Effects of molecular weight cutoff, *f/k* ratio (a hydrodynamic condition), and hydrophobic interactions on natural organic matter rejection and fouling in membranes

Jaeweon Cho, Jinsik Sohn, Heechul Choi, In S. Kim and Gary Amy

ABSTRACT

All the possible mechanisms and factors affecting flux decline, natural organic matter (NOM) rejection, and NOM transport were studied in this paper. Electrostatic exclusion (charge repulsion) was determined to be an influential factor in minimizing flux decline and membrane fouling, and in maximizing NOM rejection; the effective MWCO (membrane molecular weight cutoff) concept was used to support the notion of electrostatic interactions and to describe an apparent MWCO by a charged membrane. This allowed for a negatively-charged tight ultrafiltration (UF) membrane to be comparatively compared to a nanofiltration (NF) membrane in terms of NOM rejection. The *f/k* ratio, relating relative back-diffusional transport to convective transport, was identified as a major influential factor in terms of flux decline and NOM rejection. The effect of hydrophobicity on flux decline was not significant when the same *f/k* ratio was used for different NOM-membrane pairs. The convectional and diffusional transportation of NOM was also evaluated for NF and UF membranes using existing thermodynamic models.

Key words | *f/k* ratio, flux decline, nanofiltration, natural organic matter, ultrafiltration

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INTRODUCTION

A wide range of initial membrane studies (flux decline, natural organic matter (NOM) rejection, NOM transport) with NOM were evaluated using a cross-flow unit with nanofiltration (NF) and ultrafiltration (UF) membranes to determine influential factors and mechanisms associated with flux decline and NOM rejection. A comparison of NF and UF membranes reflects how membrane molecular weight cutoff (MWCO) affects membrane fouling and NOM rejection. Membrane MWCO is believed to be a starting point for NOM rejection by membrane filtration, because size exclusion is a primary mechanism of the membrane process. A concept of effective MWCO is introduced to consider the effects of electrostatic repulsion (Cho *et al*. 1999) and hydrodynamic operating conditions (in this paper, we used a *f/k* ratio) (Cho *et al*. 2000) on NOM rejection, with effective MWCO being much lower than expected according to the nominal MWCO provided by the manufacturer.

Hydrophobic interactions were influential factors on flux decline, according to results showing that hydrophobic NOM solution (XAD-8 resin isolate) exhibited greater flux decline than hydrophilic NOM solution (the effluent of XAD-8 resin) (Nilson & DiGiano 1996). Hydrophobic polysulfone (PSf) membranes with hydrophobic nonionic surfactants were also used to obtain relatively greater flux decline than hydrophilic membranes with the same surfactant due to the hydrophobic interactions (Yamagiwa *et al*. 1993). A stirred-cell dead-end unit was used to obtain flux declines with polyether sulfone (PES) and regenerated cellulose (RC) UF membranes (Laine *et al*. 1989). PES membranes (PM series) exhibited greater flux decline than RC membranes (YM series). According

to the above flux-decline studies, it seems likely that PSf and sulfonated PES membranes can be fouled easily by hydrophobic components due to the hydrophobicity of the membrane surface.

Polyamide thin-film-composite (TFC) membranes (NF90 from FilmTec and TFCS from Fluid Systems) were used to obtain flux declines from NOM containing natural water, along with possibly sulfonated PES membranes (NTR7450 from Hydranautics) (Allgeier *et al*. 1996). Polyamide TFC membranes exhibited very little or almost no flux declines in Ohio River water for 4–13 days, even with a recycled line. Sulfonated PES membranes showed relatively more flux decline for 4–7 days and needed frequent membrane cleaning to maintain high flux.

For a transport measurement in a cross-flow apparatus, the concentration polarization model and the Kedem-Katchalsky model by Tandon *et al*. (1994)—for small or large Peclet numbers (the ratio of convective to diffusive solute transport)—were used to evaluate NOM transport through membrane pores. When the Reynolds number (Re) is much larger than unity (Re>>1), the convective-diffusion equation can be used to represent a NOM balance between a convective transport to the membrane surface and a diffusive transport away from the membrane surface into the bulk solution (Wiesner & Chellam 1992). Because the thin concentration boundary layer can be formed (fluid velocity changes across a channel in laminar flow) due to a large Peclet and Schmidt number, a back-diffusional transport can be envisioned, defined as the back-diffusional mass transfer coefficient (k) in the concentration boundary layer. The coefficient (k) can be calculated for a laminar flow by Equation (1) (Porter 1972):

$$k = 1.62 \left(\frac{UD^2}{d_h L} \right)^{0.33} \quad \text{(cm/s)} \tag{1}$$

where U is the average velocity of the feed fluid (cm/s), D is the diffusion coefficient (cm^2/s), d_h is the equivalent hydraulic diameter (cm), and L is channel length (cm). The diffusion coefficient may be calculated from the Stokes-Einstein relationship.

A permeation flux (f, cm/s), calculated by dividing permeate volume by the surface area of membrane, can be compared with the k value to suggest an f/k ratio, representing the ratio of the NOM molecule transport by back diffusion to water molecule transport by permeate flux. It is hypothesized that a smaller f/k ratio enables NOM molecules to easily move away from the membrane surface, resulting in more NOM rejection by, and less flux-decline of, the membrane surface. Using the same f/k ratio based on an initial clean water flux, the NOM rejection and flux-decline of the PA, PES, and sulfonated PES membranes can be compared equitably even though different transmembrane pressures are used.

The primary objectives of this study are to gain a better understanding of NOM flux decline and rejection in various membranes, and to minimize and maximize these, respectively, and to determine influential factors (including NOM/membrane properties, water qualities, and operating conditions) for flux decline and NOM rejection. Based upon the f/k ratio (of which effects on NOM rejection were demonstrated only with UF membranes (Amy & Cho 1999; Cho *et al*. 2000)), equitable ways to compare NF and UF membranes in terms of NOM rejection and flux decline will be suggested in this article.

EXPERIMENTAL METHODS

NOM characterizations

Various NOM-source waters were tested in membrane experiments for flux-decline, NOM rejection, and NOM transport through the membrane pores; these sources reflect different NOM concentration levels, a range of NOM hydrophobicities and humic content (% dissolved organic carbon, DOC), and various molecular weight (MW) distributions. All of the waters tested were from drinking water sources except Twitchell water, which was derived from an agricultural drain. Baseflow Silver Lake surface water (SL-SW), Horsetooth Reservoir surface water (HT-SW), runoff SL-SW, Irvine Ranch groundwater (IR-GW), and Orange County groundwater (OC-GW), are drinking water sources, representing an increasing order of aromaticity based on their specific UV absorbance at 254 nm (SUVA = UV absorbance at 254/DOC) values.

Table 1 | NOM characteristics of source waters

Source	pH	Conductivity (μS/cm)	DOC (mg/l)	UVA (cm^{-1})	SUVA (m^{-1} mg^{-1} l)	Humic content (% of DOC)
Baseflow	6.2	21.4	2.00	0.048	2.4	43.3
SL-SW						
HT-SW	6.7	58.5	3.12	0.092	2.9	58.5
Twitchell	7.1	1,066	47.8	1.77	3.7	60.6
Runoff SL-SW	6.4	29.9	3.88	0.172	4.4	56.9
IR-GW	8.8	477	9.80	0.480	4.9	80.0
OC-GW	8.1	534	6.81	0.387	5.7	90.1

Table 2 | Membrane characteristics

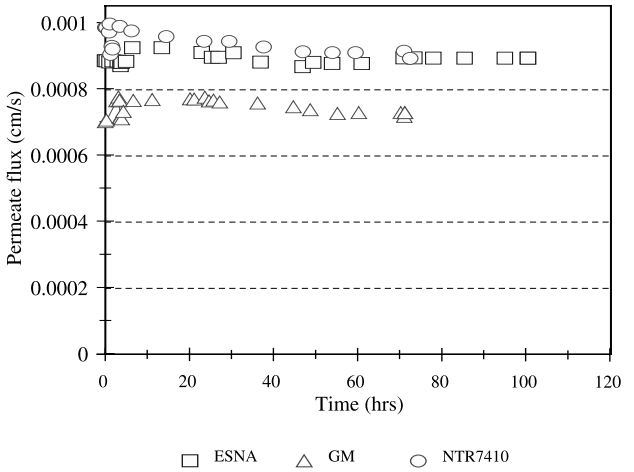
Code	MWCO (Da)*	Material	Zeta potential at pH 7	Contact angle (°)
NF45	400	Polyamide TFC	– 12.5	45.2
ESNA	250	Polyamide TFC	– 11.0	60.3
YM3	3,000	Regenerated cellulose	– 8.6	13.3
PM10	10,000	Polysulfone	– 12.7	61.7
GM	8,000	Polyamide TFC	– 17.0	54.7
NTR7410	20,000	Sulfonated PES	– 22.6	61.3
SV10	500	Cellulose acetate	– 14.8	53.3
HP09	2,000	PES	– 16.1	

*Reported by manufacturers.

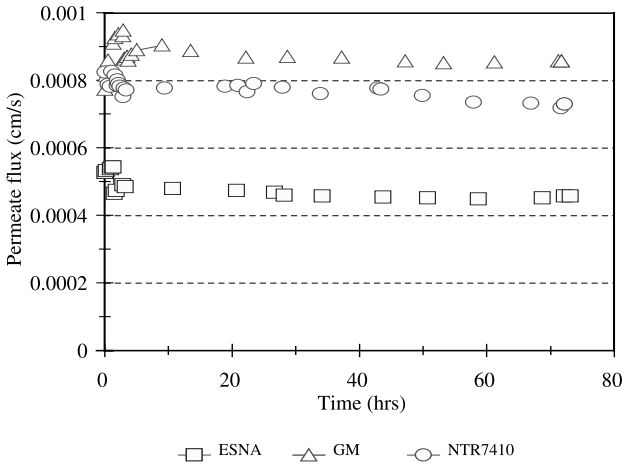
SUVA is highly correlated with aromaticity and was found to be correlated with humic content (% DOC), derived from a mass balance calculation between DOC values of feed NOM solution and the corresponding XAD-8 effluent. Humic content was well correlated with SUVA. However, it should be noted that humic content may also include ionized humic acids which reflect hydrophilicity. SUVA is also related to NOM MW because NOM with a high aromatic structure (high SUVA) generally exhibits a large MW. The Twitchell water exhibited the highest NOM concentration with a medium SUVA value. NOM characteristics and water qualities of NOM-source waters are summarized in Table 1.

Membrane characterizations

For each unique type, the membrane surface was characterized by contact angle (an index of hydrophobicity), zeta



(a) with HT-SW



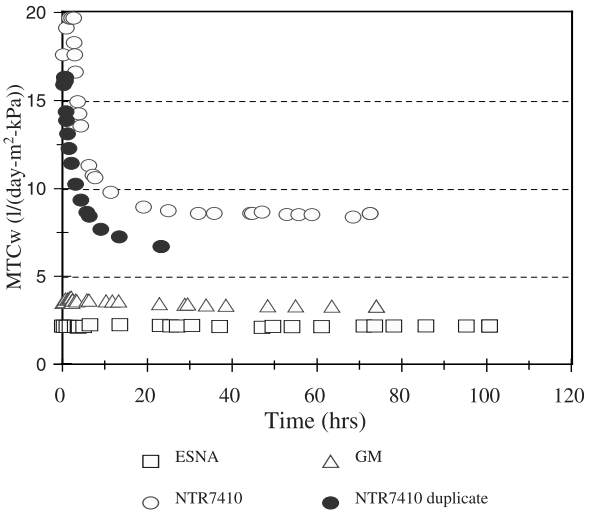
(b) with OC-GW

Figure 1 | Flux-decline: NF vs UF at the same *f/k* ratio (=1.0).

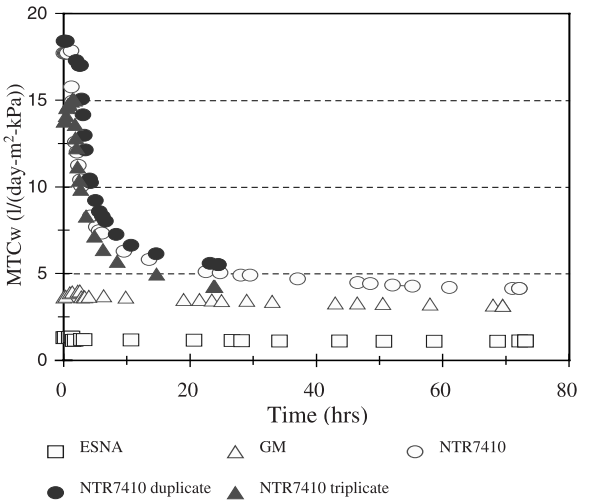
potential (for surface charge), and properties resulting from the characteristics of membrane materials, including aromatic or aliphatic structure and functional groups. As the aromatic content of the membrane surface increases, it would be expected to exhibit a greater contact angle. A membrane surface with ionizable or hydrogen bonding containing functional groups may have reduced contact angle and increased zeta potential (negatively) due to these functional groups. In the membrane characterization, only the surface charge was measured in terms of zeta potential. However, the pores of a membrane would be expected to exhibit the same charge value as the surface of the membrane based on the same material of pore and surface sites.

Contact angle is a hydrophobicity index of the membrane surface according to its material. Various membranes of different materials were provided by different manufacturers. Contact angle results for the membranes characterized by the sessile drop method are summarized in Table 2, categorized by membrane material. According to contact angle results, polysulfone, polyamide and cellulose acetate, and cellulose membranes show the greatest, intermediate, and least hydrophobicity, respectively. Cellulose membranes (containing repeating glucose units) with the least hydrophobicity would be expected to reflect the least hydrophobic interactions and thus reduce flux decline. Polyamide membranes contain aromatic rings connected by amide groups (-CO-NH-), and some of the polyamide membranes contain carboxylic groups, suggesting that amide and carboxylic groups would tend to reduce the hydrophobicity (based on contact angle) of the aromatic structure. Polysulfone (PSf) membranes are comprised of aromatic rings connected by one carbon and two methyl groups, oxygen elements, and sulfonic groups. Polyethersulfone (PES) membranes contain the same structures as PSf membranes without the one carbon and two methyl groups, indicating that a PES membrane exhibits less hydrophobicity than a PSf membrane.

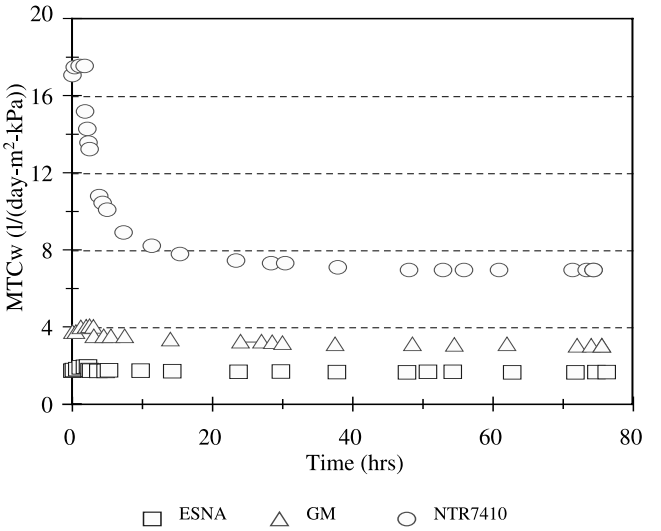
To investigate the potential for electrostatic interactions, various membranes of different materials were characterized by zeta potential (see Table 2) using a commercialized streaming potential measurement apparatus (BI-EKA, Brookhaven, New York). The sulfonated PES NTR7410 membrane exhibited the highest negative charge. The PM10, GM, ESNA, and NF45 membranes showed intermediate negative charges, and the cellulose YM3 membrane exhibited the least negative charge. The GM membrane contains carboxylic groups according to the manufacturer (Osmonics Desal). However, it could not be verified by the manufacturers whether the ESNA and NF45 membranes include any ionizable functional groups. The NTR7410 and PM10 membranes may exhibit negative charges because of their sulfonate (SO_3^-) and



(a) with HT-SW



(b) with OC-GW



(c) with runoff SL-SW

Figure 2 | Flux-decline: NF vs UF at the same pressure (=50 psi (344.7 kPa)).

sulfonite (SO_2), and sulfonite groups, respectively. The zeta potential results suggest the possibility of electrostatic repulsion for NOM rejection by charged membranes, including the GM and NTR7410 membranes.

Membrane filtration

Two types of commercial bench-scale cross-flow membrane cells (Osmonics or MiniTan) were used to evaluate flat sheet specimens. Each system was comprised of the membrane unit and feed, permeate, recycle, and waste lines. The system accommodates 155 cm^2 (for Osmonics) and 60 cm^2 (for MiniTan) flat sheet specimens under feed-flow conditions of approximately 200 to 1,000 ml/min, and cross-flow velocities of 0.01 to 0.10 m/s. These systems permit a tangential flow that simulates actual operating conditions. This system also allows the simulation of other operating conditions of pilot or

Table 3 | NOM rejection comparison of NF and UF membranes

NOM	ESNA	GM		NTR7410	
Rejection	$f/k = 1$	$f/k = 1$	$f/k = 2$	$f/k = 1$	$f/k = 10$
	$\Delta P = 50$ psi	$\Delta P = 35$ psi	$\Delta P = 50$ psi	$\Delta P = 10$ psi	$\Delta P = 50$ psi
HT-SW:					
DOC (%)	75.1 (6.4)	58.1 (5.1)	57.3 (1.6)	34.4 (2.3)	6.8 (3.7)
UVA (%)	95.5 (1.6)	77.8 (0.8)	67.6 (2.2)	44.6 (1.3)	9.4 (2.2)
OC-GW:					
DOC (%)	87.2 (4.3)	88.3 (1.1)	86.9 (1.6)	83.1 (1.2)	63.0 (4.2)
UVA (%)	97.0 (3.0)	95.9 (0.4)	93.2 (0.8)	92.0 (0.9)	66.4 (8.3)
Runoff SL-SW:					
DOC (%)	92.6 (4.8)		72.0 (1.4)		22.7 (8.5)
UVA (%)	97.9 (1.5)		83.3 (1.5)		38.0 (9.4)

*Standard deviations are indicated in parentheses.

full-scale membrane plants by designating a system recovery ratio and NOM concentration in the line in which the feed and recycle waters are mixed. The cross-flow velocity can be varied by feed-flow rate (using pump speed) and a back-pressure controller, or through the use of various feed spacers. The system recovery ratio can be controlled by a needle valve between the recycle and waste lines. Milli-Q was filtered through a flat sheet membrane until an approximation of constant flux was obtained. NOM-source water was then processed. Permeate flux, UVA_{254}, and DOC of permeate samples were monitored over time. Time average values of DOC rejection were calculated with standard deviations. The SUVA values of permeate samples were compared with those of feed samples to demonstrate preferential rejection of the aromatic components of NOM, as opposed to the rejection of non-aromatic NOM components.

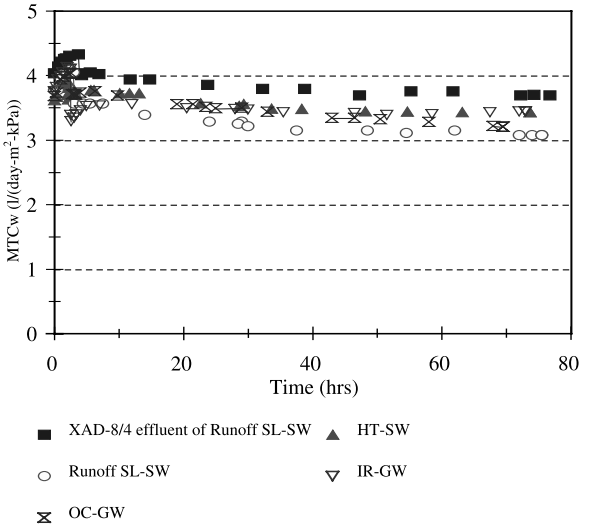
RESULTS AND DISCUSSION

Comparison of NF and UF membranes

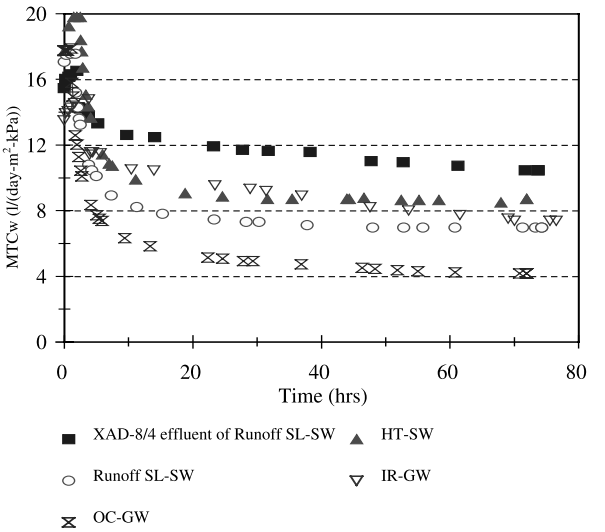
Flux-decline and NOM rejection performance of NF and UF membranes can be compared in two ways; one by using approximately the same f/k ratio (an initial hydrodynamic operating condition which was reported by Amy & Cho (1999)), which provides almost the same hydrodynamic conditions, and the other by using the same transmembrane pressure, which imparts different hydrodynamic conditions. Flux-decline trends of NF (ESNA) and UF (GM and NTR7410) membranes are compared with HT-SW and OC-GW using the same f/k ratio of 1.0 (see Figure 1 (a) & (b)). Three different membranes, each with a different pore size (based on MWCO), hydrophobicity (based on contact angle), and surface charge (based on zeta potential), exhibit almost the same slope of flux

decline versus time at the same f/k ratio. When the same transmembrane pressure (50 psi = 344.7 kPa) was used for NF and UF membranes, and different f/k ratios were used ($f/k = 1$ for ESNA, $f/k = 2$ for GM, and $f/k = 10$ for NTR7410), NF and UF membranes showed different initial permeate fluxes as well as slopes of flux decline with HT-SW, OC-GW, and runoff SL-SW (see Figure 2 (a)–(c)). However, ESNA and GM membranes showed similar flux declines compared to the NTR7410 membrane for HT-SW, OC-GW, and runoff SL-SW. It seems that NF and UF membranes are influenced by the f/k ratio in terms of flux-decline slope, without regard to different membrane properties.

NF and UF membranes can reject almost the same amount of OC-GW NOM based on DOC and UVA when the same f/k ratio was used, even with different MWCO values (see Table 3). However, this was not true for the HT-SW NOM, suggesting that a UF membrane can be used as a substitute for the NF membrane to reduce operating pressure requirements with almost the same NOM rejection for a NOM with a high SUVA (see Table 3). As the f/k ratio increases, NOM rejection by UF membranes decreases, especially for the NTR7410 with a higher MWCO value, because of a relative decrease in diffusional transport compared with convective transport through the membrane pores.



(a) GM at f/k=2



(b) NTR7410 at f/k=10

Figure 3 | NOM source effects on flux decline.

NOM source effects

UF membranes (GM and NTR7410) were tested with different NOM-source waters at the same f/k ratio (= 2.0) to demonstrate NOM source effect on flux decline. The GM membrane exhibited no significant differences in flux decline with different NOM-source waters, reflecting different values of SUVA, humic content, and feed DOC concentration (see Figure 3 (a)). When the NTR7410 membrane was tested with a relatively high f/k ratio (= 10), it showed different flux-decline patterns with different NOM-source waters (see Figure 3 (b)). HT-SW, runoff SL-SW, and IR-GW resulted in similar flux-decline trends for the NTR7410 membrane with an f/k ratio of 10, even with their different NOM characteristics. Hydrophilic NOM (XAD-8/4 effluent) derived from runoff SL-SW and OC-GW resulted in the smallest and largest flux decline due to their low DOC/low SUVA and high DOC/high SUVA, respectively. However, IR-GW with a higher DOC/higher SUVA than runoff SL-SW exhibited a flux decline similar to runoff SL-SW, and lower flux decline than OC-GW. It can be concluded that flux decline is influenced by NOM-source differences when a

Table 4 | NOM source effects on NOM rejection

	ESNA at *f/k*=1		GM at *f/k*=2		NTR7410 at *f/k*=10	
NOM source	DOC (%)	UVA (%)	DOC (%)	UVA (%)	DOC (%)	UVA (%)
Hydrophilic NOM of Runoff SL-SW			46.8 (2.9)	75.0 (2.5)	8.3 (4.2)	14.8 (10.6)
HT-SW	75.1 (6.4)	95.5 (1.6)	57.3 (1.6)	67.6 (2.2)	6.8 (3.7)	9.4 (2.2)
Runoff SL-SW	92.6 (4.8)	97.9 (1.5)	72.0 (1.4)	83.3 (1.5)	22.7 (8.5)	38.0 (9.4)
IR-SW			84.3 (1.4)	93.2 (0.6)	62.1 (4.7)	66.4 (8.8)
OC-GW	87.2 (4.3)	97.0 (3.0)	86.9 (1.6)	93.2 (0.8)	63.0 (4.2)	66.5 (8.3)

*Standard deviations are indicated in parentheses.

relatively high *f/k* ratio is used, because the high *f/k* ratio increases flux magnitude.

NOM rejection by the two UF membranes (GM and NTR7410) is influenced by NOM-source characteristics even with the same *f/k* ratio, while the NF membrane is less influenced (see Table 4). NOM with a relatively high SUVA and large humic content can be more effectively rejected by UF membranes, as opposed to NOM with a relatively low SUVA and small humic content.

Hydrophobic interaction effects

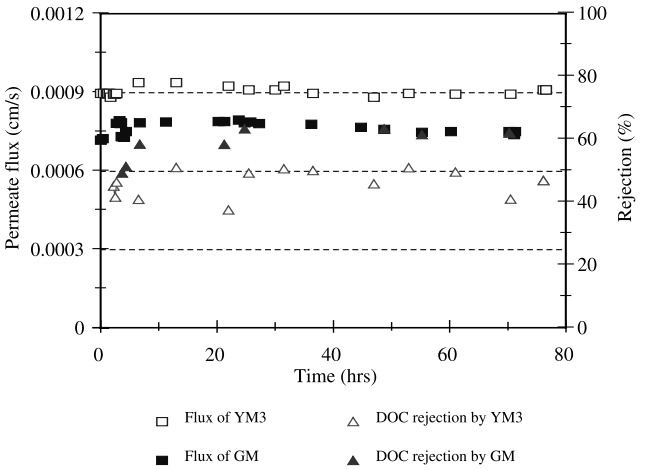
To demonstrate the hydrophobic interaction effects of the membrane surface on flux decline and NOM rejection, relatively hydrophilic (YM3) and hydrophobic (GM) membranes (based on contact angle and FTIR spectrum) were tested with the HT-SW and OC-GW containing relatively hydrophilic and hydrophobic NOM (based on SUVA and humic content), respectively. Both YM3 and GM membranes exhibited similar flux-decline behaviors with HT-SW and OC-GW (see Figure 4 (a) & (b)), even though both membranes reflect different hydrophobicity based on contact angle and different surface charge based on zeta potential (see Tables 1 and 2). However, the GM membrane rejected more NOM than the YM3 membrane with both HT-SW and OC-GW, because the GM membrane showed a higher negative charge than the YM3 membrane, representing electrostatic interactions by a negative-charged membrane.

Comparison of membrane permeate

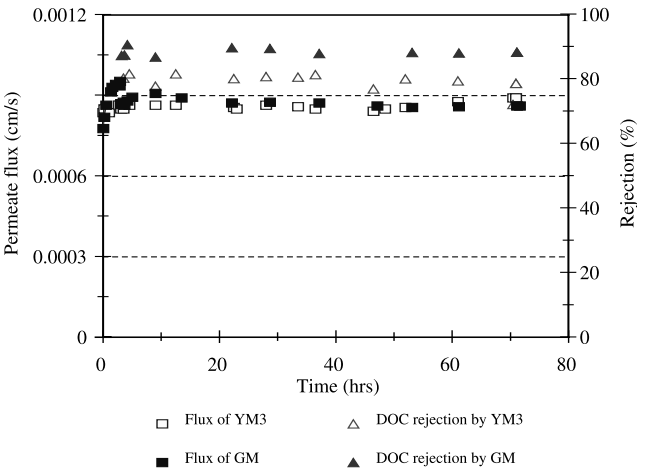
MW distributions of permeates from different membranes with different NOM-source waters and different *f/k* ratios were compared to determine which ranges of NOM MW sizes were rejected by a membrane or passed through its pores.

f/k ratio effects

To demonstrate the *f/k* ratio effect on NOM rejection and corresponding MW distribution of a permeate more closely, GM and NTR7410 membranes were tested with two NOM-source waters and different *f/k* ratios. The permeates of the two membranes were compared with feed water in terms of MW distribution. The permeate MW distributions of both membranes reflected similar shapes and fractions except for the NTR7410 with the *f/k* ratio of 9.9 (see Figure 5 (a) & (b)). This similarity indicates that larger MW NOM is not likely to be rejected when convective transport toward the membrane surface is much higher than back-diffusional transport (i.e. from a relatively high *f/k* ratio). Furthermore, larger molecular size NOM is characterized by a smaller diffusion coefficient. It



(a) with HT-SW at f/k=1



(b) with OC-GW at f/k=1

Figure 4 | Hydrophobic interactions: YM3 vs. GM.

appears that the f/k ratio does not affect NOM rejection patterns for NOM with very high SUVA values and humic content (see Figure 5 (c) & (d)). NOM constituents with MW sizes of 400 do not seem amenable to rejection by both GM and NTR7410 membranes.

NOM source effects

The MW distributions of GM permeates with different NOM-source waters were compared to demonstrate source effects on NOM rejection. They exhibited similar trends, except for the Twitchell water, reflecting a lesser fraction of smaller MW range material compared to other waters (see Figure 6). The reduced negative charge of NOM by the high ionic strength of the Twitchell water probably resulted in the decreased NOM rejection.

Effective MWCO

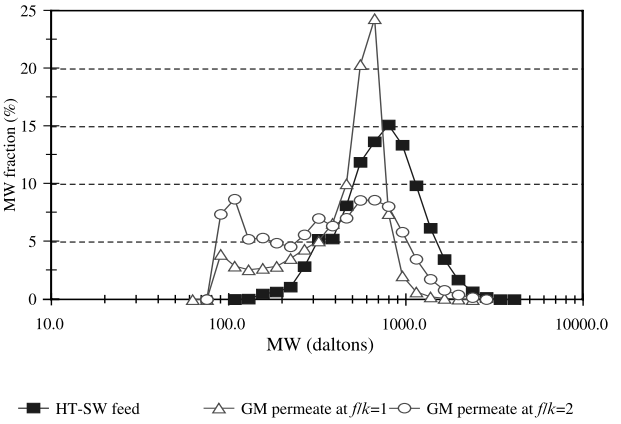
It has been shown that UF membranes showed more NOM rejection than expected, given their manufacturer-specified MWCO values, demonstrating a need for the development of a different MWCO concept: effective MWCO. As MWCO is defined as a MW which is 90% rejected by the membrane, NOM fractional rejection can be used to derive the effective MWCO; the concept is related to a certain MW size and its fractional rejection. The NOM fractional rejection data can be calculated by Equation (2) with overall NOM rejection by the membrane (Mulder 1996):

$$R_{\mathrm{Mi}} = \frac{W_{\mathrm{Mi}}(feed) - W_{\mathrm{Mi}}(perm)(1 - R_{\mathrm{overall}})}{W_{\mathrm{Mi}}(feed)} \qquad (2)$$

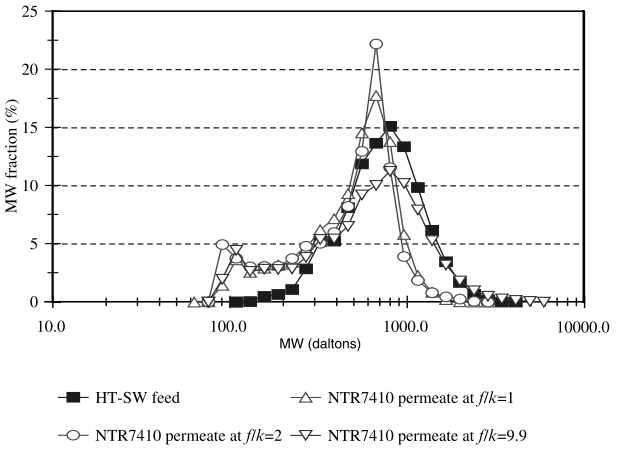
where R_{Mi} is the fractional rejection for a certain MW, W_{Mi} is the fraction of the MW, and R_{overall} is overall NOM rejection based on DOC by the charged membrane.

Various effective MWCO values of the GM membrane were compared with different NOM-source waters at an f/k ratio of 2.0 (see Table 5). Effective MWCO values are much smaller than the nominal MWCO of 8000 daltons provided by the manufacturer, resulting from the electrostatic exclusion of negatively-charged NOM constituents. The effective MWCO values for the OC-GW and Twitchell water represented the lowest and highest values due to high humic content (mostly humic acids), and high ionic strength, respectively.

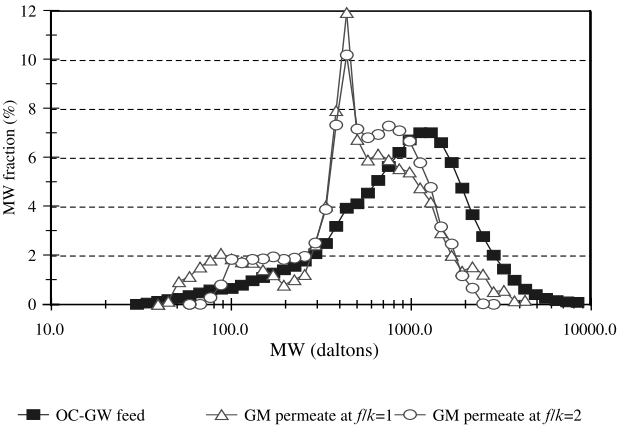
When the same pressure (50 psi = 344.7 kPa) was used for membranes with different permeabilities, the GM membrane provided better NOM rejection in terms of effective MWCO and DOC rejection than NTR7410 and YM3 membranes because of the large MWCO and higher



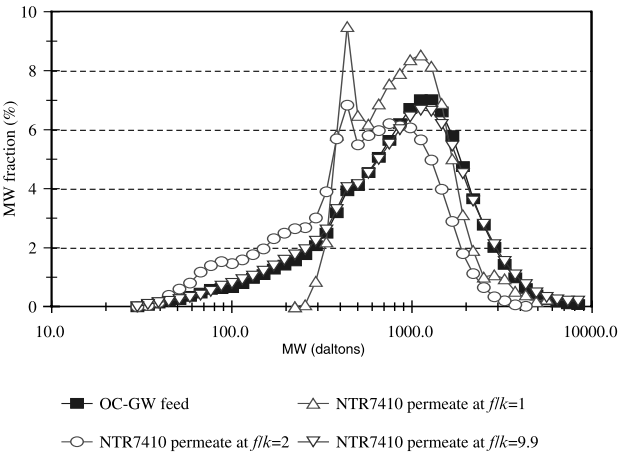
(a) by GM membrane with HT-SW at f/k=1.0 and 2.0



(b) by NTR7410 membrane with HT-SW at f/k=1.0, 2.0, and 9.9



(c) by GM membrane with OC-GW at f/k=1.0 and 2.0



(d) by NTR7410 membrane with OC-GW at f/k=1.0, 2.0, and 9.9

Figure 5 | MW distributions of permeates.

f/k ratio (NTR7410), and the less negatively-charged membrane surface (YM3), respectively (see Table 6).

To demonstrate f/k ratio effects on effective MWCO, two f/k ratios were tested for GM and NTR7410 membranes with runoff SL-SW and IR-GW to obtain effective MWCO and NOM rejection (see Table 7). For the GM membrane, the f/k ratio influenced the membrane NOM rejection performance in terms of effective MWCO. Meanwhile, the NTR7410 membrane was not influenced significantly by the f/k ratio for effective MWCO and DOC rejection with either the runoff SL-SW or IR-GW, which is probably due to the fact that the change in the f/k ratio was insignificant compared with the large MWCO and the high permeability of the NTR7410 membrane.

NOM transport

Flux-decline and NOM rejection, and associated NOM transport were tested using an Osmonic unit (the active surface area of membrane = 155 cm^2).

Flux decline and NOM rejection

Figure 7 (a)–(d) show the results of the cross-flow membrane tests with the SV10 and HP09 membranes for the

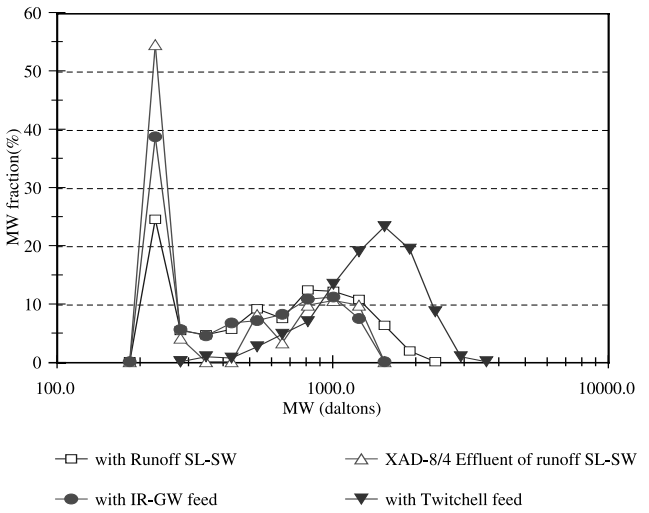


Figure 6 | MW distributions comparison of permeates by GM membrane with different NOM sources.

SL-SW and IR-GW source waters. Interestingly, there were no flux declines for all experiments, even when the relatively hydrophobic HP09 membrane was used in conjunction with the IR-GW, which contained a relatively high hydrophobic component of NOM. This is probably due to relatively low permeate flux and f/k ratio for both membranes ($f/k = 0.38$ for SV10 and $f/k = 0.34$ for HP09). It cannot be inferred that no flux-decline would continue for a long-term experiment (longer than 30 days); nevertheless, these experiments suggest the possibility of preventing significant flux decline while maintaining high rejection of NOM.

DOC rejections approached plateau-values more rapidly for SV10 than for HP09 with IR-GW. This observation is evidence that charge interactions between the membrane surface and NOM were important while DOC rejections were increasing. Meanwhile, adsorption layer roles and hydrophobic interactions are important after the plateau values for the rejection of DOC, a result probably due to the difference in negatively-charged reductions between SV10 and HP09.

UVA rejections were always higher than DOC rejections, and thus the ratios of permeate SUVA and feed water $SUVA_0$ ranged from 10% to 50%. It can therefore be concluded that aromatic (humic) components of NOM are

Table 5 | Effective MWCO values of GM membrane at f/k=2.0

	HT-SW	Twitchell	Runoff SL-SW	IR-GW	OC-GW
Effective MWCO	1,630	2,990	1,550	1,520	1,280
DOC rejection (%)	59.1	46.5	72.0	84.3	86.9

Table 6 | Effective MWCO values using the same transmembrane pressure (50 psi)

	GM at f/k=2.0	NTR7410 at f/k=9.9	YM3 at f/k=2.0
Runoff SL-SW:			
Effective MWCO	1,550	2,760	
DOC rejection (%)	72.0	31.1	
IR-GW:			
Effective MWCO	1,520	2,470	1,990
DOC rejection (%)	84.3	64.2	75.6

Table 7 | *f/k* ratio effects on effective MWCO and NOM rejection

	GM		NTR7410	
	f/k=1.0	*f/k*=2.0	*f/k*=1.0	*f/k*=2.0
Runoff SL-SW:				
Effective MWCO	900	1,550	1,380	1,370
DOC rejection (%)	61.7	72.0	33.6	37.4
IR-GW:				
Effective MWCO	900	1,520	2,130	1,940
DOC rejection (%)	88.3	84.3	83.1	74.1

preferentially rejected over hydrophilic (non-humic) components of NOM.

NOM transport

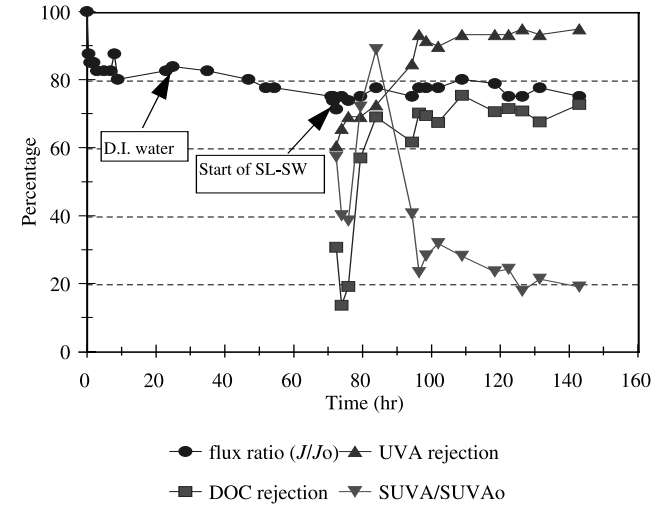
NOM transport model parameters, the reflection coefficient σ and the NOM permeability coefficient P_m, were evaluated using Equation (3) (see Table 8) (Tandon *et al.* 1994), where R_{obs} is the observed NOM removal estimated with bulk and permeate NOM concentrations.

$$\frac{1-R_{obs}}{R_{obs}} = \frac{1-\sigma}{\sigma} + \frac{P_m}{\sigma J_v} \quad (3)$$

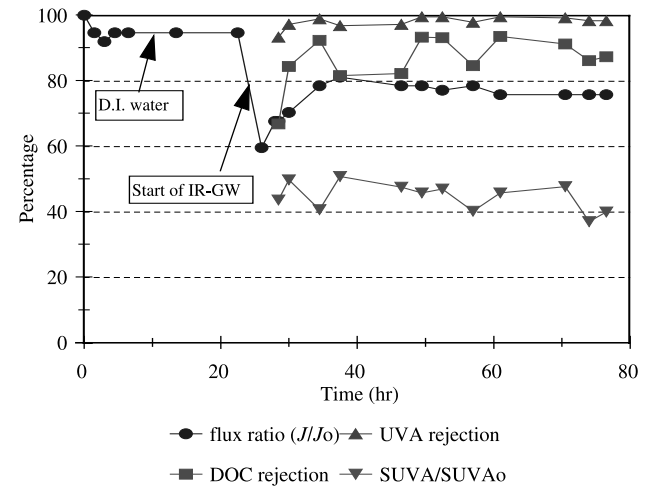
Relative NOM transports by diffusion and convection are also represented in Table 8 for the experiments with SV10/HP09 and SL-SW/OC-GW. In the four experiments, the convection transport was larger than the diffusion transmission. This is probably due to the fact that the back-diffusion velocity may reduce the diffusion transport, and the Peclet numbers (J_v/P_m) were not as small as expected because of the relatively small values of the P_m. The differences between the convection and diffusion transport were larger for HP09 than for SV10, attributable to differences in membrane MWCO. For the same membranes and different waters, the differences between the convection and diffusion transport were slightly larger for SL-SW than for OC-GW. This may be attributable to the relatively lower molecular weight and relatively greater hydrophilicity of SL-SW NOM. The reflection coefficient and permeability coefficient of the cross-flow filtration with PEG200 (average MW = 200 daltons) and SV10 are shown in Table 8.

Figures 8 and 9 show the results of permeate flux and DOC rejection trends, and NOM transport, respectively. Operational conditions were changed in the middle of the experiment to evaluate the influences of cross-membrane velocities on permeate flux and DOC rejection. The operational conditions 1, 2, and 3 correspond to cross-membrane velocity values of 0.25, 0.05, and 0.003 m/sec, respectively. Considering the molecular weight of PEG200 and the MWCO of the SV10 membrane, it was anticipated that DOC rejection would be almost zero. However, the DOC rejections were approximately 55%, which represented the cross-membrane velocity influence on the DOC rejection. As shown in Figure 8, the permeate flux was not reduced during the experiment under the different conditions. However, DOC rejections were slightly reduced as the cross-membrane velocity was changed to 0.05 m/sec from 0.25 m/sec, and DOC rejections were dramatically reduced as the cross-membrane velocity was changed to 0.003 m/sec.

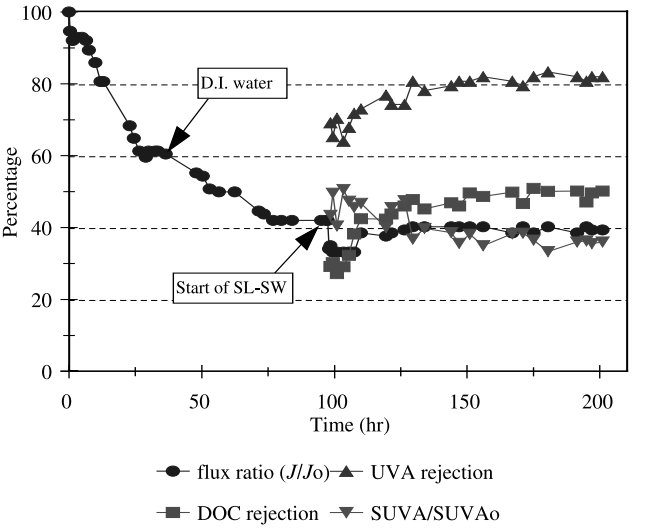
With the low cross-membrane velocity, the mass transfer coefficient decreases and concentration polarization increases, with the result that NOM transport



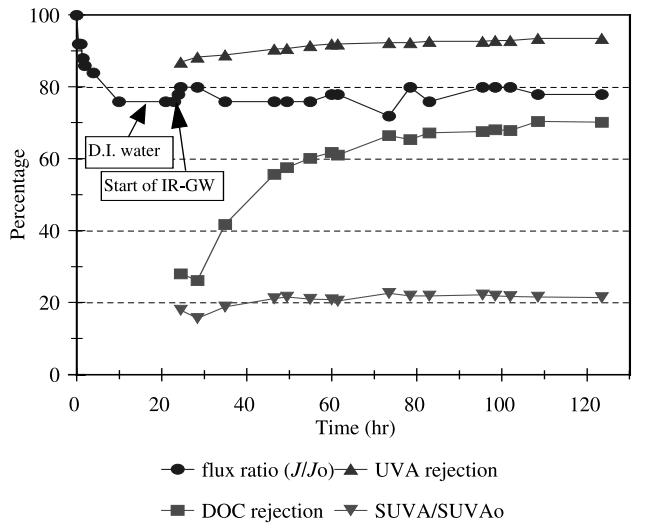
(a) with SV10 and runoff SL-SW



(b) with SV10 and IR-GW



(c) with HP09 and runoff SL-SW



(d) with HP09 and IR-GW

Figure 7 | Flux-decline and NOM rejection of cross-flow membrane test.

by diffusion (this is not k, but transport through membrane pores) is dominant over that by convection (through membrane pores). Also, the diffusion transport (through membrane pores) increases as the cross-membrane velocity decreases because the back-diffusion velocity (mass transfer coefficient) is reduced, while the convection transport slightly increases. These results can also be explained by the influence of the cross-membrane velocity on the back-diffusion velocity (mass transfer coefficient).

SUMMARY AND CONCLUSIONS

This study demonstrated several hypotheses, including membrane MWCO effects on NOM rejection, NOM

Table 8 | Reflection coefficients (σ) and NOM permeability coefficients (P_m)

				NOM solute transport		
Source	**Membrane**	σ	P_m	**Total amount ($\times 10^{-4}$ µg/sec-cm^2)**	**Diffusion (%)**	**Convection (%)**
SL-SW	SV10	0.82	0.000026	1.60	42.3	57.7
OC-GW	SV10	0.91	0.0000093	2.50	45.6	54.4
SL-SW	HP09	0.52	0.000113	3.20	34.4	65.6
OC-GW	HP09	0.81	0.000015	4.60	36.4	63.6
PEG-200	SV10	0.88	0.00024			

source effects on flux decline, and hydrophobic interactions for flux decline. MW distribution of a membrane permeate was compared with that of feed NOM-source water, either with different membranes at the same f/k ratio or with the same membrane at different f/k ratios. An effective MWCO for a membrane was introduced to obtain a more realistic index of membrane performance than a nominal MWCO provided by the manufacturer.

An NF membrane with lower MWCO exhibited greater NOM rejection for slightly hydrophilic NOM-source water than a UF membrane with higher MWCO, reflecting size exclusion for NOM rejection by the membranes. However, both NF and UF membranes showed similar NOM rejection for NOM-source water with high SUVA.

Two different UF membranes did not show significant differences in flux-decline trends with different NOM-source waters (with different aromaticity (hydrophobicity) and charge density) when the same f/k ratio was used. This result supports the f/k ratio hypothesis that the f/k ratio is a factor affecting NOM rejection and flux-decline.

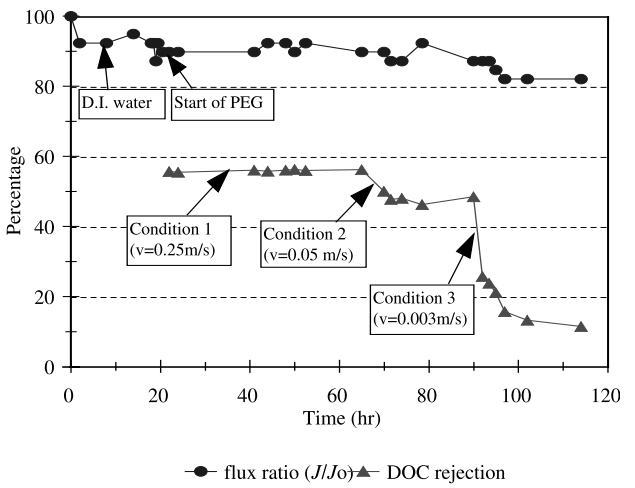


Figure 8 | Flux decline and NOM rejection of cross-flow test with SV10 and PEG200.

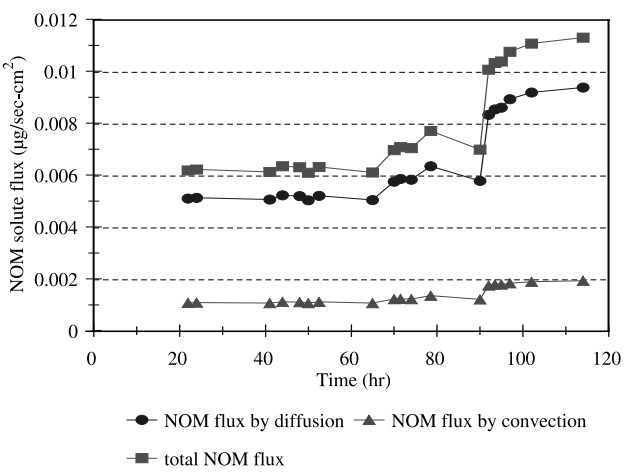


Figure 9 | NOM transport of cross-flow test with SV10 and PEG200.

Similar MW distributions for membrane permeates were found for different membranes with different MWCO values at the same f/k ratio. However, if different f/k ratios were used with the same membrane, the MW fraction of the membrane permeate at a lower f/k ratio was somewhat increased compared to that at a higher f/k ratio. This indicates that the f/k ratio is a factor in controlling NOM rejection, supporting the f/k ratio hypothesis.

Effective MWCO for negatively-charged membranes with NOM was significantly reduced from nominal MWCO (either provided by the manufacturer or calculated from a PEGs rejection test), confirming electrostatic repulsion between the negatively-charged membrane surface and NOM acids.

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