



# Effects of concentrations and types of natural organic matters on rejection of compounds of emerging concern by nanofiltration

Tse-Jung Liu, E.-E. Chang, Pen-Chi Chiang\*

Graduate Institute of Environmental Engineering, National Taiwan University, 71 Chou-Shan Rd., Taipei 106, Taiwan Tel. +886 2 3366 4381; Fax: +886 2 2362 2510; email: d96541008@ntu.edu.tw

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## ABSTRACT

Influence of water matrix on the removal of compounds of emerging concern (CECs) by nanofiltration (NF) has not been clearly delineated. In this study, rejection of eight CECs in different water matrices by NF is investigated. Two additives (humic acid and alginate) were added as natural organic matters (NOMs) to Milli-Q water to emulate raw river water and lake water. The results showed that an intermediate NOM concentration had better rejections of CECs than lower or higher concentrations in the levels of concentrations studied here. When a water matrix contained no NOM, CECs that carried negative charges gained better rejection than those that carried neutral or positive charge at pH of 7, which implies that the major mechanism of rejection is electrostatic repulsion. As the NOM concentrations in the water matrix got relatively higher, adsorption became a predominant mechanism for rejection; under these circumstances, CECs which had higher octanol–water distribution coefficient ( $k_{ow}$ ) could be adsorbed on NOMs and removed with them. The influence of NOM concentration on CEC rejection was considered and used to modify a quantitative structure-activity relationship (QSAR) model. The predicted values of the modified QSAR model were closer to the actual experimental data than those of the original model.

Keywords: Emerging contaminants; EDC; PPCP; Nanofiltration; NOM; QSAR

## 1. Introduction

Advancement of water treatment nowadays seems to provide safe potable water until the compounds of emerging concern (CECs) were detected. CECs may cause adverse impacts on organisms as shown in many previous researches [1,2]. Since the analytical techniques for identifying and quantifying trace pollutants in water are still being improved, a full list of CECs is not yet complete. In general, CECs can be categorized into two major groups: "endocrine disrupting chemicals (EDCs)" and "pharmaceuticals and personal care products (PPCPs)". Most of them cannot be effectively removed by the conventional drinking water treatment systems [3]. These CECs exist ubiquitously in aqueous media including lakes and rivers [3–5] that are often the sources for drinking water. Many advanced treatment processes have been evaluated and applied to remove CECs in the past decade [6,7] including membrane filtration. Nanofiltration (NF) has demonstrated

<sup>\*</sup>Corresponding author.

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its effectiveness among membrane filtration technologies in rejecting both EDCs and PPCPs [8–14].

NF has been shown not to have the same performance for each CEC. Many research results reported in literature indicated that the extent of CEC rejection by NF depends on physico-chemical properties of CEC, types of membrane material, electrical properties of membrane surface, operation conditions, and properties of water matrix [8,10–13,15–19]; the mechanisms of CEC rejection by NF are complicated.

Generally speaking, the main mechanisms of CEC rejection by a membrane process include electrostatic repulsion, diffusion, size exclusion, steric hindrance, hydrophobic adsorption, charge attraction, Donna exclusion, and other membrane-solute interaction [8-11,13,15,17-21]. Yoon et al. [11] discussed the relationship between octanol-water partition coefficient  $(k_{ow})$  of CEC and hydrophobic adsorption. Hydrophobic adsorption was observed between hydrophobic membranes and hydrophobic CEC. Yangali-Quintanilla et al. [13] tested the rejection of 14 CECs by clean and pre-fouled NF. The main mechanism of hydrophobic neutral compounds removal is size exclusion, and the researchers proposed electrostatic repulsion as the main mechanism for ionic compounds. The NF membrane pre-fouled with sodium alginate performed better for hydrophobic neutral compounds, but not hydrophilic neutral compounds, and hydrophilic- and hydrophobic ionic compounds. They thought that it was caused by an incipient interaction of solutes with the membrane foulant layer that resulted in less partitioning and diffusion across the membrane surface.

In terms of solution composition, presence of natural organic matters (NOMs) (1 mg/L) in the feed solution did not lead to variation in CEC (Bisphenol A, (BPA)) rejection under steady state conditions [14]. Comerton et al. [20] indicated that the adsorption of CEC (gemfibrozil) by NF could have been hindered due to the competition for adsorption sites when organic matter was present in the water matrix.

In view of the above-mentioned research results, it is clear that NOM in a water matrix and the physicochemical properties of target compounds may affect the extent of rejection of target compounds by NF. The plausible mechanisms include pore narrowing, fouling, modified electrostatic, hydrophobic/hydrophilic solute-membrane interaction and NOM-solute-membrane interaction. However, few researches discussed the interaction between NOM and CEC. This paper attempted to evaluate the effects of concentrations and types of NOMs in water matrices on CEC rejection by NF. This study intends to provide an explanation on the difference in rejection.

## 2. Materials and methods

## 2.1. Compound selection and characterization

Eight CECs were chosen based on their physicochemical properties (MW, log  $k_{ow}$ ,  $pk_a$ ) to represent six groups of organic micropollutants. These compounds are commonly found in aquatic environment all over the world [3–5,22–26]. Table 1 summarizes the structure and physico-chemical properties of the target CECs selected for this study.

## 2.2. Membrane characterization

NF270 (Dow Chemical Co., Filmtec NF270-400, Midland, MI, USA) was used in this study. The characteristics of NF270 are presented in Table 2. Pure water permeability (PWP) and molecular weight cutoff (MWCO) associated with NF270 were determined using a commercially available stainless steel crossflow membrane filtration unit (GE OSMONICS). PWP provides an indication of the maximum flux that can be achieved by the membrane and was determined by taking the slope of the average flux of Milli-Q water through the membranes as measured over a range of feed pressures. The MWCO of a membrane represents the molecular weight of a molecule that is rejected at 90% and was estimated using the solute transport technique described by Singh et al. [27] via rejection tests using solutions containing polyethylene glycol molecules (87976, Sigma-Aldrich, Oalville, ON, USA) of varying molecular weights (200, 400, 600, 1,000, and 2000 Da), but at a constant solute concentration of 10 mg/L by weight.

Membrane zeta potential was measured by using a SurPass electrokinetic analyzer (Anton Paar, Graz, Austria) following streaming current methodology described by Childress and Elimelech [28] and determined from the charge of the membrane surface. Membrane contact angle is an index of the hydrophilicity/hydrophobicity of a membrane. A contact angle can be determined to find out whether the membrane surface is hydrophilic or hydrophobic. The hydrophobicity increases with the contact angle of membrane. The static contact angle of dry membrane samples was measured in triplicate via the sessile drop technique described by Chen and Wada [29] with Mill-Q water (drop volume of approx. 10 µL) using a First Ten Angstroms dynamic contact angle analyzer (FTA200, Folio Instruments Inc., Kitchener, ON, USA).

# 2.3. Water selection and characterization

Four synthetic water samples were prepared and investigated in this study ( $W_1$ ,  $W_2$ ,  $W_3$ , and  $W_4$ ).

CEC	Structure	Molecular weight	pK <sub>a</sub> (at 25 °C)	$\log K_{\rm ow}$	Water solubility	Classified
BPA	но-СН3 -ОН	228.29	10.2 (HB-netural)	3.32	120	Group 1(G <sub>1</sub> ) $ \begin{pmatrix} MW < MWCO \\ pKa > 7 \\ log  \mathbf{k}_{ow} < 2 \end{pmatrix} $
Estron	но снз о	270.37	10.4 (HB-netural)	3.13	3.4	Group 1(G <sub>1</sub> )
SFX		253	2.1 (HL-negative)	0.89	610	Group 2(G <sub>2</sub> ) MW <mwco pKa&lt;7 log <b>k</b><sub>ow</sub>&lt;2</mwco 
CFN		194.2	6.1 (HL-netural)	-0.07	$2.16  imes 10^6$	Group 2(G <sub>2</sub> )
CBZ		236	<2 (HB-positive)	2.45	17.7	Group $3(G_3)$ MW <mwco< td=""></mwco<>
ЕМН		733.9	8.8 (HB-positive)	3.06	$2.1 \times 10^{-3}$	$\left(\begin{array}{c} p_{Ka<7} \\ \log k_{ow} > 2 \end{array}\right)$ Group 4(G <sub>4</sub> ) $\left(\begin{array}{c} MW > MWCO \\ p_{Ka>7} \end{array}\right)$
TMP	H <sub>2</sub> N N NH <sub>2</sub> O	290	7.1 (HL-netural)	0.9	400	$\left(\begin{array}{c} \log k_{\rm ow} > 2 \end{array}\right)$ Group 5(G <sub>5</sub> )
AMP	HO H	151.2	9.7 (HL-netural)	0.46	$1.4  imes 10^4$	$\frac{ V W >  V W < O}{pKa > 7}$ $\log k_{ow} < 2$ Group 6(G <sub>6</sub> ) $\frac{MW < MWCO}{pKa > 7}$ $\log k_{ow} < 2$

Table 1			
Structures and physico-chemica	l properties of the target CEC	's selected for this study	[7 11 13 16 20 21]

Membran	e Material	MWCO (Da)	NaCl retention (%)	Average pore diameter (nm)	Zeta potential (mV)	Thickness (µm)	Contact angle (°)	Roughness (R <sub>rms</sub> ) (nm)	$PWP (Lm^{-2}h^{-1}kPa^{-1})$
NF-270	Polyamide thin-film composite	300	40.0	0.84	–22 (at pH 7)	135	64.1 ± 10.5 (clean membrane)	1.279 (clean membrane)	0.16

Table 2 Characterization of NF270 used in this study

Table 3 Characteristics of the feed water

Feed water samples	$W_1$	W <sub>2</sub>	<i>W</i> <sub>3</sub>	W4
pН	$6.23 \pm 0.20$	$7.00 \pm 0.20$	$7.36 \pm 0.20$	$7.23 \pm 0.20$
Conductivity ( $\mu$ S cm <sup>-1</sup> )	$2.6 \pm 2.00$	$88.0\pm0.20$	$143.0\pm0.20$	$117.0.0 \pm 0.20$
TOC $(mgL^{-1})$	$0.41 \pm 0.22$	$3.72 \pm 0.22$	$24.06 \pm 0.22$ .	$24.13 \pm 0.22$ .
UV254 ( $cm^{-1}$ )	$0.003 \pm 0.003$	$0.040\pm0.04$	$0.210 \pm 0.04$	$0.230 \pm 0.04$
$SUVA (Lm^{-1}mg^{-1})$	$0.004 \pm 0.002$	$0.08 \pm 0.04$	$0.17 \pm 0.04$	$0.21 \pm 0.04$
CEC concentration (ng/L)	BPA:56.5	BPA:127.8	BPA:90.3	BPA:94.2
	E1:191.6	E1:159.7	E1:177.2	E1:192.5
	SFX:24.4	SFX:74.5	SFX:48.8	SFX:51.4
	CFN:161	CFN:52.8	CFN:103.1	CFN:104.9
	CBZ:231	CBZ:64.1	CBZ:171.4	CBZ:168.6
	EMH:25	EMH:4.4	EMH:13.3	EMH:19.0
	TMP:195	TMP:66.4	TMP:97.9	TMP:96.1
	AMP:81	AMP:53.6	AMP:77.1	AMP:75.8

Milli-Q water worked as a base matrix of each filtration test in this study. Each water sample ( $W_1$ ,  $W_2$ , and  $W_3$ ) was individually added with different amounts of humic acid to make sure that these samples contained different concentrations of the total organic carbon (TOC).  $W_4$  was added with alginate and had the same TOC concentration as  $W_3$  to evaluate the types of additives on CEC rejection. Characteristics of the feed water samples are presented in Table 3.

# 2.4. Filtration test

A cross-flow filtration apparatus with a flat-sheet of membrane cell made by GE was used for all filtration tests. The surface area of the membrane was 140 cm<sup>2</sup> (14.6 cm L × 9.5 cm W) and the cross-sectional area was  $1.9 \text{ cm}^2$  (9.5 cm W × 0.2 cm H). In each experiment, a new membrane (membrane sheets were stored in 1.5% of sodium meta-bisulfite, Na<sub>2</sub>S<sub>2</sub>O<sub>5</sub> to avoid oxidation and to keep them wet.) was used. It was rinsed with Milli-Q water thoroughly and then conditioned by filtering with Milli-Q water for 24 h continuously until a stable pure water permeate flux

was established before the filtration tests. Following their initial step, the pure water was replaced by a water sample in each run. Each water sample was filtered for 216 h and the permeate was sampled for analysis at 1, 8, 24, 48, 72, 96, 168, and 216 h, respectively. All the experiments were operated in a recycle mode, i.e. both permeated water and retention were recycled back to the feed reservoir. The water in the feed reservoir was about 10 L, which was enough for withdrawing the samples during the entire run. Operation conditions of filtration test were kept at filtrating pressure of 70 psi, flow rate of 0.4 L/min, and temperature of  $25 \pm 2 \,^{\circ}\text{C}$ .

Six samples from the effluent of each run were taken at 1, 24, 48, 96, 192, and 216 h for analyses of CEC concentration. The values from each run were then averaged to get the average permeate concentration. Removing efficiency of targeted compounds of each sample by NF270 was calculated by:

$$R(\%) = \left(1 - \frac{C}{C_0}\right) \times 100\% \tag{1}$$

where *C* is the CEC concentration of the permeate at a specific filtration time and  $C_0$  is the initial concentration

of the CEC spiked into each raw sample. Therefore, a  $C/C_0$  value of 1.0 indicates no rejection by the membrane, whereas a value of 0 indicates complete rejection by the membrane.

#### 2.5. Analytical method

All water samples for CEC analysis were vacuumfiltered through a 0.45 and 0.22 µm cellulose acetate membrane filter, acidified to pH 4.0 by using sulfuric acid (2N), and stored at 4°C until analysis. Oasis HLB cartridges (500 mg, 6 mL, Waters, Milford, MA, USA) used for solid phase extraction (SPE) were preconditioned with 6 mL of methanol and 6 mL of deionized (DI) water. Aliquots of 400 mL water samples were spiked with  ${}^{13}C_6$ -sulfamethazine (employed as a surrogate) and loaded to the cartridge with a flow rate of 3–6 mL/min. After sample passage, the cartridges were rinsed with 6 mL DI water to remove excess EDTA-2Na and dried under a flow of nitrogen gas. After drying, the analytes were eluted with 4 mL of methanol and 4 mL of methanol-diethylether (50:50, v/v). The elutes were collected, evaporated to dry with nitrogen stream, and reconstituted to 0.4 mL with 25% aqueous methanol. The final solutions were filtered through a 0.45 µm PVDF membrane filter.

were analyzed following a method CECs developed by National Taiwan University (NTU) and conducted repeatedly for three times [5]. All analyses were conducted at an NTU laboratory using an Applied Biosystem LC/MS/MS system (Sciex API 4000) with an Agilent 1200 LC (Agilent Technologies, Palo Alto, CA, USA) equipped with a Phenomenex Luna  $C_{18}$  column (150 × 4.6 mm, 5 µm). The method detection limits (MDLs) of these compounds are from 1 to 10 ng/L. The TOC was analyzed by using a TOC analyzer (O.I. Analytical Model 1010, TX, USA) with an autosampler (O.I. Analytical Model 1051) for raw water samples, following the NIEA W532.51C (Taiwan Environment Analysis Laboratory, 2000). The MDLs for dissolved organic compounds was 0.22 mg/L. Surface characterization of clean and fouled membranes was observed by scanning electron microscope (SEM, Hitachi S-2400) with working voltage of 20 kV. The functional groups of raw and fouled membranes were identified by Fourier transform infrared spectroscopy (Thermo Nicolet NEXUS470) with a MCT/A detector operated from 650 to  $4,000 \,\mathrm{cm}^{-1}$ .

# 2.6. Modification of a QSAR model

There were few models for prediction of CECs rejection by NF available in literature. A general quantitative structure–activity relationship (QSAR) equation was developed by Yangali-Quintanilla et al. [30,31] for predicting the rejection of CECs by NF. Principal component analysis, partial least square regression, and multiple linear regressions (MLR) were applied to develop a general QSAR equation that involves membrane characteristics, filtration operating conditions, and CEC properties, which is:

$$Rejection = 265.150 \text{ eqwidth} - 117.356 \text{ depth} + 81.662 \text{ length} - 5.229 \log D - 0.272 \text{ MWCO} - 62.565$$
(2)

The definitions and units of the variables mentioned above and the range of a QSAR application are referred to in the previous research by Yangali-Quintanilla et al. [30]. The rejection efficiencies of CEC in different NOM concentrations were considered to modify the QSAR model. MLR was applied to the 144 pieces of rejection data. The operation conditions of the filtration tests were within the range of a general QSAR model.

#### 3. Results and discussions

# 3.1. Influence of NOM concentration on rejection

Averaged rejection of samples ( $W_1$ – $W_3$ ) with different NOM concentrations (0.41, 3.72, and 24.0 mg/L) are shown in Fig. 1. For  $W_1$  test, the rejection of PPCP group showed extreme results. The one that carried negative charge at pH 7 and had lower log  $k_{ow}$  values sulfamethoxazole (SFX) and caffeine (CFN) had better



Fig. 1. The average rejections of CEC in water matrix with different NOM concentrations.

rejection than those that carried positive or neutral charge. It implies that the predominant mechanism was electrostatic repulsion. The better rejection relied on the structure of PPCP functional group that has higher electronegativity, which could be adsorbed on the surface of NF270 via hydrogen bonds. Even for erythromycin (EMH), which had similar physicochemical properties as SFX and CFN, the rejection was not as good. It could be concluded that the water solubility of EMH was much lower in water matrix. Therefore, the rejection of PPCP was not significant with low concentration of NOM.

The results from  $W_1$  to  $W_3$  of tests showed that different NOM concentrations in water matrix had a great impact on NF270 rejection for most CEC. In the  $W_1$  and  $W_2$  tests, the CEC rejections significantly increased with an increase in NOM concentration, except for SFX,  $E_1$ , and BPA. The results also showed that CEC had similar *pk*a value (from 7.1 to 9.7), higher than the pH of water matrix at 7, and carried a positive or neutral charge in water matrix with a significant increment of rejection (EMH, acetaminophen [AMP], and trimethoprim [TMP]). It was worth to mention that those categorized as EDCs (including  $E_1$  and BPA) had higher rejection (>78%) compared with others due to their high values of log  $k_{ow}$  (>3) [32,33] and neutral charge, which made EDCs to get more easily adsorbed on NF270 surface.

Comparing  $W_2$  with  $W_3$  tests, the rejection of each CEC was significantly greater. As the content of NOM (humic acid) moderately existed in water matrix, the interaction between CEC and organic matters frequently occurred, which made hydrophobic adsorption as the critical mechanism. As the NOM concentration in water matrix ( $W_3$ ) was larger than that of  $W_2$ , fouling phenomenon occurred easily, which resulted in worse rejection than the moderate NOM that existed in the water matrix ( $W_2$ ). The result is similar to a previous study which suggested that fouling causes a decline of bulk electricity by the double electric layer compression [10]. This could also be resulted from concentration polarization [27] or decreasing adsorption sites of NF270 [20].

In accordance with the results of  $W_1$ ,  $W_2$ , and  $W_3$  (see Table. 4), there is a strong correlation between the NOM concentration and rejection. EDC ( $G_1$ ) and the

Table 4 The relationships between flux and TOC concentration

	T							
$R^2$	EMH	AMP	TMP	CBZ	CFN	SFX	E <sub>1</sub>	BPA
Linearity	0.070	0.530	0.448	$2  imes 10^{-6}$	0.014	0.038	0.907	0.911
Logarithm	0.425	0.905	0.852	0.182	0.281	0.356	0.533	0.540



Fig. 2. Characterization of functional groups of tested NF270 by FTIR.



Fig. 3. SEM photographs of fouling on NF 270 surface from the rejection of (a)  $W_1$ , (b)  $W_2$ , and (c)  $W_3$  filtration tests.

minority of PPCP (AMP and TMP) have higher linearity between *R* (%) and NOM (TOC) concentrations, which are  $R^2 > 0.9$  and  $R^2 > 0.4$ , respectively. Furthermore, AMP and TMP have a better logarithmic correlation between *R* (%) and NOM (TOC) concentration ( $R^2 > 0.85$ ) than linearity due to their lower values of log  $k_{ow}$ . For EMH, carbamazepine (CBZ), CFN, and SFX, there is poor and no correlation between *R* (%) and TOC concentration.

Four types of functional groups, including carboxyl, amino, hydroxyl, and phosphate group were identified as the most important moieties in adsorption of organic matter [34,35]. The existence of these functional groups is favorable for the adsorption of CECs. Each tested NF270 with different sample waters were investigated by FTIR as shown in Fig. 2. By comparing the raw NF270 with those in filtration tests, functional groups such as carboxylic acids and amine group, which could offer adsorption sites, increased on the NF270 surface with increasing NOM concentrations in water matrices. The results partly explain that the rejections of CEC by NF270 in W<sub>2</sub> or W<sub>3</sub> were better than those in  $W_1$ . It implies that hydrophobic adsorption is the major mechanism when a membrane is fouled.

## 3.2. Observation of membrane surface

Fig. 3 shows the SEM photography of fouling. The cake could be easily observed on the NF270 surface ( $W_3$ ), which was much thicker than those of  $W_1$  and  $W_2$ . The surface of NF270 used to filter  $W_1$  sample was almost the same as that of raw NF270, which was rough and without any impurity. Fouling phenomenon could be seen on the membranes of NF270 used to filter  $W_2$  and  $W_3$  samples in the form of cake which could provide adsorptive sites, narrow membrane

pore sizes, and offer an electrostatic function to increase the rejection. However, too much fouling in NF270 membrane used for  $W_3$  would cause a stronger double electric layer decompression.

#### 3.3. The relationship between flux and rejection

The relationship between the flux rate and rejection is shown in Fig. 4. The results showed that there was an inverse proportion between the flux and rejection of certain CECs, such as EMH, AMP, and TMP, as the existence of NOM. It was because of the reason that EMH in water matrix had a lower concentration than other CEC, which made the rejection not obvious. On the other hand, the flux decline could serve as an indicator of fouling. It means that a fouled membrane or longer filtration time would result in better rejection of CEC.

# 3.4. Influence of water matrix on rejection

Humic acid and alginate were, respectively, added into Milli-Q water to simulate river- and lake- source water in this research ( $W_3$  and  $W_4$ ). The average rejections of CEC in these two types of water matrices are shown in Fig. 5. The water matrix with humic acid  $(W_3)$  showed better CEC rejection than the one with alginate (W<sub>4</sub>) of the same TOC concentration, except for EMH and CFN. This result is similar to the findings of a previous study [35]. The structures of humic acid and alginate are similar, but the structural formula of humic acid is more complicated and larger that potentially makes the interactions between its functional groups more than alginate. Therefore, CECs with a higher electronegativity of functional groups (EMH and CFN) could combine with alginate's functional groups through adsorption via Hbond [15].



Fig. 4. The relationship between CEC rejection and flux of (a)  $W_{1}$  (b)  $W_{2}$  (c)  $W_{3}$  and (d)  $W_{4}$  tests.

The FTIR results of  $W_3$  and  $W_4$  filtered by NF270 are shown in Fig. 6. These results indicated that there were more OH groups, but less C–O functional groups in alginate compared with humic acid. Therefore, it was evident that adding humic acid as NOM provided more adsorption sites for CEC. It was interesting to note that addition of alginate could enhance the rejection of CECs that have extreme physicochemical properties (CFN and EMH).

## 3.5. Influence of CEC properties on rejection

Impacts of CEC properties on their removal depend on the existence of NOM in water matrix. When the NOM concentration was low, the electrostatic repulsion was the major mechanism. It means that the CEC with a pka value lower than the environment pH could have a better rejection by NF270. On the contrary, as NOM concentration became relatively high, log  $k_{ow}$  of CEC played an important role in the



Fig. 5. Comparison of CEC rejection in different water matrices (TOC = 24 mg/L).



Fig. 6. Characterization of functional groups of tested NF270 applied to  $W_3$  and  $W_4$  by FTIR.



Fig. 7. Comparison of authentic values: the predicting rejections of raw QSAR and modified QSAR.

process and determined whether CEC could be removed by adsorption. Functional groups of CEC were also important, since they played a role of a joint between CEC and NOM or membrane. There was no obvious impact of MW on CEC rejection [21]. Even EMH has similar  $k_{ow}$  value as  $G_1$ , their rejection were different in this study.

## 3.6. Modification of a QSAR model

The results showed a significant relationship between TOC concentration and CEC rejection for several CECs (AMP,  $E_1$ , and BPA;  $R^2 > 0.5$ ). Overall, a logarithm regression fits the data better than a linear regression. The general QSAR model was modified based on MLR analysis of the 144 data points as:

$$Rejection = 265.150 \text{ eqwidth} - 117.356 \text{ depth} + 81,662 \text{ length} - 5.229 \log D - 0.272 \text{ MWCO} + 6.353 \log \text{ TOC} - 63.288 \pm 5.2956$$
(3)

where TOC represents the NOM concentration with a unit of mg/L.

Comparisons of the predicted values of the original and the modified QSAR with the actual experiments are shown in Fig. 7. The figure shows that the actual rejection values were generally higher than the values predicated by the original QSAR model, but were close to the values predicated by the modified QSAR model.

#### 4. Conclusions

The rejections of eight CEC (six groups) by NF270 in different water matrices were examined in this study. The physico-chemical properties of CECs and types and concentration of NOM impacted the CEC rejections significantly. The extent of rejection correlated strongly with compound charge for the Milli-Q water sample. It also correlated well with  $k_{ow}$  values of the CEC when a moderate amount of NOM existed. In general, the

rejection of CEC increased with an increase in NOM concentration between 4 and 24 mg/L of TOC. Two mechanisms, electrostatic repulsion and hydrophobic adsorption played an important role in lower and moderate NOM concentrations. Some CECs, including CBZ, CFN, and EMH had a slight decrease in rejection under higher NOM concentration (TOC = 24 mg/L). The removal mechanisms could be the double electric layer depression and a competition for adsorption sites from the organic matter in the water matrix.

The water sample added with alginate showed better rejections of CECs with extreme physico-chemical properties. It implies that extent of rejection of CECs by NF was determined by physico-chemical properties of both CECs and the membrane. In this study, CECs which had moderate values of MW (close to MWCO), pka (>10), log  $k_{ow}$  (>3), water solubility (30-400 mg/L), positive or neutral charge, and high electronegativity functional groups in the water matrix were expected to have better rejection (>70%). Besides,  $G_1$  (EDC) had a better rejection (>90%) than those in the PPCP. To effectively remove CECs from drinking water supplies, a membrane process can be tandem with other advanced processes to produce potable water with CEC concentrations below the safety limits [6,7,37,38]. Hence, the types and concentrations of NOM play important roles in the removal of CECs by NF.

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#### References

- O.A. Jones, J.N. Lester, N. Voulvoulis, Pharmaceuticals: A threat to drinking water? Trends Biotechnol. 23 (2005) 163–167.
- [2] L. Ma, Endocrine disruptors in female reproductive tract development and carcinogenesis, Trends Endocrinol. Metab. 20 (2009) 357–363.
- [3] S.D. Kim, J. Cho, I.S. Kim, B.J. Vanderford, S.A. Snyder, Occurrence and removal of pharmaceuticals and endocrine disruptors in South Korean surface, drinking, and waste waters, Water Res. 41 (2007) 1013–1021.
- [4] S. Dagnino, B. Picot, A. Escande, P. Balaguer, H. Fenet, Occurrence and removal of endocrine disrupters in wastewater treatment plants for small communities, Desalin. Water Treat. 4 (2009) 93–97.
- [5] A. Yu-Chen Lin, Y. Tsung-Hsien, L. Cheng-Fang, Pharmaceutical contamination in residential, industrial, and agricultural waste streams: Risk to aqueous environments in Taiwan, Chemosphere 74 (2008) 131–141.

- [6] V. Yangali-Quintanilla, S. Kyu Maeng, T. Fujioka, M. Kennedy, Z. Li, G. Amy, Nanofiltration vs. reverse osmosis for the removal of emerging organic contaminants in water reuse, Desalin. Water Treat. 34 (2011) 50–56.
- [7] D. Dolar, K. Kosutic, D. Mutavdzic, B. Kunst, Removal of emerging contaminants of industrial origin by NF/RO—a pilot scale study, Desalin. Water Treat. 6 (2009) 197–203.
- [8] J. Radjenovic, M. Petrovic, F. Ventura, D. Barceló, Rejection of pharmaceuticals in nanofiltration and reverse osmosis membrane drinking water treatment, Water Res. 42 (2008) 3601–3610.
- [9] F. Neira Ruiz, A. Arcos Arevalo, B. Jimenez Cisneros, Operating conditions and membrane selection for the removal of conventional and emerging pollutants from spring water using nanofiltration technology: The Tula Valley case, Desalin. Water Treat. 42 (2012) 117–124.
- [10] A.R.D. Verliefde, S.G.J. Heijman, E.R. Cornelissen, G. Amy, B. Van der Bruggen, J.C. van Dijk, Influence of electrostatic interactions on the rejection with NF and assessment of the removal efficiency during NF/GAC treatment of pharmaceutically active compounds in surface water, Water Res. 41 (2007) 3227–3240.
- [11] Y. Yoon, P. Westerhoff, S.A. Snyder, E.C. Wert, Nanofiltration and ultrafiltration of endocrine disrupting compounds, pharmaceuticals and personal care products, J. Membr. Sci. 270 (2006) 88–100.
- [12] K. Kimura, T. Iwase, S. Kita, Y. Watanabe, Influence of residual organic macromolecules produced in biological wastewater treatment processes on removal of pharmaceuticals by NF/RO membranes, Water Res. 43 (2009) 3751–3758.
- [13] V. Yangali-Quintanilla, A. Sadmani, M. McConville, M. Kennedy, G. Amy, Rejection of pharmaceutically active compounds and endocrine disrupting compounds by clean and fouled nanofiltration membranes, Water Res. 43 (2009) 2349–2362.
- [14] L. Braeken, R. Ramaekers, Y. Zhang, G. Maes, B. Van der Bruggen, C. Vandecasteele, Influence of hydrophobicity on retention in nanofiltration of aqueous solutions containing organic compounds, J. Membr. Sci. 252 (2005) 195–203.
- [15] M. Ali Zazouli, H. Susanto, S. Nasseri, M. Ulbricht, Influences of solution chemistry and polymeric natural organic matter on the removal of aquatic pharmaceutical residuals by nanofiltration, Water Res. 43 (2009) 3270–3280.
- [16] V. Yangali-Quintanilla, A. Verliefde, T.-U. Kim, A. Sadmani, M. Kennedy, G. Amy, Artificial neural network models based on QSAR for predicting rejection of neutral organic compounds by polyamide nanofiltration and reverse osmosis membranes, J. Membr. Sci. 342 (2009) 251–262.
- [17] M. Ribau Teixeira, M. João Rosa, The impact of the water background inorganic matrix on the natural organic matter removal by nanofiltration, J. Membr. Sci. 279 (2006) 513–520.
- [18] C. Bellona, J.E. Drewes, X. Pei, G. Amy, Factors affecting the rejection of organic solutes during NF/RO treatment—a literature review, Water Res. 38 (2004) 2795–2809.
  [19] K.O. Agenson, T. Urase, Change in membrane performance
- [19] K.O. Agenson, T. Urase, Change in membrane performance due to organic fouling in nanofiltration (NF)/reverse osmosis (RO) applications, Sep. Purif. Technol. 55 (2007) 147–156.
- [20] A.M. Comerton, R.C. Andrews, D.M. Bagley, P. Yang, Membrane adsorption of endocrine disrupting compounds and pharmaceutically active compounds, J. Membr. Sci. 303 (2007) 267–277.
- [21] K. Kimura, S. Toshima, G. Amy, Y. Watanabe, Rejection of neutral endocrine disrupting compounds (EDCs) and pharmaceutical active compounds (PhACs) by RO membranes, J. Membr. Sci. 245 (2004) 71–78.
- [22] M. Clara, B. Strenn, O. Gans, E. Martinez, N. Kreuzinger, H. Kroiss, Removal of selected pharmaceuticals, fragrances and endocrine disrupting compounds in a membrane bioreactor and conventional wastewater treatment plants, Water Res. 39 (2005) 4797–4807.

- [23] J.B. Ellis, Pharmaceutical and personal care products (PPCPs) in urban receiving waters, Environ. Pollut. 144 (2006) 184–189.
- [24] M.J. Gómez, M.J. Martínez Bueno, S. Lacorte, A.R. Fernández-Alba, A. Agüera, Pilot survey monitoring pharmaceuticals and related compounds in a sewage treatment plant located on the Mediterranean coast, Chemosphere 66 (2007) 993–1002.
- [25] J.T. Yu, E.J. Bouwer, M. Coelĥan, Occurrence and biodegradability studies of selected pharmaceuticals and personal care products in sewage effluent, Agric. Water Manag. 86 (2006) 72–80.
  [26] M. Carballa, F. Omil, T. Ternes, J.M. Lema, Fate of pharmaceutical
- [26] M. Carballa, F. Omil, T. Ternes, J.M. Lema, Fate of pharmaceutical and personal care products (PPCPs) during anaerobic digestion of sewage sludge, Water Res. 41 (2007) 2139–2150.
- [27] S. Singh, K.C. Khulbe, T. Matsuura, P. Ramamurthy, Membrane characterization by solute transport and atomic force microscopy, J. Membr. Sci. 142 (1998) 111–127.
- [28] E. Amy, Childress, Menachem Elimelech, effect of solution chemistry on the surface charge of polymeric reverse osmosis and nanofiltration membranes, J. Membr. Sci. 119 (1996) 253–268.
- [29] J.D. Chen, N. Wada, Edge profiles and dynamic contact angles of a spreading drop, J. Colloid Interface Sci. 148 (1992) 207–222.
- [30] V. Yangali-Quintanilla, A. Sadmani, M. McConville, M. Kennedy, G. Amy, A QSAR model for predicting rejection of emerging contaminants (pharmaceuticals, endocrine disruptors) by nanofiltration membranes, Water Res. 44 (2010) 373–384.

- [31] V. Yangali-Quintanilla, A. Sadmani, M. McConville, G. Amy, A QSAR (quantitative structure-activity relationship) approach for modelling and prediction of rejection of emerging contaminants by NF membranes, Desalin. Water Treat. 13 (2010) 149–155.
- [32] H.E. Keenan, A. Sakultantimetha, S. Bangkedphol, Environmental fate and partition co-efficient of oestrogenic compounds in sewage treatment process, Environ. Res. 106 (2008) 313–318.
- [33] M. Mänttäri, L. Puro, J. Nuortila-Jokinen, M. Nyström, Fouling effects of polysaccharides and humic acid in nanofiltration, J. Membr. Sci. 165 (2000) 1–17.
- [34] F. Liu, S. Teng, R. Song, S. Wang, Adsorption of methylene blue on anaerobic granular sludge: Effect of functional groups, Desalination 263 (2010) 11–17.
- [35] Š.K. Das, P. Ghosh, I. Ghosh, A.K. Guha, Adsorption of rhodamine B on *Rhizopus oryzae*: Role of functional groups and cell wall components, Colloids Surf. B 65 (2008) 30–34.
- [36] J. de Koning, D. Bixio, A. Karabelas, M. Salgot, A. SchÃĂfer, Characterisation and assessment of water treatment technologies for reuse, Desalination 218 (2008) 92–104.
- [37] F. Saravia, F.H. Frimmel, Role of NOM in the performance of adsorption-membrane hybrid systems applied for the removal of pharmaceuticals, Desalination 224 (2008) 168–171.