



Identifying the rejection mechanism for nanofiltration membranes fouled by humic acid and calcium ions exemplified by acetaminophen, sulfamethoxazole, and triclosan

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ABSTRACT

This research investigated the fouling effect of humic acid and humic acid/calcium ions on the rejection of three target compounds, i.e., acetaminophen, sulfamethoxazole, and triclosan, by two nanofiltration (NF) membranes. A modified Hermia fouling model was used to describe the fouling process. The effects of solute and membrane characteristics on the rejection and flux decline at various pH levels and with various foulants were also investigated. Results show that fouling mechanisms include complete blocking and gel layer formation. The presence of humic acid and humic acid/calcium ions may positively influence the rejection of hydrophilic compounds and neutral compounds rejected only by size exclusion. The experimental rejections of solute by the NF270 membrane correlate well with the theoretical rejection model in which only size exclusion was considered. For NF membranes with pore sizes larger than the solutes (e.g., the NTR7450 membrane), the rejection could be determined from the model combining both size exclusion and electrostatic exclusion.

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1. Introduction

Pharmaceuticals and personal care products (PPCPs) are chemical products used by individuals for personal health or cosmetic reasons or by agribusiness to enhance the growth or health of livestock [1]. Three PPCPs, namely, acetaminophen, sulfamethoxazole, and triclosan, are of particular importance because of their widespread use as an analgesic/antipyretic, as an antibiotic, and in household products such as soap, deodorant and mouthwash, respectively. These chemical products have frequently been detected in surface waters in Taiwan [2].

Membrane filtration processes, such as nanofiltration (NF) and reverse osmosis, play an important role in the production of high-quality reclaimed water when small organic compounds, (e.g., pesticides, endocrine disruptors and pharmaceutically active compounds) are removed. From the twenty-first century, NF has been used as an attractive alternative to conventional wastewater treatment technology for the removal of organic micropollutants including PPCPs and endocrine-disrupting compounds (EDCs) from

aquatic environments [3–8]. Many water treatment and purification plants are using NF instead of reverse osmosis because of NF's low power consumption and higher flux. For example, Radjenović et al. [7] studied the removal of thirty-one compounds by an NF membrane in a full-scale drinking water treatment plant and found an overall performance observed rejection (the difference between the feed and the permeate over the permeate stream) of >85% for almost all of the pharmaceuticals investigated.

The rejection of membrane filtration is influenced by membrane properties, solute properties, and feed water characteristics [9–11]. Many researchers have concluded that NF removes organic solutes through three main mechanisms, i.e., size exclusion, electrostatic repulsion, and adsorption. Yoon et al. investigated the removal of twenty-seven EDC/PPCP compounds by NF and ultrafiltration membranes from various drinking water sources and showed that size exclusion could be dominant for EDC/PPCPs rejection when steady-state operation was achieved [12]. Verliefde et al. investigated the removal of twenty compounds by two different NF membranes, and the results showed that with negatively charged membranes, electrostatic exclusion leads to an increase in the rejection of negatively charged solutes [8]. Adsorption mechanism is important only for hydrophobic compounds under electrostatically neutral condition [13]. However, the contribution of adsorption could be neglected since the adsorption

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Table 1
Properties of NF270 and NTR7450 membranes used in this study.

Membrane	NF270	NTR7450
Manufacturer	Dow FILMTECH™	Nitto Denko
Material	Polyamide	Sulfonated polyethersulfon
MWCO ^a	300	550
Water permeability (1/m ² h × 10 ⁻⁵ /Pa)	11	12
Max. temperature (°C)	35	40
Max. pressure (10 ⁵ Pa)	17	30
Thickness (mm)	0.2	0.2
Pore radius (nm) ^b	0.43	0.7
pH-range	3–9	2–11

^a Determined by polyethylene glycols method [21].

^b Determined by Spiegler and Kedem membrane transport model [20].

capacity of NF membrane is low, e.g., 0–2.5 ng/cm² for 27 EDC/PPCP compounds [12], or up to 0.5 mmol/m² for diclofenac and ibuprofen [14].

Although NF membranes can produce very high quality water, membrane fouling is inevitable in full-scale membrane filtration during long-term operation [15]. Recently, many reports have indicated that fouling may change membrane surface properties, i.e., contact angle, zeta potential and surface morphology, which could affect the rejection mechanisms of the NF membrane [16–18]. It is clear that NF membrane fouling may change the surface properties and therefore may affect the rejection mechanisms, i.e., size exclusion, electrostatic exclusion, and adsorption [13,19].

Zazouli et al. studied the removal of five pharmaceuticals by two commercial NF membranes with alginate as the model foulant, and revealed that for the smallest molecules with moderate polarity exhibited a decrease of rejection due to the fouling layer [17]. Although many studies found that pharmaceuticals may be removed by NF membranes, the effect of fouling on the performance of the process must be considered [8,16–18]. Certainly, the complexity of fouling on rejection mechanisms needs further study.

The objectives of this work were: (1) to investigate the effects of fouling, by humic acid and calcium ions, on membrane filtration (flux and rejection) and surface characteristics (contact angle, roughness, and zeta potential); (2) to determine the rejection mechanisms, i.e., size exclusion, electrostatic repulsion for the removal of three PPCPs; and (3) to identify the influence of fouling on each mechanism in rejection of the target compounds.

2. Materials and methods

2.1. Membrane characterization

Two NF membranes, i.e., NF270 and NTR7450, manufactured by Dow Filmtech and Nitto Denko, respectively, were used in this study. The NF270 membrane is a polyamide thin-film membrane, and the NTR7450 membrane has a composite structure consisting of an active layer (50–250 nm thick) on top of an asymmetric

Table 2
Characteristics of the organic compounds used for the establishment of the relationship between MW and mass transfer coefficient.

Target compound	CAS Number	Molecular formula	IUPAC name	Molecular weight	Acidity (pK _a) ^a	Log K _{ow} ^a	Diffusivity (× 10 ⁻⁹ m ² /s) ^b
Acetaminophen	103-90-2	C ₈ H ₉ NO ₂	<i>N</i> -(4-hydroxyphenyl)-ethanamide	151	9.4	0.46	0.94
Sulfamethoxazole	726-46-6	C ₁₀ H ₁₁ N ₃ O ₃ S	4-amino- <i>N</i> -(5-methylisoxazol-3-yl)-benzenesulfonamide	253	5.5	0.89	0.77
Triclosan	3380-34-5	C ₁₂ H ₇ Cl ₃ O ₂	5-chloro-2-(2,4-dichlorophenoxy)phenol	290	7.9	4.76	0.58

^a Reference [37].

^b Determined by ACDLABS 12 software with the same aqueous condition as filtration test.

polysulfone support (50 nm thick), backed by a layer of unwoven polyester fibers (200 nm thick). Detailed properties of the two membranes are shown in Table 1. The molecular weight cut-off (MWCO) of the membrane was estimated using polyethylene glycols with molecular weights ranging from 200 to 1500. The polyethylene glycols concentration in the feed and permeate stream were analyzed to obtain the molecular weight distribution curve. In general, the molecular weight of polyethylene glycols rejection for 90% is defined as the MWCO of the membrane. In this study, the rejection curves indicated that the MWCO of NF270 and NTR7450 was about 300 and 550 Da, respectively.

The pore size of the membrane can be evaluated using the Spiegler and Kedem membrane transport model described by Wang et al. [20]:

$$R_r = \frac{\sigma 1 - \exp(-((1 - \sigma)/P)J_v)}{1 - \sigma \exp(-((1 - \sigma)/P)J_v)} \quad (1)$$

where R_r is the intrinsic rejection; P is the solute permeability; J_v is the permeate water flux; and σ the reflection coefficient is defined as:

$$\sigma = 1 - \left(1 + \frac{16r_s^2}{9r_p^2}\right) \left(1 - \frac{r_s}{9r_p}\right)^2 \left[2 - \left(1 - \frac{r_s}{r_p}\right)^2\right] \quad (2)$$

where r_s is the Stokes radius of the compound, and r_p is the membrane pore radius.

The estimated pore radius of NF70 and NTR7450 membranes was 0.48 nm, and the average pore radius of the NF270 membrane was calculated as 0.43 and 0.70 nm, respectively. The details of the procedure can be referenced in our previous study [21].

Scanning electron microscopy (SEM) (JEOL, JSM-6330F Field Emission Gun SEM, Japan) was used to observe the morphological properties of the membrane. Both the clean and fouled membranes were sputtered with a nanometer layer of platinum to enhance the surface conductivity before SEM observation.

The contact angle of water on the membrane was measured according to the sessile drop method at room temperature using an automatic contact angle meter (Model CA-VP, Kyowa Interface Science Co., Japan). This was done by dropping distilled water on each membrane sample at ten random sites, and the average value was used to calculate the contact angle.

2.2. Chemicals and analytical methods

Acetaminophen, sulfamethoxazole, and triclosan were selected as the target compounds. For acetaminophen, sulfamethoxazole, and triclosan, respectively, the molecular weight is 151, 253, and 290 g/mol; the pK_a is 9.4, 5.5, and 7.9; and the log K_{ow} is 0.46, 0.89, and 4.76. Detailed physicochemical parameters of the three target compounds are shown in Table 2. Differences in hydrophobicity (expressed as log K_{ow}, the logarithm of the octanol/water partitioning coefficient) and charge characteristics were chosen to enable

assessment of the influence of hydrophobic interactions and charge on rejection.

The concentration of the target compounds was analyzed with a high-performance liquid chromatograph equipped with a C-18 column that was 4.6 mm in diameter, 150 mm in length, and 5 μm in pore size, respectively. An ultraviolet detector was used to measure the concentration of all target compounds. The wavelength was 254, 280 and 225 nm for acetaminophen, sulfamethoxazole and triclosan, respectively. The mobile phase consisted of methanol and KH_2PO_4 buffer solution. The injection volume of each sample was 25 μL . The detection limit of each target compound was 0.01 mg/L, which was approximately 2% of the feed solution.

2.3. Filtration test

A cross-flow module was used for the filtration test. The surface area of the membrane was 140 cm^2 (14.6 cm \times 9.5 cm), and the cross-sectional area was 1.9 cm^2 (9.5 cm \times 0.2 cm). The membranes were stored in a 1.5% (w/w) sodium meta-bisulfite ($\text{Na}_2\text{S}_2\text{O}_5$) solution to prevent them from oxidizing and desiccating. Before the filtration test, the membrane was pre-compacted with Milli-Q water for at least 16 h to reach steady-state permeate flux.

The permeate flow rate was measured with a digital scale connected to a computer with continuous recording capability. The amount of material deposited on the membrane was then calculated with discrete differentiation. The cross-velocity and transmembrane pressure were 0.3 m/s and 690 kPa (100 psi), respectively. Constant ionic strength was maintained throughout the experiment using 10^{-2} M of NaCl. The performance of the membrane was determined through the permeate flux and the target compound rejection. The concentration of target compounds in the permeate and feed were measured at fixed time intervals (0, 1, 2, 3, 4, 5, 6, 12, 16, 20, and 24 h) for each target compound.

Humic acid (Aldrich), a surrogate natural organic matter (NOM), was used to foul the membrane. Humic acid at a concentration of 20 mg/L was prepared with either Milli-Q water or a solution containing 1 mM of calcium ion (calcium chloride, J.T. Baker). The fouling layer was established in 24 h of continuous filtration operation at a constant pH of 8 ± 0.1 . Target compounds at an initial concentration of 500 $\mu\text{g/L}$ were used in each filtration test.

2.4. Determination of the rejection mechanism

2.4.1. Size exclusion and electrostatic repulsion

In this study, the Spiegler–Kedem equation was used to determine the extent of rejection by size exclusion and electrostatic repulsion. Note that the intrinsic rejection (or real rejection) is not the same as the observed rejection R and is difficult to determine. The film theory model can be used to relate R and R_r via the following equation [22]:

$$\frac{1 - R_r}{R_r} = \frac{1 - R}{R} \times \exp\left(\frac{-J_v}{k}\right) \quad (3)$$

where k is the mass transfer coefficient of the solute across the pore of the membrane.

Substituting Eq. (1) into Eq. (3) and rearranging yields the following equation:

$$R = \frac{1}{(1 - \sigma)/\sigma[1 - \exp((\sigma - 1)/P)]J_v \exp((J_v)/k) + 1} \quad (4)$$

The SHP (steric-hindrance pore) model includes steric hindrance, and the reflection coefficient and the solute permeability are as follows:

$$\sigma = 1 - \left(1 + \frac{16}{9}\lambda^2\right)(1 - \lambda)[2 - (1 - \lambda)^2] \quad (5)$$

Table 3

Effect of humic acid and calcium on the membrane for NF270 and NTR7450 membranes.

Membrane	Foulants	Membrane characterization/performance	
		Contact angle ($^\circ$)	Flux decline (%)
NF270	Clean	23	1
	Humic acid	62	15
	Humic acid/ Ca^{2+}	68	20
NTR7450	Clean	77	2
	Humic acid	62	35
	Humic acid/ Ca^{2+}	64	47

$$P = D_s(1 - \lambda)^2 \frac{A_k}{\Delta x} \quad (6)$$

where λ is the ratio of solute to pore radius; D_s is the solute diffusivity; and $A_k/\Delta x$ is the ratio of membrane porosity to membrane thickness.

Electrostatic exclusion was included by the TMS (Teorell–Meyer–Sievers) model in which the membrane parameters can be expressed as follows:

$$\sigma = 1 - \frac{2}{(2\alpha - 1)\xi + (\xi^2 + 4)^{1/2}} \quad (7)$$

$$P = D_s(1 - \sigma) \frac{A_k}{\Delta x} \quad (8)$$

where α is the transport number of cations in free solution, and ξ is the ratio of the fixed charge density to the electrolyte concentration.

3. Results and discussions

3.1. Characteristics of the fouled membranes

3.1.1. Changes of surface properties and flux decline

Fig. 1 shows the SEM images of NF270 and NTR7450 membranes after filtration operation for 24 h using feed solutions containing foulants such as humic acid and humic acid/ Ca^{2+} at pH 8. As expected, few particles were deposited on the clean membrane surface (Fig. 1a and d). On the other hand, an obvious cake layer formed on the membrane surface when humic acid (Fig. 1b and e) and calcium (Fig. 1c and f) were present in the feed solution. The results demonstrated that fouling was more severe when calcium was present in the feed solution. Previous studies have shown that divalent ions such as calcium, which have a strong potential to form complexes with NOM, are capable of forming bridges between membrane surfaces and NOM [23,24]. That is, the presence of calcium ions could cause more severe organic fouling due to its intermolecular bridging and charge neutralization capacity, which enhance the cross-linkage between the organic foulants and the membrane surface. The fact that more severe flux declines occurred in NOM fouling with divalent ions systems was reported in a number of studies [25–27]. In addition, the membrane pore size could affect the extent of fouling, e.g., more severe fouling occurred with larger membrane pores than with smaller ones [24].

Contact angle is an indicator of the hydrophobicity of membrane surfaces, with a larger contact angle correlating with a more hydrophobic surface ($>90^\circ$) and a smaller contact angle correlating with a more hydrophilic surface ($<90^\circ$). In Table 3, the contact angle of the NF270 membrane increased after fouling, indicating that the fouling layer rendered the membrane more hydrophobic. It was reported that a membrane with a larger contact angle could retain and adsorb more hydrophobic compounds than one with a smaller contact angle [13]. On the other hand, the contact angle of the NTR7450 membrane decreased after fouling, indicating that the NTR7450 membrane became more hydrophilic.

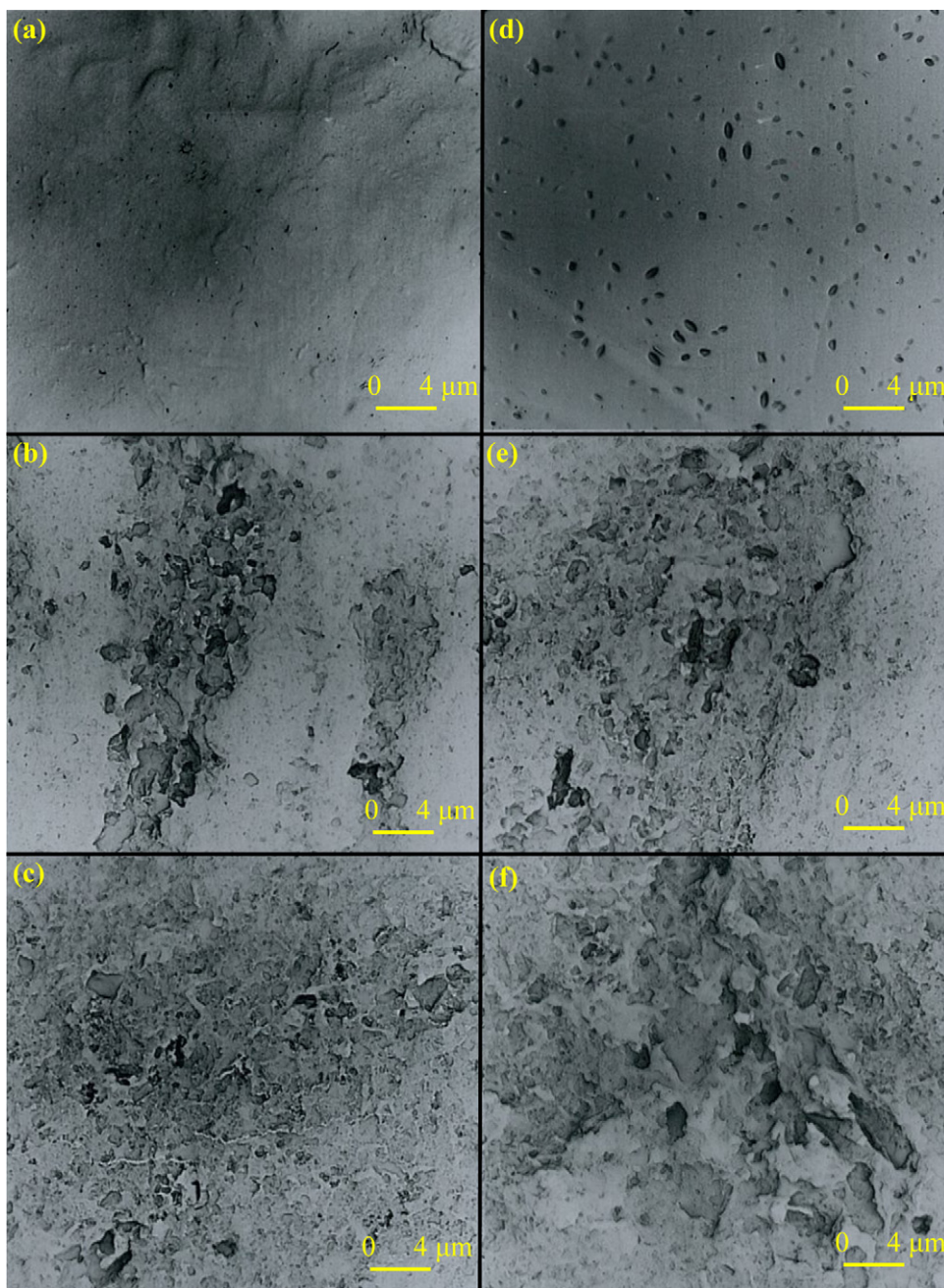


Fig. 1. SEM images of N270 and NTR7450 membranes operated at (a) clean/NF270, (b) humic acid/NF270, (c) humic acid + Ca²⁺/NF270; (d) clean/NTR7450, (e) humic acid/NTR7450, and (f) humic acid + Ca²⁺/NTR7450.

The effect of fouling on the contact angle of membrane surface has been studied [16,28,29]. Bellona et al. indicated that the effect of organic fouling on the characteristics of the membrane was found to be membrane dependent, e.g., the NF-90 membrane became more hydrophilic and negatively charged, whereas the NF-270 membrane became more hydrophobic and less negatively charged [30]. Some studies in the literature have reported that the adsorption of humic acid onto the membrane surface can increase the hydrophobicity of the fouled membrane surface [16,28]. In addition, membrane surface characteristics play a significant role in fouling during the initial phase of filtration. Rough and hydrophobic membranes with high permeability displayed more severe initial specific flux decline largely due to membrane compaction and

adsorption of hydrophobic organic matter, whereas the smooth and hydrophilic membrane exhibited high and constant specific flux [31].

Fig. 2 shows the variation of flux with time. For NF270, Fig. 2a, the flux declines were smooth in humic acid and humic acid/Ca²⁺ fouling. In contrast, NTR7450 (Fig. 2b) exhibited a sudden flux decline at the first 5 h. After that, the flux decline rate became slow and smooth. The decline ratio after equilibrium is shown in Table 3. The flux decline after 24 h filtration was found to be approximately 15% and 20% for the NF270 membranes fouled by humic acid and humic acid/Ca²⁺, respectively. The flux decline of the NTR7450 membrane was approximately 35% and 47% in the presence of humic acid and humic acid/Ca²⁺ in the feed solution, respectively.

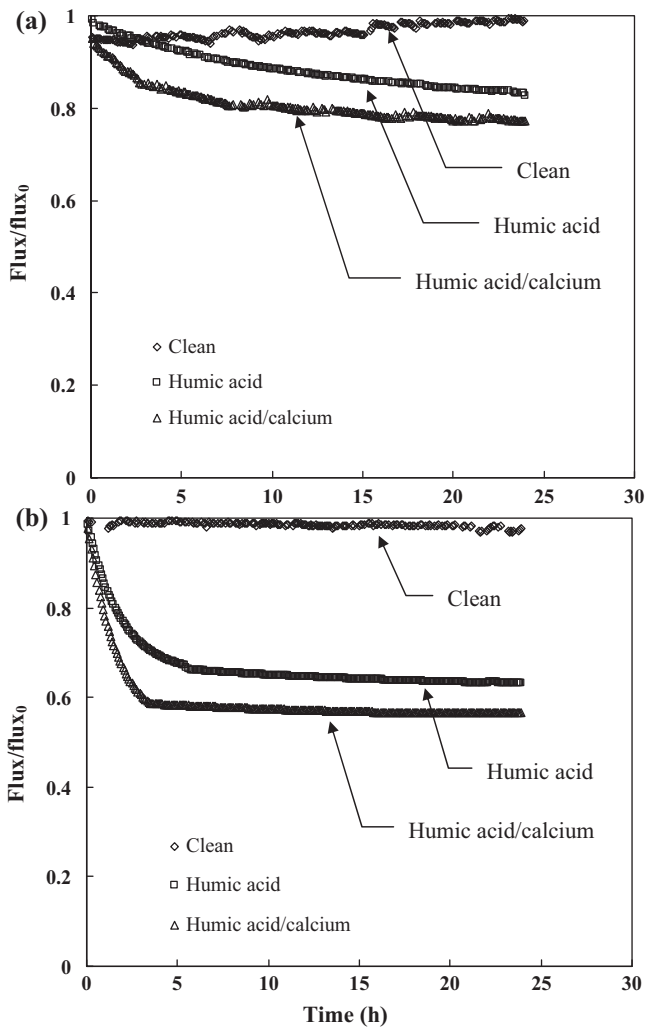


Fig. 2. Flux with time for (a) NF270, and (b) NTR7450 membranes.

3.1.2. Fouling mechanism

The fouling mechanism was assessed using the modified Hermia model [32]. According to this model, there are four main types of fouling: complete blocking, intermediate blocking, standard blocking, and cake formation. Complete blocking occurs when the size of foulants is similar to the membrane pore size, which results in reducing the number of open pores without particles depositing on the membrane surface in the first place. Intermediate blocking is somewhat similar to complete blocking, i.e., a single particle can precipitate on other particles to form multi-layers, and it can directly block some membrane surfaces, resulting in an increase in cake thickness. Standard blocking is similar to adsorption, by which the particles approaching the membrane are adsorbed and deposited on the internal pore wall, thereby reducing the pore volume. In cake formation, foulants deposit on the particles that already block the pores and result in cake formation.

For the sake of simplicity, the degree of model fitness (R^2) was used mainly to determine the fouling mechanisms that could explain the experimental data rationally, and the results are shown in Table 4. The fitting results showed that the standard blocking model correlated poorly, with low R^2 values in all cases, whereas cake-layer formation could be applied to all fouling conditions. It should be mentioned that both complete blocking and intermediate blocking also had good correlations (≥ 0.9) in all cases, which implied that the fouling mechanisms were very complex and that fouling could not be attributed to a single mechanism.

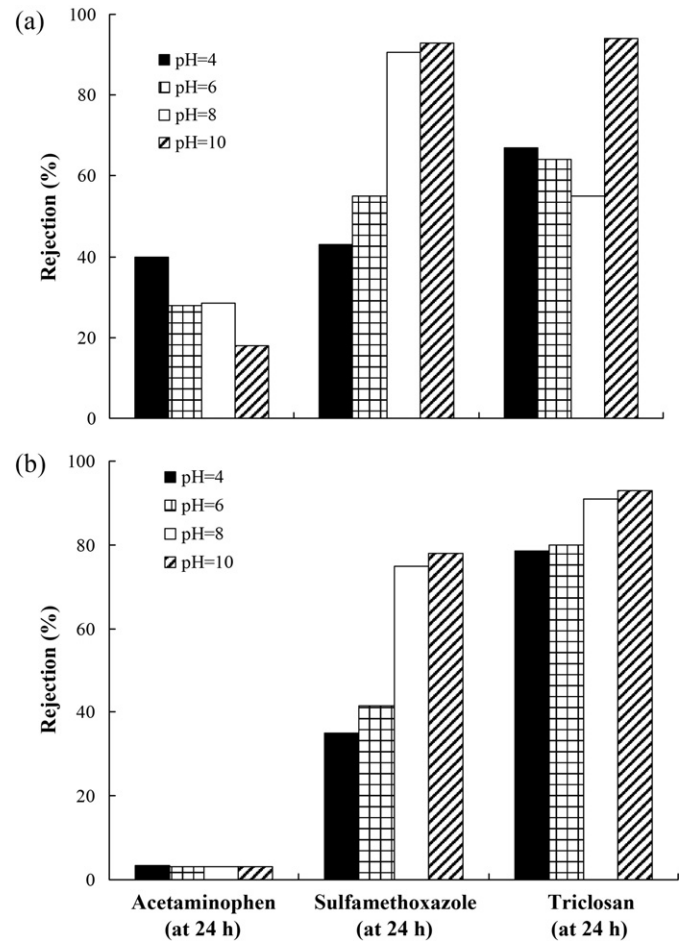


Fig. 3. Rejections of acetaminophen, sulfamethoxazole and triclosan as a function of pH (4, 6, 8, and 10) by (a) NF270 and (b) NTR7450 membranes.

This was due to the wide range of the molecular weight distribution of the humic acid. For instance, the sudden flux decline observed in Fig. 3 could be explained by the evidence of two-stage fouling, i.e., pore blocking and cake layer formation. The rapid fouling was due to pore blocking, in which most membrane pores are blocked quickly at the beginning of filtration, whereas the slow fouling was attributed to cake layer formation. Both complete and intermediate blocking would proceed more rapidly than cake layer formation owing to fewer particles being needed to achieve blocking. On the other hand, cake layer formation was the predominant fouling mechanism after the pores became blocked, which could result in concentration polarization and lower solute rejection as reported in the literature [16,28].

In summary, the change of the surface characteristics under each fouling condition was as follows: (1) after fouling the contact angle increased for the NF270 membrane but decreased for the NTR7450 membrane; and (2) membranes fouled by humic acid/ Ca^{2+} could cause a severer flux decline, in which the initial rapid fouling was due to pore blocking, whereas the second-stage fouling was attributed to cake layer formation.

3.2. Rejection of target compounds

3.2.1. Effect of pH

In this study, the effect of pH on rejection was investigated at various pH values (4, 6, 8, and 10) and the results are shown in Fig. 3. The isoelectric point of the NF270 and NTR7450 membranes was approximately 4, which indicates that the membrane surface

Table 4
Goodness of data fitting (R^2) by the Hermia model.^a

Membrane	Foulant	Complete blocking (CB)	Intermediate blocking (IB)	Standard blocking (SB)	Cake-layer formation (CF)	Proposed fouling mechanisms
NF270	Humic acid	0.931	0.895	0.042	0.936	CF and CB
	Humic acid/Ca ²⁺	0.901	0.903	0.051	0.947	CF and IB
NTR7450	Humic acid	0.973	0.925	0.076	0.934	CB and CF
	Humic acid/Ca ²⁺	0.904	0.933	0.086	0.952	CF and IB

^a Operated at constant cross-flow velocity of 0.3 m/s, and TMP of 690 kPa.

exhibits negative zeta potential. For acetaminophen, the rejection by NF270 membrane (Fig. 3a) decreased with increasing pH from 4 to 10. This relatively lower rejection was also reported by other study [33] which was due to the strong solute-membrane affinity [31]. However, Zazouli et al. reported a contrary result in which the acetaminophen rejection increased as the pH increased [17]. On the other hand, the rejections by NTR7450 membrane were very low under all pH values (Fig. 3b), which imply that the electrostatic repulsion was not the major mechanism controlling the rejection within this pH range.

For sulfamethoxazole, the rejections increased when the pH increased from 4 to 10 by both membranes. It was noted that the membrane became negatively charged as pH increased, whereas the sulfamethoxazole with a pK_a of 5.5 was deprotonated to anionic ions as the pH increased from 4 to 10. Consequently, electrostatic repulsion could bring about further rejection. It was reported that the NF270 membrane had high rejection of sulfamethoxazole at pH above 8 for virgin membranes, since electrostatic repulsion was the major rejection mechanism of negatively charged solutes [34]. The similar observation was also found in the rejection of triclosan, i.e., the highest rejection occurred at pH 10. It was thus concluded that the rejection due to electrostatic repulsion was increased significantly, once the pH exceeded the pK_a (7.9).

3.2.2. Effect of fouling

The rejection of the three target compounds by the fouled NF270 and NTR7450 membranes is shown in Figs. 4 and 5, respectively. The results showed that fouling caused an increase in rejection of acetaminophen for the two membranes (Figs. 4a and 5a). In addition, the presence of humic acid/Ca²⁺ exhibits higher rejection than that of humic acid only, which was consistent with the findings reported by Xu et al. [19] and Nghiem et al. [28] It suggests that membranes fouled by humic acid and humic acid/Ca²⁺ might create a hindrance layer resulted in increasing solute rejection. Since acetaminophen was a neutral molecule at pH 8, electrostatic repulsion might not play an important role in its rejection. However, contrary results also have been reported by Zazouli et al. who revealed that acetaminophen would be enriched on/in the polar alginate layer and more easily diffuse through the membrane barrier to the permeate side, thus decreasing the observed rejection [17]. The discrepancy in rejection for the fouled and unfouled NF270 membrane for acetaminophen could be explained through the interactions between the solute and the membrane surface as well as cake-enhanced concentration polarization [30]. Although fouling enhanced the rejection of acetaminophen, it also reduced the flux and therefore is not beneficial to the total membrane process.

Figs. 4b and 5b show the rejection of sulfamethoxazole by the fouled NF270 and NTR7450 membranes, respectively. It is apparent that fouling by humic acid/Ca²⁺ could decrease the solute rejection more than fouling with humic acid due to an increase in concentration polarization in the humic acid/Ca²⁺ system. It was reported that cake formation might cause concentration polarization and thus significantly affect sulfamethoxazole rejection [18,24,28]. In general, the effect of organic fouling on the membrane characteristics was found to be membrane dependent [30]. In this study, it

was expected that membrane fouling by humic acid increased the negative charge and therefore increased the rejection of negatively charged compounds. On the other hand, the fouling layer might act as a secondary membrane so as to increase rejection [24,35].

A similar finding was also observed with the rejection of triclosan by the fouled NTR7450 membrane. As shown in Fig. 5c, the extent of decrease in rejection by the membrane fouled by humic acid/Ca²⁺ was greater than that fouled by humic acid. Based on contact angle measurement, results also showed that the NTR7450 membrane became more hydrophilic after fouling, which could explain the decreased rejection by adsorption. In contrast, as shown in Fig. 4c, the rejection of triclosan by the fouled NF270 membrane did not vary with time. For hydrophilic non-ionic target compounds, e.g., triclosan, the main rejection mechanism (size exclusion) did not change after fouling even though the fouling layer might change the total amount of rejection [36]. In conclusion, the influence of fouling on solute rejection could be interpreted in terms of three distinct aspects, i.e., pore restriction, changes in membrane surface characteristics, and cake-enhanced concentration polarization. For pore restriction, the membrane was fouled by pore blocking, which could considerably enhance solute rejection, especially for a comparatively loose membrane [28]. This effect was attributed to the narrowed pores by fouling, which resulted in size exclusion becoming more dominant [6]. However, the same authors also indicated that there was a marked decrease in the rejection of larger solutes. Since the removal of larger organics was mainly by size exclusion for the virgin membranes, the diffusion of adsorbed pollutants across the fouled membrane played a prominent role in their transfer through and then lowered the rejection thereafter.

3.3. Determination of the rejection mechanism

Fig. 6a shows the observed and predicted solute rejection by NF270 and NTR7450 membranes. The predicted rejection by the SHP model correlated well with the observed value of the NF270 membrane but was underestimated for the NTR7450 membrane, which implies that size exclusion in the NF270 membrane was more predominant than in the NTR7450 membrane. Since acetaminophen was removed mostly by size exclusion (attributed to its low $\log K_{ow}$ and neutral properties), the error of adsorption could be neglected. In general, the SHP model was applicable only to describing size exclusion as the rejection mechanism, rather than electrostatic repulsion. In other words, electrostatic repulsion should be considered in the model prediction because the humic acid that adsorbed onto the membrane surface could increase the negative charge of the membrane, resulting in increasing the electrostatic repulsion for negatively charged solutes.

Fig. 6b shows the predicted rejection of the three target compounds by the combined model, i.e., the SHP model (size exclusion) coupled with the TMS model (electrostatic repulsion). Results showed that the predicted results of the three compounds by the SHP model (Fig. 6a) were almost identical to that by combined model (Fig. 6b), which implied that the contribution of electrostatic repulsion by the NF270 membrane was insignificant in comparison of size exclusion. On the other hand, the prediction for

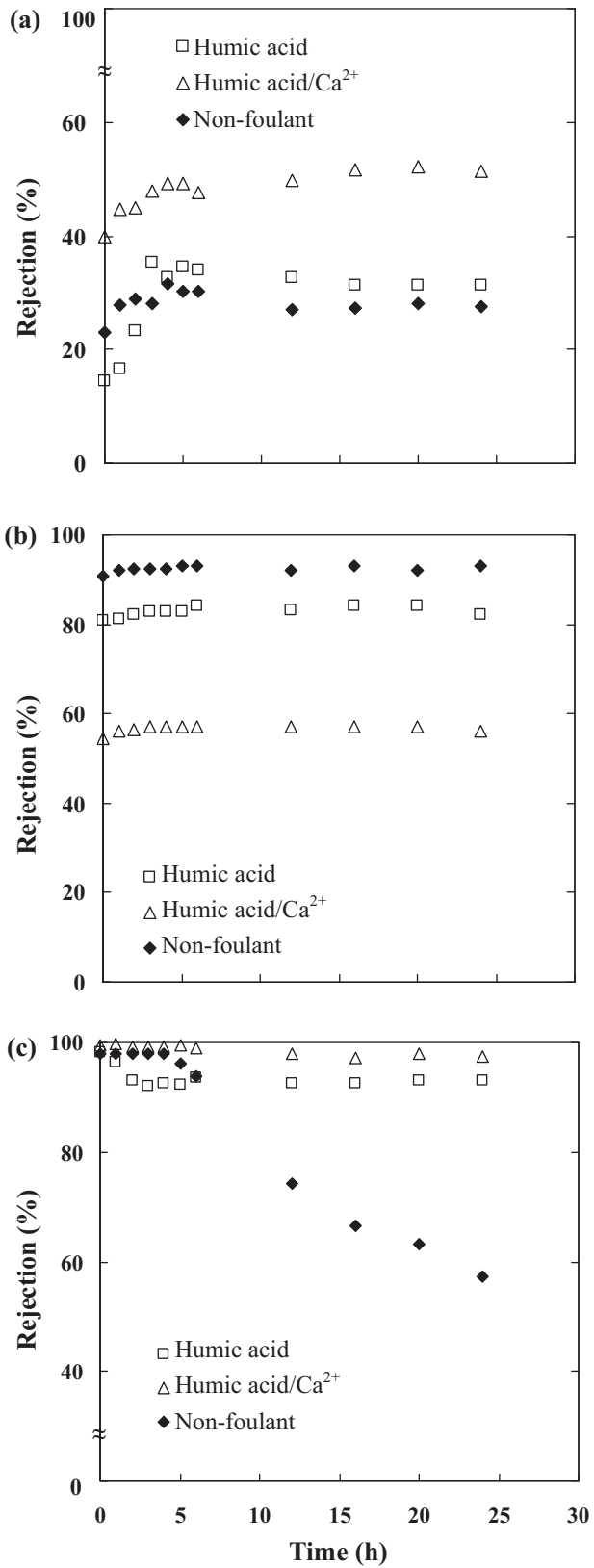


Fig. 4. Rejection of (a) acetaminophen, (b) sulfamethoxazole, and (c) triclosan as function of foulant by NF270 membrane, at pH 8, transmembrane pressure 690 kPa, and cross-flow velocity 0.30 m/s.

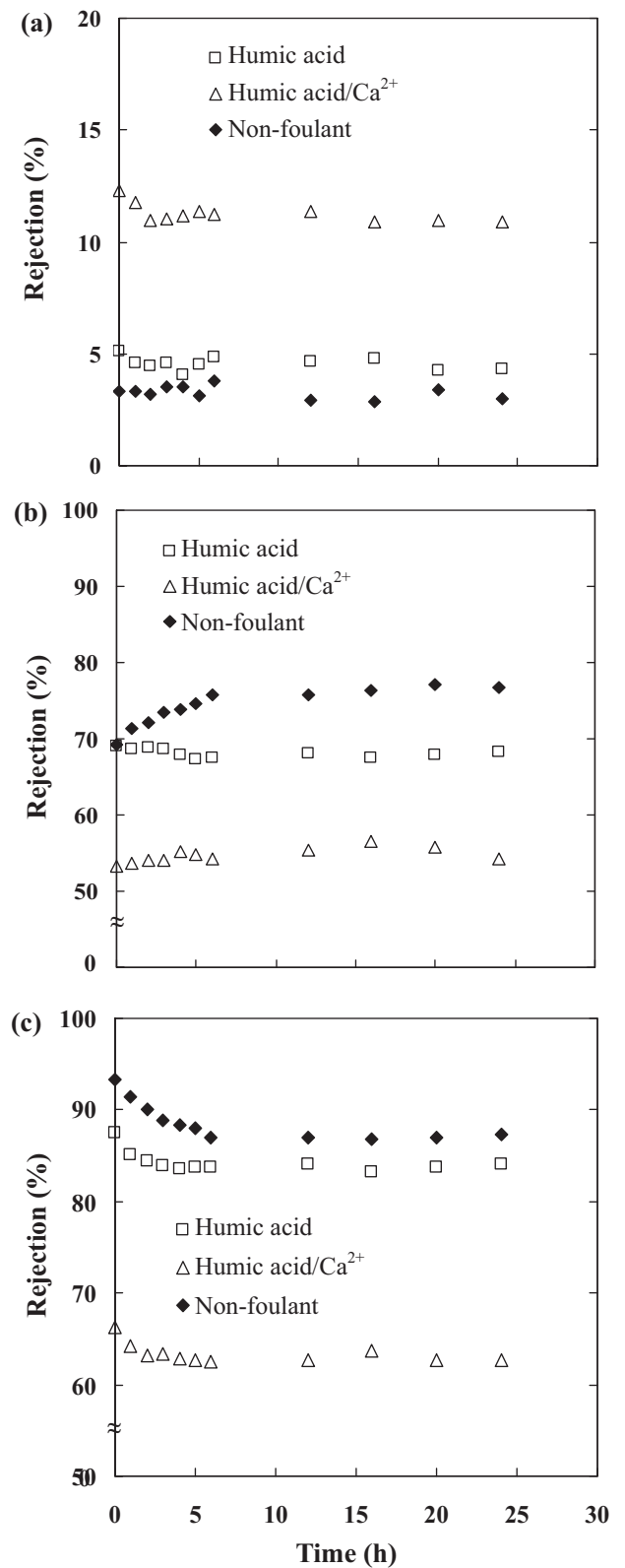


Fig. 5. Rejection of (a) acetaminophen, (b) sulfamethoxazole, and (c) triclosan as function of foulant by NTR7450 membrane, at pH 8, transmembrane pressure 690 kPa, and cross-flow velocity 0.30 m/s.

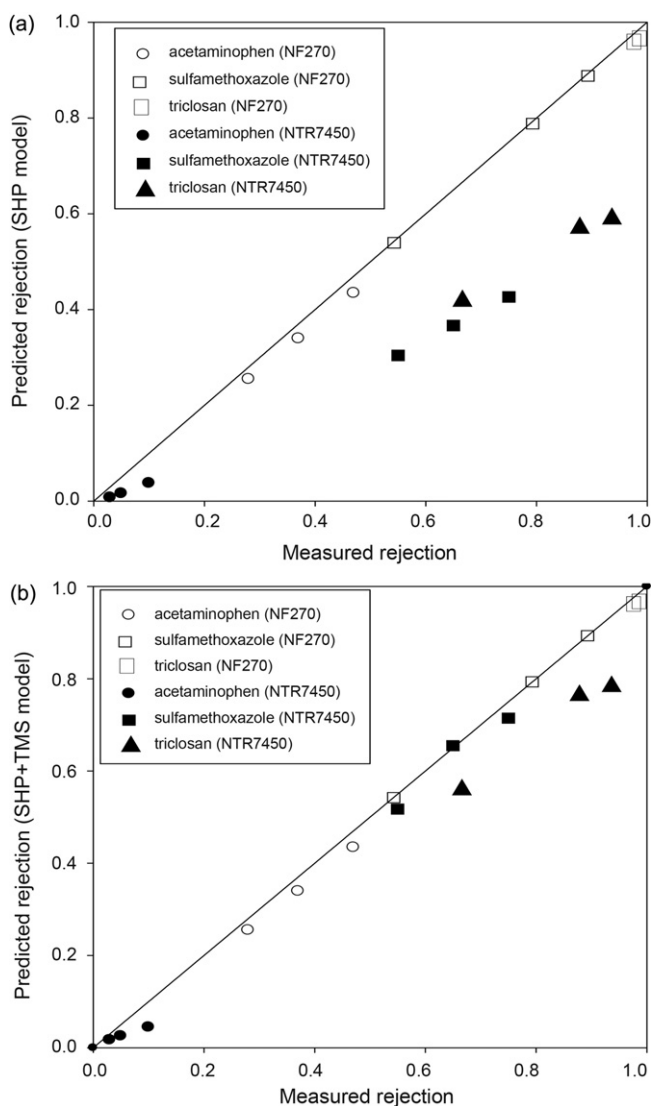


Fig. 6. Rejection of target compounds predicted by (a) SHP, and (b) combined (SHP+TMS) model.

sulfamethoxazole and triclosan rejection of the NTR7450 membrane was much improved by the combined models, which indicated that electrostatic repulsion should play an important role for the NTR7450 membrane. It also suggests that the adsorption mechanism should be introduced to the combined model to increase the prediction precision for target compounds with highly hydrophobic (low K_{ow}) solutes in our future research work.

4. Conclusions

The two membranes fouled with humic acid were attributed to complete blocking and cake-layer formation, while membranes fouled with humic acid/ Ca^{2+} were attributed primarily to cake-layer formation with elements of pore blocking. Discrepancies existed in the influence of fouling on the rejection of three target compounds by the two membranes. For small and neutral-charged target compounds, e.g., acetaminophen, the presence of humic acid and calcium ions increased rejection due to an extra hindrance layer provided by the foulants. In contrast, fouling of the membranes decreased the rejection of larger target compounds, e.g., sulfamethoxazole and triclosan, because the concentration

polarization was enhanced by the presence of humic acid or calcium ions.

The predicted rejection by the SHP model correlated well with the measured rejection of the NF270 membrane but was underestimated for the NTR7450 membrane, implying that the contribution of size exclusion was more dominant on the NF270 membrane than on the NTR7450 membrane. On the other hand, the rejection of sulfamethoxazole and triclosan by the NTR7450 membrane could be estimated more precisely when electrostatic exclusion was introduced, suggesting that electrostatic repulsion played a more functional role in determining rejection by the NTR7450 membrane. It suggests that the change in the membrane surface characteristics could affect both electrostatic repulsion and adsorption, which should be validated through an adsorption isotherm test in our future research work.

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