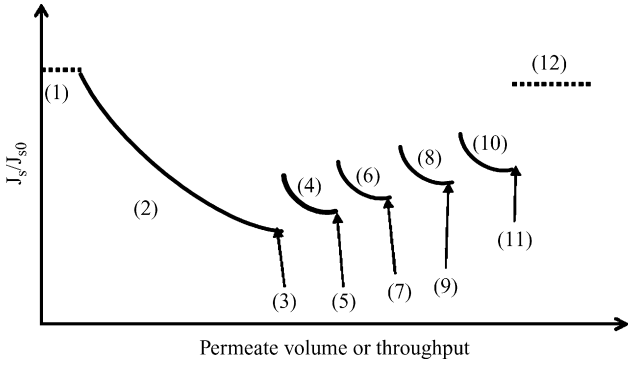

Fig. 2 – Diagram of filtration protocol adopted in the study. The operating conditions of each step is provided in the text.

2.4. *Filtration protocol*

As illustrated in Fig. 2, each filtration experiment included the following steps: (1) membrane rinsing and determination of clean membrane specific flux (J_{s0}) by filtering ultrapure water, (2) operation of clean membranes using natural water (designated as feedwater) at a specified permeate flux, (3) permeate backwash at permeate flux A, (4) operation of the backwashed membrane for 5 min using feedwater, (5) permeate backwash at permeate flux B, (6) operation of membrane for another 5 min using feedwater, (7) permeate backwash at permeate flux C, (8) operation of the membrane for a third 5 min period using feedwater, (9) 2 min of caustic backwash at permeate flux A, (10) operation of the membrane for a fourth 5 min period using feedwater, (11) 2.2 min of chlorine backwash and 30 min soaking time, (12) measurement of specific flux by filtering ultrapure water. The experimental hydraulic conditions were carefully controlled in the membrane fouling experiments in order to distinguish the effects of NOM source and operating flux. It is noteworthy that the effects of permeate flux on NOM fouling were interpreted through three separate runs with varying permeate fluxes, while those of backwash flux were tested by three consecutive backwash steps (Steps 3, 5, and 7) with three subsequent fouling or permeability tests (Steps 4, 6, and 8). The range of filtration fluxes was chosen based on the typical fluxes recommended by the manufacturers, while the fluxes for hydraulic backwashing were chosen as 1–2 times the highest flux used during the filtration.

2.5. *Size-exclusion chromatography*

Water samples generated during fouling experiments were collected for NOM characterization using a size-exclusion chromatography (SEC) technique. The utilization of dual real-time detectors made it possible to distinguish organic fractions by both UV absorbance and dissolved organic carbon (DOC). The former is mostly specific to humic substances with aromatic structures, while the latter is a measure of both humic and non-humic organic materials. Water sampled in each fouling experiment included the feed raw water, the permeate, the permeate backwash water, the caustic backwash water, and the retentate water (only for submerged, outside-in PVDF membranes). The instrumentation and operating protocol of SEC have been described elsewhere (Lee et al., 2004). The HMW or polysaccharide (PS) peak is related to the concentration of polysaccharides and other HMW compounds such as proteins. The relative amount of the HMW NOM in water samples was estimated by integrating the peak area of the PS peak (10–50 kDa) based on the DOC responses. The absolute concentration of this fraction was then calculated by using the standard calibration curves established for each NOM source.

3. Results and discussion

3.1. *Effects of NOM source on fouling*

In order to compare fouling data obtained with natural waters containing different concentrations of DOC, membrane fouling profiles are plotted as a function of the total amount of DOC delivered to a unit surface area of membrane. The total amount of delivered DOC was calculated based on permeate

throughput and feedwater DOC. Fig. 3 shows the variation of membrane fouling obtained with different sources of NOM. Given the similar mass loading of DOC and regardless of the type of membrane, the Scottsdale secondary effluent resulted in the greatest membrane fouling; Tampa Bay water produced the least. Considering the dominant NOM component of the waters, these data suggest that, under conditions employed in the study, EfOM exhibited the highest fouling potential, allochthonous NOM had the lowest fouling potential on LPHF membranes tested, and autochthonous NOM lay between the two. Another comparison was made between White River water and Scottsdale water since both contained a similar percentage of the hydrophilic fraction of NOM (36% versus 40%, cf. Table 1). As shown in Fig. 3, the two PVDF membranes were fouled at roughly the same rate by these two waters, which appeared to be consistent with the premise that the hydrophilic fraction of NOM contributes to most of the NOM fouling (Carroll et al., 2000). However, the two PES membranes showed a different pattern. The Scottsdale effluent caused substantially more fouling of these two membranes than White River water, suggesting that the analytical distinction of NOM hydrophilicity is probably insufficient for the interpretation of different fouling behaviors of NOM for all LPHF membranes. Therefore, the related results obtained in previous studies may be specific to the type of the membranes used.

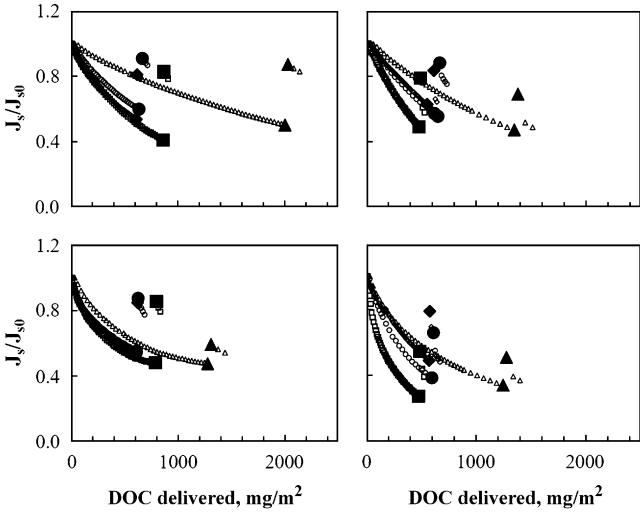

Fig. 3 – Fouling of PVDF1 (left, top), PVDF2 (left, bottom), PES1 (right, top), and PES2 (right, bottom) membranes by Tampa Bay (triangle), White River (diamond), Twente Canal (circle), and Scottsdale (square) NOM. Experiments with PVDF membranes were conducted at permeate and backwash fluxes of 109 LMH, and experiments with PES membranes were conducted at a permeate flux of 102 LMH and a backwash flux of 136 LMH. The break in the fouling curve indicates the operation of the permeate backwash.

3.2. *Effects of permeate flux on fouling*

The decrease of membrane specific flux at 450 mg C/m^2 delivered DOC is plotted as a function of permeate flux in Fig. 4. The fouling of the four membranes did not increase significantly with increasing permeate flux as shown in the figure, indicating the absence of critical permeate flux for their fouling by NOM. A more important observation in the figure is the relative importance of NOM source in membrane fouling. For instance, comparing Tampa Bay water to Scottsdale effluent, the loss of normalized specific flux (J_s/J_{s0}) with the PVDF1 increased by approximately 25%; however, an increase in fouling of only 10% (or less) was observed as the result of changes in permeate flux over a range of 54–109 LMH. Thus, the type of water or the source of NOM had a greater impact on membrane fouling than operating flux. Further, the

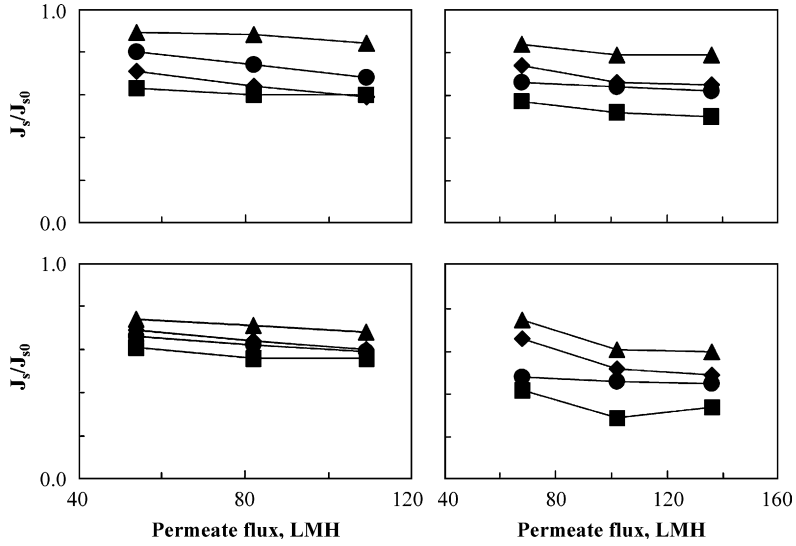

Fig. 4 – Fouling of PVDF1 (left, top), PVDF2 (left, bottom), PES1 (right, top), and PES2 (right, bottom) membranes by Tampa Bay (triangle), White River (diamond), Twente Canal (circle), and Scottsdale (square) NOM at a delivered DOC of 450 mg/m^2 and various permeate fluxes.

change in fouling with increasing flux was greatest for Scottsdale and Tampa Bay waters, which have the greatest and least hydrophilic fractions, respectively. This suggests that hydrophilic fraction is poorly correlated to fouling, at least for the PVDF membranes studied. As shown in Fig. 4, the effects of permeate flux on the fouling of PVDF2, PES1, and PES2 membranes by different natural waters, in general, showed similar trends as observed with the PVDF1 membrane, i.e., water type or NOM source had a greater impact on the loss of membrane specific flux than permeate flux.

The findings noted above are different from earlier studies with regard to the presence of critical flux in membrane fouling (Field et al., 1995; Vigneswaran et al., 2000). The difference is likely to result from the difference in the properties of the major foulants and the range of permeate fluxes tested. Since the hydraulic conditions used in the study were chosen based on real-world practice, the relationship between filtration fluxes and membrane fouling are likely to represent the practical performance of these commercial LPHF membranes.

Fig. 4 shows that an increase of permeate flux often resulted in increase in membrane fouling and the magnitude of the change was specific to each membrane and water combination, which indicates that the permeate flux effect was indeed associated with the type of water being treated. However, it is difficult to establish a clear relationship between NOM source and the presence of critical permeate flux for NOM fouling.

The effect of permeate flux on hydraulically irreversible fouling was not pronounced. Therefore, it is not discussed herein. This may be due to the low transmembrane pressure required to reach the desired permeate flux employed in the study. As found by Crozes et al. (1997), the threshold transmembrane pressure for this effect to manifest itself was approximately 0.85–1 bar, which was rarely exceeded in this study.

3.3. *Effect of NOM sources and backwash fluxes on hydraulically irreversible fouling*

Hydraulic reversibility of NOM fouling reflects the possibility of fouling control using permeate backwash, which has been a common practice and the most economical method for large-scale LPHF membrane systems. In this study, hydraulically irreversible fouling (HIF) was defined using the normalized specific flux observed 1 min after permeate backwash (cf. Fig. 2). Fig. 5 illustrates the HIF of the two PVDF membranes and the two PES membranes as a function of backwash flux. For the two PVDF membranes, the figure shows that NOM source had a greater impact on the HIF than backwash flux, which was similar to the results observed in the forward flux membrane experiments (cf. Fig. 4). The normalized specific flux after backwash varied over a range of 0.80–0.92 for the PVDF1 membrane and 0.60–0.92 for the PVDF2 membrane with different sources of waters, indicating some difference in response of the two PVDF membranes. This difference may relate to different structural properties of the two membranes, e.g., membrane pore sizes (0.02 μm for PVDF1 and 0.1 μm for PVDF2). The same maximum normalized specific flux (approximately 0.92) was observed for both PVDF membranes on the same water (Twente Canal) but at different backwash fluxes. For the two PES membranes, the HIF of two PES membranes was also affected by the NOM source, with a greater effect observed than that for PVDF1 and an effect similar to that for PVDF2. Of particular interest is the greater difference in HIF between PES1 and PES2 at all

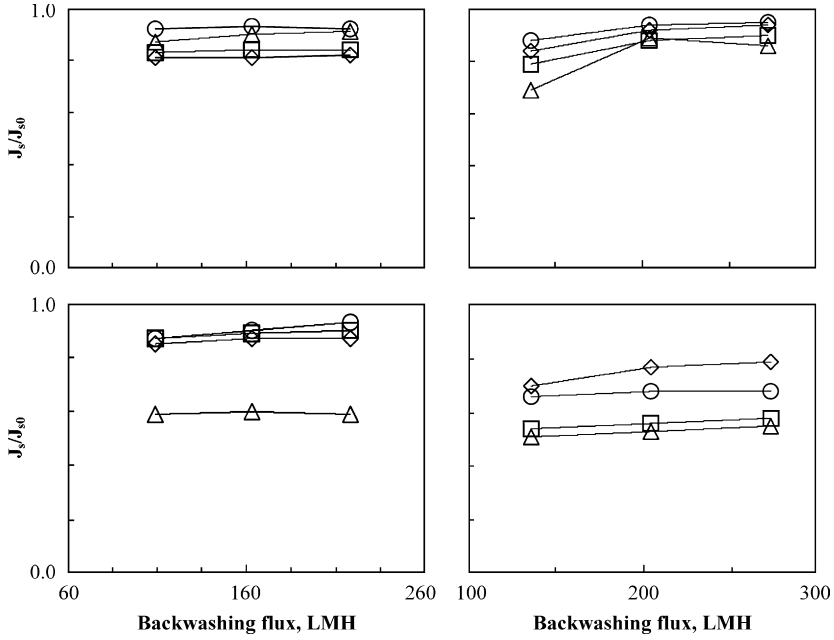

Fig. 5 – Effect of backwash flux and NOM source on the hydraulically irreversible fouling of PVDF1 (left, top), PVDF2 (left, bottom), PES1 (right, top), and PES2 (right, bottom) membranes. All runs were conducted at a permeate flux of 109 LMH for PVDF membranes and 102 LMH for PES membranes. The symbols represent Tampa Bay (triangle), White River (diamond), Twente Canal (circle), and Scottsdale (square) NOM.

backwash fluxes (cf. Fig. 5). This difference may be attributable to the incorporation of a hydrophilizing agent, polyvinylpyrrolidone (PVP), into the formulation of PES1, but not into that of PES2. Overall, the most dramatic impact of backwash flux on HIF was observed in the fouling of the PES1 membrane by Tampa Bay water, where the normalized specific flux increased by approximately 0.18 with increasing backwash flux. However, this difference was still less than that caused by the variation of water sources, i.e., approximately 0.20 for PES1 and 0.26 for PES2 membranes.

Fig. 5 also shows that the HIF caused by Tampa Bay water (representative of allochthonous NOM) equaled or even exceeded those caused by the other three waters, except for the PVDF1 membrane. This differs from what is shown in Fig. 4, where Scottsdale water (secondary effluent) produced the most total fouling. These results suggest that, although allochthonous NOM may cause less total fouling when normalized for DOC delivered, the fouling may be more resistant to reversal by backwashing (i.e., less hydraulically reversible) as compared to other sources of NOM. This finding is important to the evaluation of the fouling potential of different source waters as HIF is often ignored in many related bench-scale studies.

HIF directly reflects the loss of membrane permeability immediately after permeate backwash. It also impacts the fouling of membrane systems in the subsequent filtration of natural waters. This latter aspect was investigated by calculating the decreasing rate of the normalized specific flux after each of three sequential backwashes (cf. Fig. 2). The data were then normalized to the decreasing rate of the normalized specific flux observed with a clean membrane after the first 5 min of the filtration. The greater the normalized value, the faster the specific flux declines compared to a clean membrane. The results from experiments conducted at a permeate flux of 102–109 LMH for the four membranes studied are presented in Fig. 6. As shown in the figure, the two PES and the two PVDF membranes responded differently to the variation of backwash fluxes. The relative decrease of specific flux was reduced by a factor of 2–5 as the backwash flux doubled (from 136 to 272 LMH) in the case of PES membranes. In comparison, the relative decrease of specific flux remained at around one for the two PVDF membranes, regardless of the variation of backwash flux (ranging from 109 to 218 LMH). This difference between PVDF and PES membranes was observed consistently for all natural waters evaluated in the study. Therefore, it appeared not to be solely a result of the NOM source. However, it is unclear if this difference is attributable to membrane materials (PVDF versus PES) or membrane configurations (submerged, outside-in versus pressurized, inside-out). Meanwhile, the PVDF1 membrane has similar pore size as the two PES membranes, but it behaved similar to the PVDF2 membrane that has larger pore size in terms of the backwash effect. This suggests that pore size is probably not important in this case.

3.4. *Behaviors of colloidal NOM in membrane fouling*

Water samples collected from filtration experiments were characterized using SEC with DOC and UV detection (SEC-DOC/UV). It was found that the chromatographs of NOM for these water samples usually showed three distinct peaks in terms of the DOC response (cf. Fig. 7). The HMW (PS) peak appeared in a MW range of 10–50 kDa, the middle MW (humic substances) peak in a range of 1–10 kDa (mostly 1–5 kDa), and the low MW (low MW acids) peak in a range of several hundred daltons or less. Comparatively, the medium MW (humic substances) peak appeared dominant in terms of the UV response, while the other two peaks were almost negligible. The reference compounds used for the SEC were polyethylene glycol (PEG) with different MWs. The hydrodynamic radius of 30 kDa PEG is approximately 5.5 nm as calculated using the following relationship (Berestovsky et al., 2001):

$$\bar{r}_h(\text{in nm}) \approx MW^{1/2}(\text{in kDa}).$$

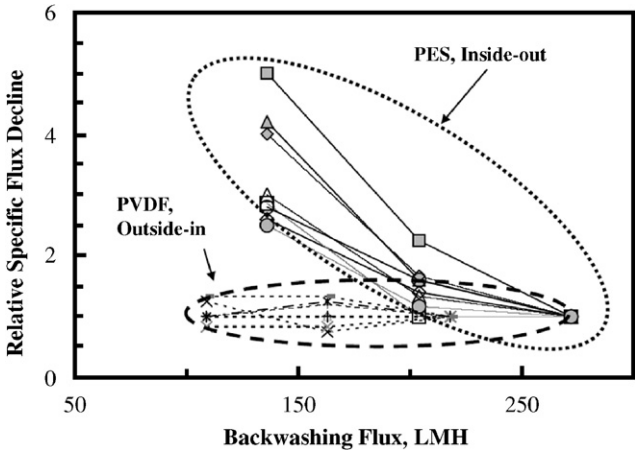

Fig. 6 – Relative decrease in specific flux as a function of permeate backwash flux for four membranes with different materials and configurations. The two ovals indicate two distinctive regions for PVDF, outside-in, and PES, inside-out membranes, respectively.

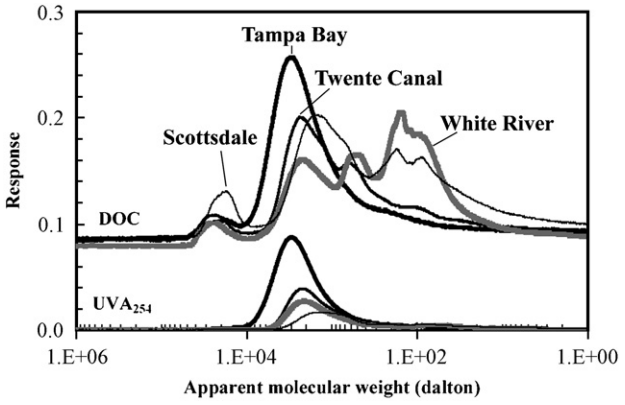

Fig. 7 – SEC-DOC/UV chromatograph of four natural waters used in the study. The upper and the lower curves were based on the response of the DOC detector and the UV detector, respectively.

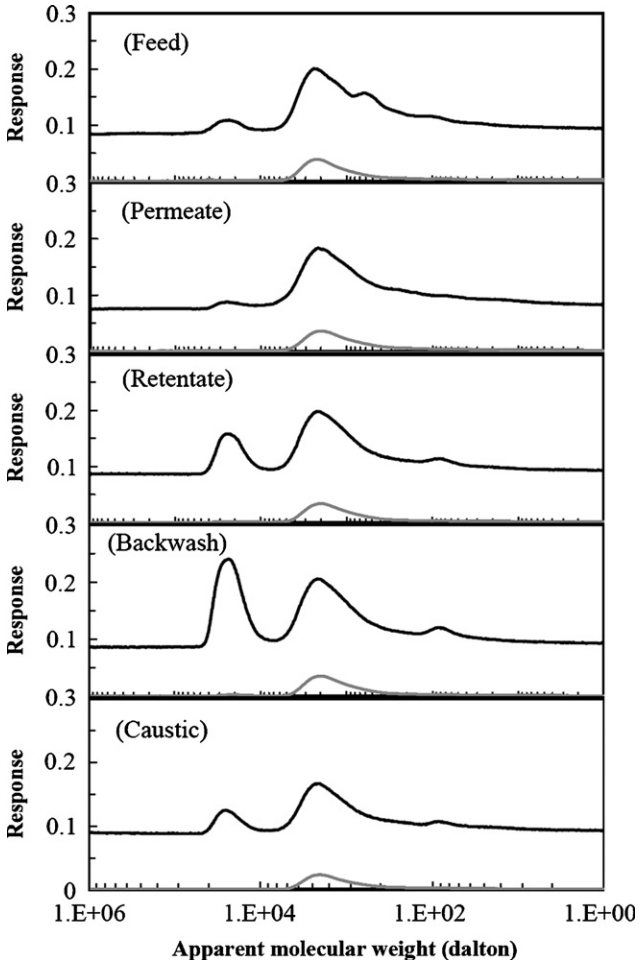

Fig. 8 – SEC-DOC/UV responses for Twente Canal water filtered with the PVDF2 membrane.

Aquatic materials of this size are indeed in the defined size range of colloids (1 nm–1 μm). Chemically, the HMW (polysaccharide) peak represents HMW macromolecules (PSs and proteins) and possibly colloidal NOM as well. These organic substances are usually classified as "non-humic" in character (Lee et al., 2004), but the aggregates of some humic substances may also fit into this size range as found with different water samples (Huang, 2006).

Fig. 8 is an example of the SEC-DOC/UV responses of different samples collected in a fouling experiment. As shown in the figure, the most extensive differences were observed for the HMW peak, while the other two peaks remained mostly unchanged. During the filtration of Twente Canal water, HMW/colloidal NOM in the feedwater was partially retained by the PVDF2 membrane, observed as a decrease of the HMW peak from the feed raw water to the permeate. Meanwhile, for this submerged membrane, some HMW/colloidal NOM rejected by the membrane did not attach to the membrane surface, but remained in the bulk liquid phase, resulting in the concentration of these NOM in the retentate sample. Thereafter, backwashing of the fouled membrane removed some of the HMW/colloidal NOM on the membrane surface as the high MW peak increased dramatically for the backwash water sample. The remaining HMW/colloidal NOM was further removed from the membrane surface during the caustic backwash, evidenced by the appearance of a distinctive HMW peak in the chromatograph. On the other hand, the medium and low MW peaks were fairly consistent for all samples, indicating little if any rejection or adsorption of these NOM fractions by the PVDF2 membrane. Similar trends were observed with other membrane and water combinations.

Table 2 summarizes the PS-DOC (corresponding to the HMW peak) for all waters employed in this study. This table clearly shows that the trend observed during the filtration of Twente Canal water using the PVDF2 membrane was similar for all other membrane and water combinations, suggesting that the relevance of colloidal/HMW NOM in the fouling of LPHF membranes is likely to be universal for the LPHF membranes used in water treatment. Similar trends have also been observed by other researchers (Lin et al., 1999). Since the retention and removal of colloidal/HMW NOM were always coincident with the loss and restoration of a membrane-specific flux (i.e., permeability), it is probable that colloidal/HMW NOM was most responsible for the hydraulically reversible fouling of the LPHF membranes evaluated in this study. Colloidal/HMW NOM may also play an active role in chemically reversible fouling as suggested by the correlation between caustic restoration of HIF and the presence of colloidal NOM in the caustic backwash water (cf. Fig. 8 and Table 2).

The role of colloidal NOM in the fouling of low-pressure membranes has been found in many other bench-scale studies involving different types of natural surface waters and wastewater effluents as introduced previously. This study found that colloidal NOM may have a similar role in the fouling of commercially available LPHF membranes. The mechanisms of the fouling induced by colloidal NOM were usually considered as a combination of membrane pore blocking at initial stage and cake layer formation afterwards (Yuan et al., 2002; Costa et al., 2006). The importance of colloidal NOM in fouling was thought to be primarily associated with their relative large sizes as compared with other NOM components. The importance of the relative size of NOM and membrane pores in membrane fouling was observed by Costa et al. (2006) and Lee et al. (2006). However, because the relative sizes of NOM and membrane pores appeared to be similar for the three UF membranes studied, i.e., PVDF1, PES1, and PES2, the size effect itself seems insufficient in explaining the membrane specificity of water fouling potential and the variable reversibility of fouling found in this study.

Other studies with respect to membrane modification have demonstrated that membrane fouling may be reduced by treating membrane surfaces in a variety of approaches (Kilduff et al., 2005), especially hydrophilization (Maartens et al., 2000) or ionization (Carroll et al., 2002), because these approaches can mitigate the attachment of foulants on membrane surfaces. Therefore, it is necessary to consider the effect of "chemical attachment" and its coupled effects with the relative size of NOM.

According to the findings of a related modeling study (Huang, 2006), the extent of irreversible fouling is determined by both the relative size of colloidal NOM and the presence of

Table 2 – DOC for HMW/colloidal NOM in different water samples, calculated from SEC-DOC results. (unit: mg C/L)

Membrane	Water	Feed	Permeate	Backwash	Caustic	Retentate
PVDF1	White River	0.21	n.a.	3.34	n.a.	0.68
	Tweente Canal	0.51	0.28	3.01	0.72	1.22
	Tampa Bay	0.44	n.a.	n.a.	n.a.	n.a.
	Scottsdale	0.39	0.23	3.17	0.40	n.a.
PVDF2	White River	0.21	0.19	3.47	n.a.	0.95
	Tweente Canal	0.51	0.29	2.95	0.66	1.38
	Tampa Bay	0.44	n.a.	n.a.	n.a.	n.a.
	Scottsdale	0.39	0.16	4.52	0.47	n.a.
PES1	White River	0.21	0.18	1.79	n.a.	n.a.
	Tweente Canal	0.51	0.28	2.63	1.01	n.a.
	Tampa Bay	0.44	0.28	2.65	1.02	n.a.
	Scottsdale	0.39	0.24	4.39	0.74	n.a.
PES2	White River	0.21	0.18	2.18	n.a.	n.a.
	Tweente Canal	0.51	0.29	2.93	1.09	n.a.
	Tampa Bay	0.44	0.18	3.16	3.21	n.a.
	Scottsdale	0.39	0.30	3.70	0.81	n.a.

Note: "n.a." means that data are unavailable.

stable colloid-membrane attachment, and therefore, a critical size range exists for "sticky" aquatic substances (approximately 10–100 nm, depending on membrane pore size) to be effective in blocking membrane pores and causing fouling. This to a great extent explains why the extents of irreversible NOM fouling were significantly different for the membranes studied since the stickiness of colloidal NOM may be different for various membranes with similar pore sizes. Quantitative information with respect to the interactions between NOM and LPHF membrane surfaces is rarely available in the literature as compared with reverse osmosis and nanofiltration membranes. This makes it difficult to comprehensively interpret the effect of NOM source and hydrodynamic conditions on colloidal NOM fouling of LPHF membranes observed in this study. Therefore, better characterization of colloidal NOM and LPHF membranes will be necessary for the better understanding of the fouling results and relevant interactions.

4. Conclusions

The fouling of LPHF membranes by different types of NOM is an important and challenging topic in the area of water and wastewater treatment. This study systematically explored the impact of NOM source and hydrodynamic operating conditions on the fouling of representative LPHF membranes. Fouling profiles as well as hydraulic reversibility of NOM fouling were evaluated in a series of bench-scale experiments. More information on the mechanism of fouling was obtained through the characterization of NOM in related water samples.

The major findings of the study can be summarized as follows:

(1) Given a similar amount of NOM delivered to membrane surface, wastewater EfOM (Scottsdale secondary effluent) caused the most severe total fouling for all membranes evaluated; allochthonous NOM (Tampa Bay water) caused the least. However, fouling by EfOM was, for the most part, hydraulically reversible. In comparison, allochthonous NOM produced the least amount of total fouling, but the hydraulic irreversible fouling was greater as compared to other types of NOM (except for PVDF1, the sole PVDF UF membrane).
(2) An increase in permeate flux promoted the fouling for all combinations of membranes and NOM sources, but the impact was less significant than NOM source. The presence of critical permeate flux for membrane fouling was not observed.
(3) The impact of backwash flux on hydraulic reversibility of fouling was specific to both membrane type and NOM source. However, the relative decline in the decreasing rate of specific flux as a function of backwash flux was greater for the inside-out PES than for the outside-in PVDF membranes.
(4) SEC-DOC/UV results revealed the retention and the detachment of HMW organic materials on LPHF membranes during filtration and backwash, coincident with the loss and the hydraulic restoration of membrane permeability. The other two NOM fractions, humic substances and low molecular weight acids, elucidated in this research, may also play a role in fouling, but their impact was less apparent.
(5) The response of the two PVDF membranes to NOM fouling was more similar than for the two PES membranes, despite the more significant difference in pore size of the former. This greater variability in PES membrane response is possibly attributed to the presence of PVP, a hydrophilizing agent, in the PES1 membrane.

It is evident from this study that the effects of NOM source on the fouling of LPHF membranes was affected by the

presence of certain fraction(s) of NOM, rather than all organic substances in natural waters. Further, these effects can also vary with different types of LPHF membranes. The fouling potential of each water source is usually specific to the type of membrane used. Therefore, better characterization of both membranes and NOM is necessary for a complete understanding of the fouling mechanism of LPHF membranes. In comparison, the effects of hydrodynamic conditions are important, but to a lesser extent, than NOM source.

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REFERENCES

Berestovsky, G.N., Ternovsky, V.I., Kataev, A.A., 2001. Through pore diameter in the cell wall of *Chara corallina*. J. Exp. Bot. 52 (358), 1173–1177.

Carroll, T., King, S., Gray, S.R., Bolto, B.A., Booker, N.A., 2000. The fouling of microfiltration membranes by NOM after coagulation treatment. Water Res. 34 (11), 2861–2868.

Carroll, T., Booker, N.A., Meier-Haack, J., 2002. Polyelectrolyte-grafted microfiltration membranes to control fouling by natural organic matter in drinking water. J. Membr. Sci. 203 (1-2), 3–13.

Chellam, S., Jacangelo, J.G., 1998. Existence of critical recovery and impacts of operational mode on potable water microfiltration. J. Environ. Eng.-ASCE 124 (12), 1211–1219.

Cho, J., Amy, G., Pellegrino, J., 2000. Membrane filtration of natural organic matter: factors and mechanisms affecting rejection and flux decline with charged ultrafiltration (UF) membrane. J. Membr. Sci. 164 (1-2), 89–110.

Cho, J., Sohn, J., Choi, H., Kim, I.S., Amy, G., 2002. Effects of molecular weight cutoff, *J/k* ratio (a hydrodynamic condition), and hydrophobic interactions on natural organic matter rejection and fouling in membranes. J. Water Supply Res. Technol. Aqua 51 (2), 109–123.

Costa, A.R., de Pinho, M.N., Elimelech, M., 2006. Mechanisms of colloidal natural organic matter fouling in ultrafiltration. J. Membr. Sci. 281 (1–2), 716–725.

Crozes, G.F., Jacangelo, J.G., Anselme, C., Laine, J.M., 1997. Impact of ultrafiltration operating conditions on membrane irreversible fouling. J. Membr. Sci. 124 (1), 63–76.

Fan, L.H., Harris, J.L., Roddick, F.A., Booker, N.A., 2001. Influence of the characteristics of natural organic matter on the fouling of microfiltration membranes. Water Res. 35 (18), 4455–4463.

Field, R.W., Wu, D., Howell, J.A., Gupta, B.B., 1995. Critical flux concept for microfiltration fouling. J. Membr. Sci. 100 (3), 259–272.

Hester, J.F., Mayes, A.M., 2002. Design and performance of foul-resistant poly(vinylidene fluoride) membranes prepared in a single-step by surface segregation. J. Membr. Sci. 202 (1–2), 119–135.

Hong, S., Elimelech, M., 1997. Chemical and physical aspects of natural organic matter (NOM) fouling of nanofiltration membranes. J. Membr. Sci. 132 (2), 159–181.

Howe, K.J., Clark, M.M., 2002. Fouling of microfiltration and ultrafiltration membranes by natural waters. Environ. Sci. Technol. 36 (16), 3571–3576.

Huang, H., 2006. Microfiltration membrane fouling in water treatment: impact of chemical attachments. Ph.D. Dissertation, Johns Hopkins University.

Kilduff, J.E., Mattaraj, S., Zhou, M.Y., Belfort, G., 2005. Kinetics of membrane flux decline: the role of natural colloids and mitigation via membrane surface modification. J. Nanoparticle Res. 7 (4-5), 525–544.

Kimura, K., Hane, Y., Watanabe, Y., Amy, G., 2004. Irreversible membrane fouling during ultrafiltration of surface water. Water Res. 38 (14–15), 3431–3441.

Lee, N., Amy, G., Croué, J.-P., Buisson, H., 2004. Identification and understanding of fouling in low-pressure membrane (MF/UF) filtration by natural organic matter (NOM). Water Res. 38 (20), 4511–4523.

Lee, N., Amy, G., Croue, J.P., 2006. Low-pressure membrane (MF/UF) fouling associated with allochthonous versus autochthonous natural organic matter. Water Res. 40 (12), 2357–2368.

Lin, C.-F., Huang, Y.-J., Hao, O., 1999. Ultrafiltration processes for removing humic substances: effect of molecular weight fractions and PAC treatment. Water Res. 33 (5), 1252–1264.

Maartens, A., Swart, P., Jacobs, E.P., 2000. Membrane pretreatment: a method for reducing fouling by natural organic matter. J. Colloid Interface Sci. 221 (2), 137–142.

Mosqueda-Jimenez, D.B., Narbaitz, R.M., Matsuura, T., 2004. Impact of membrane surface modification on the treatment of surface water. J. Environ. Eng.-ASCE 130 (12), 1450–1459.

Roberts, K.A., Santschi, P.H., Leppard, G.G., Marcia West, M., 2004. Characterization of organic colloids from surface and ground waters at the actinide-contaminated Rocky Fats Environmental Technology Site (RFETS), Colorado, USA. Colloids Surf. A: Physicochem. Eng. Aspects 244 (6), 105–111.

Schafer, A.I., Schwicker, U., Fischer, M.M., Fane, A.G., Waite, T.D., 2000. Microfiltration of colloids and natural organic matter. J. Membr. Sci. 171 (2), 151–178.

Seidel, A., Elimelech, M., 2002. Coupling between chemical and physical interactions in natural organic matter (NOM) fouling of nanofiltration membranes: implications for fouling control. J. Membr. Sci. 203 (1–2), 245–255.

Taniguchi, M., Kilduff, J.E., Belfort, G., 2003. Low fouling synthetic membranes by UV-assisted graft polymerization: monomer selection to mitigate fouling by natural organic matter. J. Membr. Sci. 222 (1-2), 59–70.

US-EPA, 2001. Low-pressure Membrane Filtration for Pathogen Removal: Application, Implementation and Regulatory Issues. United States Environmental Protection Agency, Cincinnati, OH.

Vigneswaran, S., Kwon, D.Y., Ngo, H.H., Hu, J.Y., 2000. Improvement of microfiltration performance in water treatment: is critical flux a viable solution? Water Sci. Technol. 41 (10–11), 309–315.

Yuan, W., Kocic, A., Zydney, A.L., 2002. Analysis of humic acid fouling during microfiltration using a pore blockage-cake filtration model. J. Membr. Sci. 198 (1), 51–62.