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Factors governing the rejection of trace organic contaminants by nanofiltration and reverse osmosis membranes

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ABSTRACT

This study aimed to elucidate key factors governing the rejection of trace organic contaminants (TrOCs) by nanofiltration (NF) and reverse osmosis (RO) membranes. The rejection of 16 selected hydrophilic and hydrophobic TrOCs by an NF and an RO membranes was evaluated at different solution pH values using a cross-flow NF/RO filtration system. An analytical technique consisting of solid phase extraction followed by gas chromatography and mass spectrometry detection was used for the analysis of the TrOCs. In general, rejection increased in the order of decreasing membrane permeability, increasing molecular weight (or equivalent molecular width) of the TrOCs, and increasing hydrophilicity. Adsorption of hydrophobic TrOCs to the membrane could be observed based on a mass balance calculation. However, the correlation between adsorption and log D value (the logarithm of the octanol-water distribution coefficient) of the TrOCs (which indicates their hydrophobicity) observed in this study was rather weak. This is due to the adsorption being not only dependent on hydrophobicity, but also on other physicochemical aspects of TrOCs and the membrane material, such as molecular size, charge of the compounds, pore size, charge, and surface roughness properties of the membranes. Therefore, the results suggest that these factors may also govern the adsorption (and subsequently rejection) of TrOCs to NF/RO membranes.

Keywords: Trace organic contaminants; Nanofiltration; Reverse osmosis; Rejection mechanisms; Adsorption

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1. Introduction

Over the last 100 years, many synthetic chemicals have been developed and used for different purposes in industry, agriculture, medicine, and science. The use of these compounds has brought about many significant social and economic benefits such as various medical breakthroughs and an increase in agricultural crop yields. However, a number of these synthetic

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compounds have been released into the environment due to their widespread use [1]. As a result, different classes of trace organic contaminants (TrOCs) including endocrine-disrupting chemicals (EDCs), pharmaceutically active compounds (PhACs), disinfection by products (DBPs), and personal care products have been found in leachate from landfill sites, groundwater, surface water, drinking water treatment plants, and wastewater treatment plants effluents [2–4]. More recently, the occurrence at trace levels (usually at μg/L or ng/L levels) of these organic contaminants in different water resources has attracted the attention of both scientific and regulatory communities. Several of these compounds are suspected carcinogens, while others have estrogenic properties with the potential to adversely affect the endocrine system of biota [5,6]. Therefore, the removal of these organic contaminants in water treatment processes is a high priority. As part of the approach to solve this problem, advanced treatment technologies are an essential component for the removal of micropollutants in drinking water treatment and water reclamation processes [7]. In particular, nanofiltration (NF) and reverse osmosis (RO) membrane filtration processes have demonstrated promising results and are an attractive technology for the rejection removal of EDCs, PhACs, and DBPs from the aquatic environment because of its high rejection efficiency for most of these contaminants in water and wastewater, which can be achieved without the addition of other chemicals [8,9]. In recent years, there has been widespread application of NF and RO for the effective rejection of TrOCs in the treatment of municipal wastewater and other water sources [10,11].

The rejection of TrOCs by NF and RO membranes can be governed by several mechanisms. These include size exclusion, adsorption onto the membrane surface, diffusion across the membrane, and electrostatic interaction [12,13]. In addition, there are a number of factors that may influence their rejection including the physicochemical properties of the compounds, characteristics of the membrane, operating conditions, and feedwater composition [13,14]. In particular, the feed solution pH can be considered as one of the most important parameters influencing the hydrophobicity, the adsorption, and the chemical speciation of dissociable organic compounds as well as the membrane surface charge during the experiment. Therefore, pH is expected to affect the effective rejection of organic compounds [15,16]. In a major study of the rejection of estrone using NF and RO membranes, Schäfer et al. [15] concluded that adsorption is the major mechanism for estrone rejection at the initial stages of filtration and that rejection of estrone was considerable affected by solution pH above its pK_a value. A number of previous studies had found that hydrophobic TrOCs were strongly adsorbed to the membrane over a relatively long period of time. At the initial stages of filtration, the overriding rejection mechanism for these compounds was adsorption. When the adsorption of compounds onto the membrane had reached equilibrium, size exclusion would then become the dominant rejection mechanism [17,18]. Moreover, Braeken et al. [19] and Arsuaga et al. [20] observed a decrease in rejection with increasing compound hydrophobicity due to adsorption onto the membranes during filtration. Additionally, Nghiem et al. [8,21] found that the solution pH affected the hydrophobicity and net charge of selected PhACs and that this influenced their adsorption and rejection throughout the experiment by NF membranes. Furthermore, Boussu et al. [22] argued that charged TrOCs were better rejected at pH 10 than at pH 3. More recently, Schäfer et al. [23] reported that rejection of estradiol at pH 11 stabilized at 85%, while at pH 7 rejection was only 60%. This was attributed to the occurrence of charge repulsion between the negatively charged NF and RO membranes and the negatively charged estradiol, leading to greater rejection at pH 11 compared to pH 7. In another investigation, Verliefde et al. [12] suggested that rejection of negatively charged and neutral pharmaceuticals under different pH conditions in surface water using NF membranes was relatively high (>75%), with rejection of negatively charged pharmaceuticals being typically higher. These results could again be attributed to the electrostatic interactions between these organic compounds and charged membranes. Although these recent studies have explored the removal of TrOCs by NF and RO membranes and underlying mechanisms under different pH conditions, the current understanding of the rejection of these compounds remains rather limited. Moreover, among the various rejection mechanisms, the influence of adsorption of organic compounds onto the NF and RO membranes is still difficult to quantify. Therefore, a complete understanding of the adsorption mechanism of trace organics onto NF and RO membranes as well as the effective rejection of these compounds in treatment processing is still a challenging issue and requires further study.

The objectives of the current work are to study the adsorption of the selected TrOCs onto the NF270 and ESPA2 membranes at different pH values (4.7, 7, and 11) and evaluate their effective rejection. Experiments were conducted using a laboratory scale cross-flow NF/RO cell membrane filtration system with 16 selected hydrophilic and hydrophobic TrOCs. These compounds have a wide range of physicochemical properties and represent major classes of contaminants. The results enable the evaluation of the role of adsorption on rejection performance of trace organic compounds during NF and RO separation.

2. Materials and methods

2.1. NF and RO membranes

A loose NF membrane NF270 and a low pressure RO membrane ESPA2 were selected for this investigation. The NF270 membrane was supplied by Dow-Filmtec (Minneapolis, MN), and the ESPA2 membrane was purchased from Hydranautics (Oceanside, CA). According to the manufacturers, they are thin-film composite polyamide membranes with a high flux at low pressure and have been widely used in water and wastewater treatment processes. In addition, the application of these membranes to TrOCs rejection has been investigated by many researchers over recent years. The flat sheet membrane samples were stored dry.

The main characteristics of NF270 and ESPA2 membranes have been previously described in the literature. NF270 membranes have a relatively smooth surface, reflected by its relatively low roughness value (8.55 nm) [24], whereas the ESPA2 membrane exhibited large-scale surface roughness (80.22 nm) [25]. Another parameter frequently used to estimate TrOC rejection is the pore size. According to Alturki et al. [26], the average pore diameter of the NF270 membrane is 0.84, nm while the ESPA2 membrane may be assumed to have no pores at all. On the other hand, it is interesting to note that the zeta potential characterization could provide a qualitative insight into the charge properties of the membrane active layer. According to Nghiem et al. [8] and Li et al. [25], the isoelectric point values of the NF270 and ESPA2 membranes are around pH 3.5 and pH 4, respectively. They are consequently net positively charged when the pH of the solution is lower than this isoelectric point value, and are negatively charged when pH is higher. Therefore, both these membranes are negatively charged at all pH values used in the current study. These properties would be expected to significantly affect adsorption and rejection of several TrOCs during the experiment. These will be explained and discussed in detail in the Sections 3.2 and 3.3.

2.2. TrOCs, analytical chemicals and reagents

The target TrOCs, for this research have been chosen from the major classes of EDCs, PhACs and DBPs. They have diverse physicochemical properties such as hydrophobicity, charge, solubility, and molecular size. A stock solution was prepared at a concentration of 1 mg/mL in pure methanol. A working solution of these TrOCs was also prepared in pure methanol. Both these solutions were stored in a freezer at −18°C prior to use.

Chemical solutions and feedwaters were prepared with Milli-Q water. Both the solvents used for solid-phase extraction (SPE) and analysis of samples, including methanol and dichloromethane, were purchased from Sigma-Aldrich (Sydney, Australia). Internal standard of bisphenol A-d_{16} and N,O-bis (trimethylsilyl) trifluoroacetamide (BSTFA) containing 1% of trimethylchlorosilane (TMCS). Pyridine is used in the derivatization process. All reagents and chemicals were purchased from Sigma-Aldrich (Sydney, Australia).

2.3. Cross-flow NF/RO membrane filtration system

A cross-flow membrane filtration system was used in this study (Fig. 1). The system consisted of a stainless steel NF/RO membrane cell with an effective surface area of 40 cm^2 (4 cm × 10 cm) with a channel height of 2 mm, and a stainless steel feed reservoir of 10 L. A Hydra-Cell pump (Wanner Engineering Inc., Minneapolis, MN) capable of providing a maximum pressure of 6,800 kPa and a flow rate of 4.2 L/min was used. The temperature of the experimental solution was controlled by a chiller/heater (Neslab RTE 7) equipped with a stainless steel heat exchanger coil submersed in a stainless steel feed reservoir. A digital flow meter (Optiflow 1,000; Agilent Technologies, Palo Alto, CA) connected to a PC was utilized to measure permeate flow, and the crossflow was monitored with a manual flow meter.

2.4. Experimental protocol

All experiments were performed in background buffer solutions under three different pH conditions (pH 4.7, 7, and 11) and conducted over 24 h. Before use, all the membrane samples were rinsed with tap water and Milli-Q water to remove any preservative layer. Subsequently, they were compacted using Milli-Q water at 1,000 kPa for the NF270 membrane and 1,800 kPa in the case of the ESPA2 membrane for at least one hour until a stable permeate flux has been obtained. The background buffer solution was then added to the feed reservoir and made up to the total feed volume of 10 L. For the experiment at pH 4.7, an acetate buffer solution containing 1 mM of $CaCl_2$, 5.5 mM of CH_3COOH, and 5.5 mM of CH_3COONa was

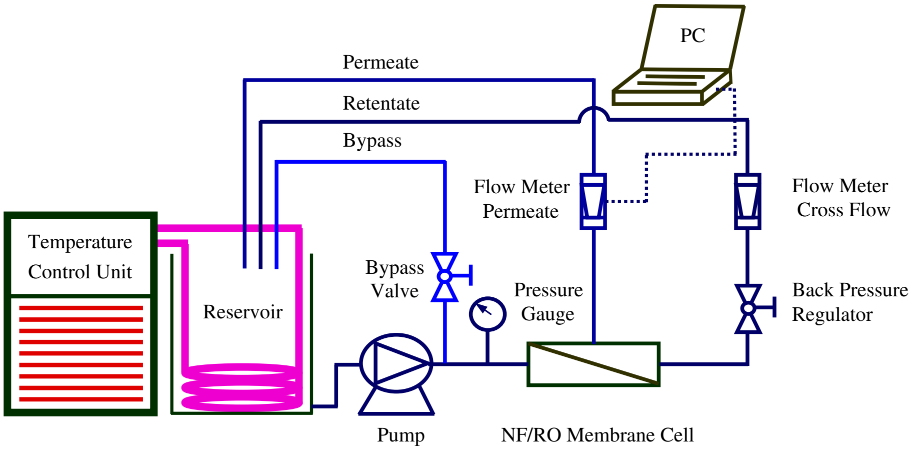

Fig. 1. Schematic diagram of the NF/RO filtration system.

utilized. A phosphate buffer solution containing10 mM of NaCl, 1 mM of $CaCl_2$, and 1 mM of NaH_2PO_4 was used for the experiment at pH 7. The pH 11 experiment was conducted in a carbonate buffer solution, which contained 0.2 mM of NaCl, 0.3 mM of $NaHCO_3$, and 4.5 mM of Na_2CO_3. During the experiment, the feed reservoir temperature and cross-flow velocity were kept constant at 20 ± 0.1˚C and 42 cm/s, respectively. The permeate flux was set to the manufacturer's quoted nominal membrane flux of 42 L/m^{2}h throughout the experiment. Both permeate and retentate were recirculated to the feed reservoir. A mixture of 16 selected trace organics was then added to the feed reservoir to obtain a concentration of 25 µg/L of each. To maintain the feed solution pH during the experiment, a certain amount of 0.2 M of CH_3COOH, 1 M of NaOH, and 1 M of Na_2CO_3 was added to adjust the solution pH for the experiment at pH 4.7, pH 7, and pH 11, respectively. Approximately, 100 mL of feed and permeate samples were taken at specific times. Samples were stored in clean glass bottles, wrapped in aluminum foil, and stored in the fridge for subsequent extraction and GC/MS analysis.

The effective rejection was defined as R (%): $R = 100 \times (1 - \frac{C_p}{C_f})$, Where C_f and C_p were the feed and the permeate concentrations, respectively.

Adsorption of TrOCs (A, %) onto the membranes at the end of filtration stage was determined by mass balance: $A = 100 \times (1 - \frac{C_{f2}}{C_{f1}})$, Where C_{f1} and C_{f2} were the initial and final organic compound concentration in the feed solution, respectively.

2.5. Analytical methods

The Oasis HLB SPE cartridges (6 mL, 200 mg, Waters, Milford, MA, USA) for extraction of the TrOCs in feed and permeate samples were used in this investigation. The feed and permeate samples of 100 mL were allowed to reach room temperature and adjusted by 4 M sulfuric acid to pH range between 2 and 3. Before the samples were extracted, the SPE cartridges were conditioned sequentially by 7 mL dichloromethane and methanol (1:1, v/v), 7 mL methanol, and about 2 × 7 mL reagent water on a vacuum manifold at a flow rate of 2 mL/min. Subsequently, the samples were passed through the cartridges with a flow rate of 2 mL/min. The loaded cartridges were washed with 6 × 7 mL of Milli-Q water and dried under vacuum for 30 min along with a stream of nitrogen. The SPE columns containing the TrOCs were eluted with 7 mL methanol followed by 7 mL dichloromethane and methanol (1:1, v/v) at a flow rate of 1–5 mL/min. The elution volume was then evaporated to dryness under a gentle stream of nitrogen in a water bath at 40˚C. An amount of 200 µL methanol solution containing 5 µg bisphenol A-d_{16} was utilized to dissolve the extracted residues and was transferred into 1.5 mL vials before further evaporation to dryness under a gentle nitrogen stream. Finally, the derivatization of the dried residues in the vials was performed by adding 100 µL of BSTFA (N,O-bis (trimethylsilyl) trifluoroacetamide) (1% TMCS) and 100 µL of pyridine (dried with KOH solid). The conditions of the derivatization reaction were 30 min at 60–70˚C. The derivatives were allowed to cool to room temperature before analysis by GC-MS [27].

A Shimadzu GCMS-QP5000 system consisting of a Shimadzu AOC 20i autosampler and a Phenomenex Zebron ZB-5 (5% diphenyl–95% dimethylpolysiloxane) capillary column (30 m × 0.25 mm ID, df = 0.25 µm) was used to determine the concentrations of the organic compounds. Helium was used as the carrier gas at a constant flow rate of 1.3 mL/min. The GC oven temperature program was conducted as follows: 100°C for 1 min, first ramp 10°C/min to 175°C, 3 min at 175°C, second ramp 30–210°C, third ramp 2°C/min to 228°C, fourth ramp 30–260°C, fifth ramp 3°C/min to 290°C, 3 min at 290°C. The injector port and the temperature of the GCMS interface were set at 280°C. A sample volume of 1 μL was injected in splitless mode.

The MS was obtained by electron impact ionization in full-scan mode from 50 to 600 of m/z, and later on in selected ion monitoring mode for qualitative determinations. The most abundant ions of each organic compound were selected from its spectrum for quantification, in accordance with previous studies [28,29]. A series of standard TrOCs at 1, 10, 50, 100, 500, and 1,000 ng/mL and a bisphenol A-d_{16} internal standard were prepared for the instrument calibration. The calibration curves obtained for each compound had correlation coefficients greater than 0.99. The detection limits and quantification limits for analytes were estimated with the signal-to-noise (s/n) ratio higher than 3 and higher than 10, respectively.

A Metrohm model 744 pH Meter was calibrated before beginning of an experiment and utilized to measure the feed solution pH for the duration of the experiment.

3. Results and discussion

3.1. Properties of TrOCs

The major physicochemical properties of the target organic contaminants are shown in Table 1. The compounds selected for this investigation exhibited considerable difference in their physicochemical properties. These compounds have low molecular weight, ranging between 138.12 and 314.42 g/mol for salicylic acid and 17β-estradiol acetate, respectively. However, they are markedly different in their dissociation constants (pK_a) and hydrophobicity properties. Most TrOCs are weak acids and will dissociate into an ionic form at pH above the pK_a. Based on the pK_a values of the selected organic compounds listed in Table 1, it can be seen that carbamazepine is uncharged and exists in a neutral form at all pH conditions of the experiment, whereas salicylic acid, diclofenac, ibuprofen, and pentachlorophenol are mostly deprotonated, resulting in negative charge. At pH 4.7, all the other organic contaminants are uncharged and exist mostly as a neutral species. When the experiments are performed at pH 7, gemfibrozil has a net negative charge, whereas the other TrOCs are uncharged. At pH 11, carbamazepine is uncharged, while all the other organic compounds are negatively charged.

The intrinsic hydrophobicity of TrOCs is a key factor governing their adsorption onto the membrane surface and their rejection by the NF/RO process [23,30]. The hydrophobicity of TrOCs is often expressed as the logarithm of the octanol-water distribution coefficient, log *D* or the logarithm of the octanol-water partition coefficient, log K_{ow}. However, log *D* appears to be a better hydrophobicity indicator than log K_{ow} and can be used to evaluate the hydrophobicity of TrOCs at any pH value [26,31,32]. This is because TrOCs often contain basic or acidic groups. They can, thus, exist in a neutral form or charged species (ionised) depending on the solution pH. For ionizable solutes, the hydrophobicity is dependent on the percentage of uncharged versus charged species, and thus it depends strongly on pH. Log K_{ow} is defined only for neutral solutes and describe the partitioning of the neutral form between the aqueous and organic (hydrophobic) phases. Since log *D* is defined for all neutral and charged compounds, it reflects the true hydrophobicity behavior of an ionizable compound in a solution at a given pH value or range. Log *D* can be calculated from the pK_a and log K_{ow} of TrOCs, and thus, it is accepted as one of the principal parameters to evaluate hydrophobicity of TrOCs at any pH value [14,33]. According to Wells [32] and Alturki et al. [26], TrOCs with log *D* equal to 3 or higher are generally referred to as hydrophobic. TrOCs with log *D* below 3 are referred to as hydrophilic. At pH 4.7, some of the TrOCs examined here are hydrophobic due to their high log *D* values (ranged between 3.03 and 6.14 for ibuprofen and 4-n-nonylphenol, respectively). Data in Table 1 indicate that the log *D* of salicylic acid, ibuprofen, gemfibrozil, diclofenac, pentachlorophenol, and triclosan decreases, while the log *D* of other compounds do not change as the pH increases from 4.7 to 7. However, when the pH increases to 11, except for carbamazepine, the log *D* value of all other TrOCs decreases, leading to a variation in their hydrophobicity behavior. By contrast, there are only three TrOCs in which at hydrophilic as reflected by their log *D* being lower than 3, varying from 0.31 to 2.53, namely salicylic acid, carbamazepine, and estriol. At pH 11, however, there are only still five target compounds with hydrophobic properties: 17α-ethinylestradiol, 17β-estradiol, 4-tert-octylphenol, 17β-estradiol acetate, and 4-n-nonylphenol with their log *D* values vary from 3.28 to 5.23, while numerous other compounds are hydrophilic. At pH 7, the number of target compounds with hydrophilic and hydrophobic properties is nearly equivalent. The changes in hydrophobicity and other physicochemical properties of the

Table 1
Physicochemical properties of the selected TrOCs

Organic compounds	CAS number	Molecular formula	Molecular weight (MW) (g/mol)	Log K_{ow}[a]	pK_a[a]	Log D[b]			Molecular dimension (nm)[c]		
						pH 4.7	pH 7	pH 11	Length	Width	Height
Salicylic acid	69-72-7	$C_7H_6O_3$	138.12	2.011	3.01	0.31	−1.13	−5.98	0.615	0.354	0.577
Ibuprofen	15687-27-1	$C_{13}H_{18}O_2$	206.28	3.502	4.41	3.03	0.94	−3.09	0.900	0.354	0.561
Gemfibrozil	25812-30-0	$C_{15}H_{22}O_3$	250.33	4.302	4.75	4.03	2.07	−1.95	0.972	0.354	0.670
Diclofenac	15307-86-5	$C_{14}H_{11}Cl_2NO_2$	296.15	4.548	4.18	3.91	1.77	−2.27	0.829	0.354	0.767
Carbamazepine	298-46-4	$C_{15}H_{12}N_2O$	236.27	1.895	13.94	1.89	1.89	1.89	0.818	0.354	0.676
Pentachlorophenol	87-86-5	C_6HCl_5O	266.34	5.115	4.68	4.80	2.85	−1.21	0.659	0.354	0.640
4-tert-butylphenol	98-54-4	$C_{10}H_{14}O$	150.22	3.397	10.13	3.40	3.40	2.47	0.735	0.354	0.505
4-tert-octylphenol	140-66-9	$C_{14}H_{22}O$	206.32	5.180	10.15	5.18	5.18	4.27	0.822	0.354	0.595
4-n-nonylphenol	104-40-5	$C_{15}H_{24}O$	220.35	6.142	10.15	6.14	6.14	5.23	1.179	0.354	0.519
Triclosan	3380-34-5	$C_{12}H_7Cl_3O_2$	289.54	5.343	7.80	5.34	5.28	2.14	0.926	0.354	0.602
Bisphenol A	80-05-7	$C_{15}H_{16}O_2$	228.29	3.641	10.29	3.64	3.64	2.85	0.876	0.354	0.570
Estrone (E1)	53-16-7	$C_{18}H_{22}O_2$	270.37	3.624	10.25	3.62	3.62	2.80	0.697	0.340	0.693
17β-estradiol (E2)	50-28-2	$C_{18}H_{24}O_2$	272.38	4.146	10.27	4.15	4.15	3.34	0.697	0.340	0.693
Estriol (E3)	50-27-1	$C_{18}H_{24}O_3$	288.38	2.527	10.25	2.53	2.53	1.71	0.751	0.340	0.693
17α-ethinylestradiol (EE2)	57-63-6	$C_{20}H_{24}O_2$	296.40	4.106	10.24	4.11	4.11	3.28	0.788	0.356	0.693
17β-estradiol acetate (E2Ac)	1743-60-8	$C_{20}H_{26}O_3$	314.42	5.111	10.26	5.11	5.11	4.30	0.947	0.354	0.842

[a] Scifinder Scholar, [b] calculated by the equation: $\log D_{(pH)} = \log K_{ow} - \log\left(1 + 10^{(pH - pK_a)}\right)$, [c] calculated using Molecular Modeling Pro^{TM} Plus software.

compound at different pH values may have significant implications for the rejection mechanisms of these TrOCs.

3.2. Rejection of trace organics by NF/RO membranes

The difference in rejection efficiency of neutral and negatively charged TrOCs after 24 h of filtration using the NF270 and ESPA2 membranes at three pH values of pH 4.7, 7, and 11 is illustrated in Figs. 2 and 3. In most cases, the rejection efficiency of the TrOCs by the ESPA2 membrane was considerably higher than the NF270 membrane. These rejection values were up to 98% at pH 4.7 and were up to 100% at both the pH 7 and pH 11 for the ESPA2 membrane, while the corresponding maximum values for the NF270 membrane were 86, 98, and 99% at pH 4.7, pH 7, and pH 11, respectively. These could be due to the NF270 membrane having larger pore size than the ESPA2 membrane. Because of the very small pore size of the ESPA2 membrane, TrOCs do not significantly penetrate into the membrane pores, resulting in their adsorption occurring mainly at the membrane surface. Consequently, the diffusion of these compounds across the membrane was very limited, leading to the high rejection efficiencies observed. Consistent with these findings, William et al. [34] and Nghiem and Schäfer [35] observed that because of the narrow pores of RO membranes, hydraulic resistance reduced the penetration of trace organics, and adsorption could only occur at the surface of the membranes, resulting in a higher rejection. In addition, better rejection of TrOCs by RO compared to NF membranes has been reported in the literature [36,37].

In general, rejection values for most negatively charged compounds were higher than the rejection values for neutral compounds at all experimental pH conditions for the two membranes. This is explained by the electrostatic repulsion mechanism. Negatively charged TrOCs exhibit a lower concentration at the membrane surface due to the charge repulsion, leading to a higher rejection, whereas for neutral TrOCs, no charge interactions with the membrane surface exist. In most investigations on electrostatic interactions, it was already reported that there is an increase in rejection of negatively charged compounds compared with neutral compounds by NF and RO membranes due to electrostatic repulsion between the negatively charged solute and the negatively charged membrane [12,21]. It is, however, noteworthy that some hydrophobic neutral and hydrophobic negatively charged compounds with a high log *D* value showed lower rejections. Indeed, as illustrated by Figs. 2 and 3 for NF270 membrane, rejection of hydrophobic neutral compounds such as 4-tert-butylphenol, bisphenol A, 4-tert-octylphenol, and triclosan were observed to be relatively low (below 50%) at pH 4.7. At pH 7, rejection efficiencies of bisphenol A, 4-tert-octylphenol, and 4-n-nonylphenol were approximately 37, 59, and 47%, respectively. Similarly, for hydrophobic negatively charged species such as ibuprofen and pentachlorophenol, their rejection efficiency was only about 3 and 0%, respectively, at pH 4.7. Lower rejection efficiency for several hydrophobic neutral and hydrophobic negatively charged compounds also occurred with the ESPA2 membrane, namely 4-tert-butylphenol and 4-n-nonylphenol were only rejected approximately of 58 and 36%, respectively, at pH 7. At pH 11, 4-n-nonylphenol was rejected approximately of 53%. These phenomena can be attributed to the dominance of adsorption as a rejection mechanism. Hydrophobic TrOCs adsorbed onto the membranes, resulting in an increase partitioning of these compounds into the membranes and therefore a rise in transport through the membranes, resulting in a reduced rejection. Kimura

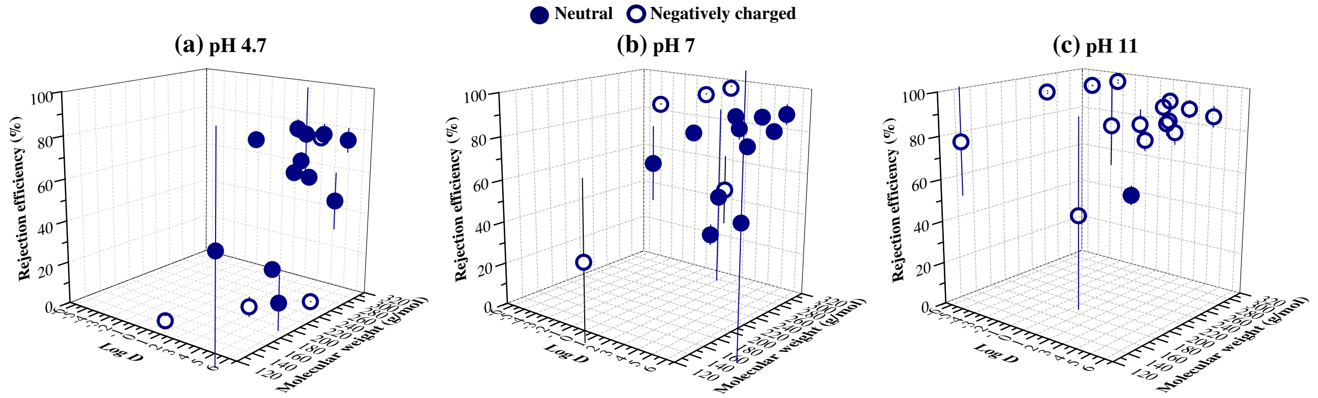

Fig. 2. Correlation between rejection efficiency after 24 h of filtration, log *D*, and molecular weight of TrOCs by the NF270 membrane at pH 4.7, pH 7, and pH 11.

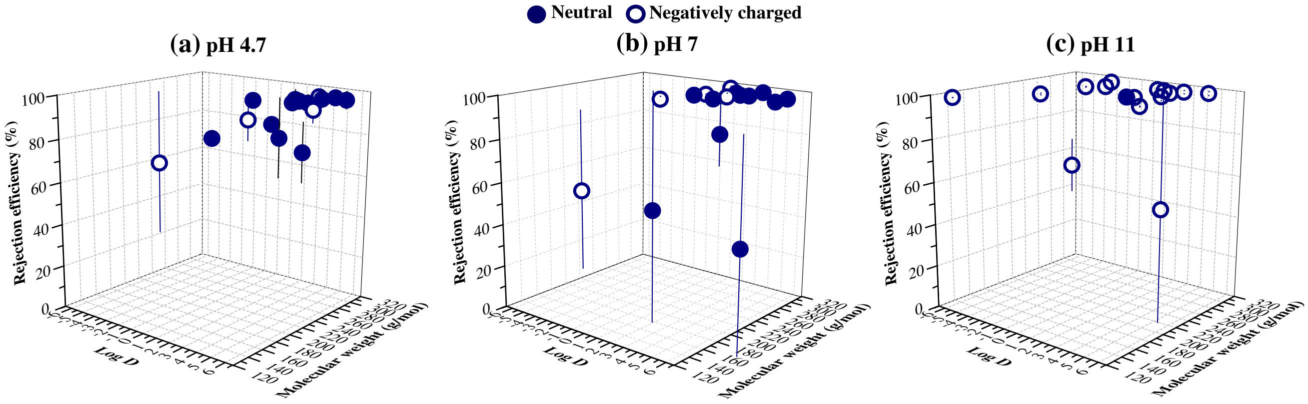

Fig. 3. Correlation between rejection efficiency after 24 h of filtration, log *D*, and molecular weight of TrOCs by the ESPA2 membrane at pH 4.7, pH 7, and pH 11.

et al. [38] and Hu et al. [7] concluded the same from their study.

Findings in this study also showed that there was a good correlation between rejection of hydrophilic neutral and hydrophilic negatively charged compounds with their molecular weight for both the NF270 and ESPA2 membranes at all pH conditions used. Generally, larger molecular weight compounds have higher rejection than small molecular weight compounds on size exclusion grounds. These results confirmed the observations of Yangali-Quintanilla and coworker [39,40], who also demonstrated that there was a strong correlation between molecular weight and the rejection for hydrophilic compounds. Conversely, for hydrophobic neutral and hydrophobic negatively charged compounds, there was little or no correlation between their rejections with molecular weight. This can be attributed to mainly adsorption and electrostatic repulsion at high pH. This is in agreement with previous studies [14,41]. Adsorption mechanism of hydrophilic and hydrophobic TrOCs onto NF and RO membranes will be discussed in detail in the following section.

3.3. Adsorption of trace organics to NF/RO membranes

Adsorption levels of both hydrophilic and hydrophobic organic compounds illustrated in Figs. 4 and 5 are listed in order of increasing log *D*. It can be observed that at all pH conditions for both the NF270 and ESPA2 membranes, most of the hydrophobic TrOCs significantly adsorbed onto the membranes after 24 h of filtration, while the hydrophilic organic compounds exhibited much lower and more variable adsorption levels. They adsorbed much less compared to hydrophobic species and many compounds did not adsorb onto the membrane at all pH conditions used. For example, except for some specific hydrophobic and hydrophilic compounds, adsorption levels of hydrophobic compounds approximately ranged from 14 to 94% for the NF270 membrane and from 79 to 94% in the case of the ESPA2 membrane at the pH 7. The corresponding values for hydrophilic compounds were approximately in the range of 0–32% for the NF270 membrane and in the range of 0–12% in the case of the ESPA2 membrane. These study results could be explained by the specific interactions between the TrOCs and membranes surface. The hydrophobic TrOCs showed significant affinity with the membranes, leading to an increased partitioning and a facilitated transport of them onto the membranes, resulting in their strong adsorption onto these membranes. In contrast, hydrophilic TrOCs have a lower affinity for the membranes, displayed by their relatively low log *D* values (<3). As a result, they were adsorbed less compared to more hydrophobic species and many compounds did not adsorb to the membrane at the end of filtration stage at all pH conditions. These results were in general agreement with numerous previous studies [15,21,22,42].

However, it was somewhat surprising that there was no linear correlation between adsorption and log *D* of organic compounds as can be seen from the correlation coefficient values of R^2 in Figs. 4 and 5. Several specific hydrophobic compounds showed lower adsorption levels, whereas higher adsorption levels of several hydrophilic compounds were also found in this investigation. In fact, the adsorption of several hydrophobic organics onto the NF270 membrane was observed to be lower than expected or showed no adsorption at all based on their log *D* value alone, namely 17β-estradiol (0%) and 17α-ethinylestradiol (approximately 2%) at pH 11. This trend was also similar to the adsorption of some hydrophobic compounds onto the ESPA2 membrane at this pH

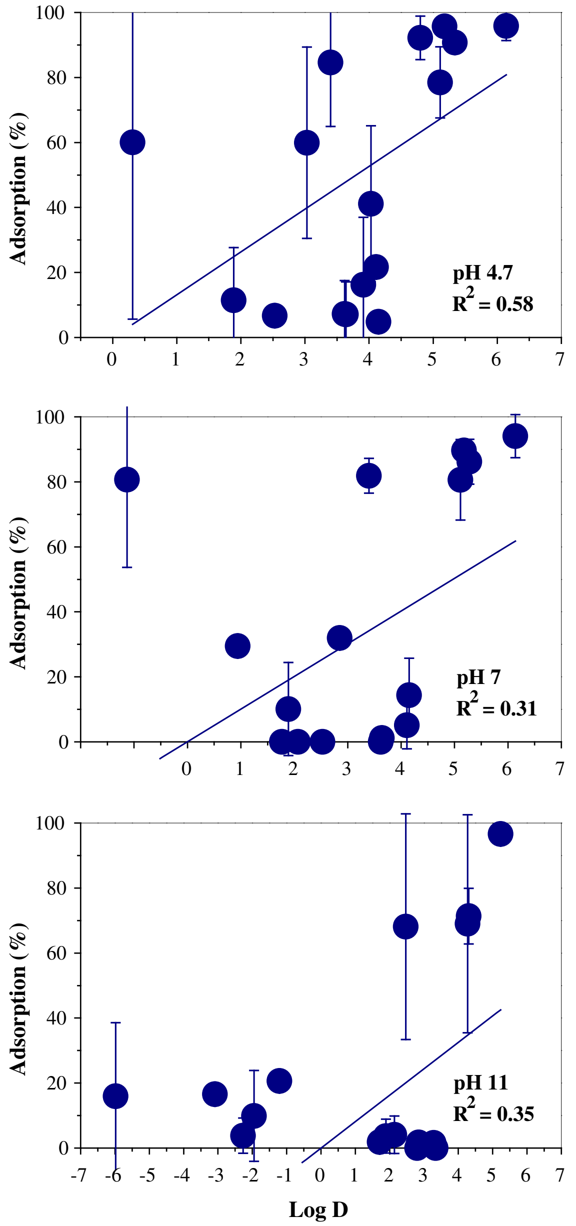

Fig. 4. Adsorption of TrOCs to the NF270 membrane as a function of log *D*.

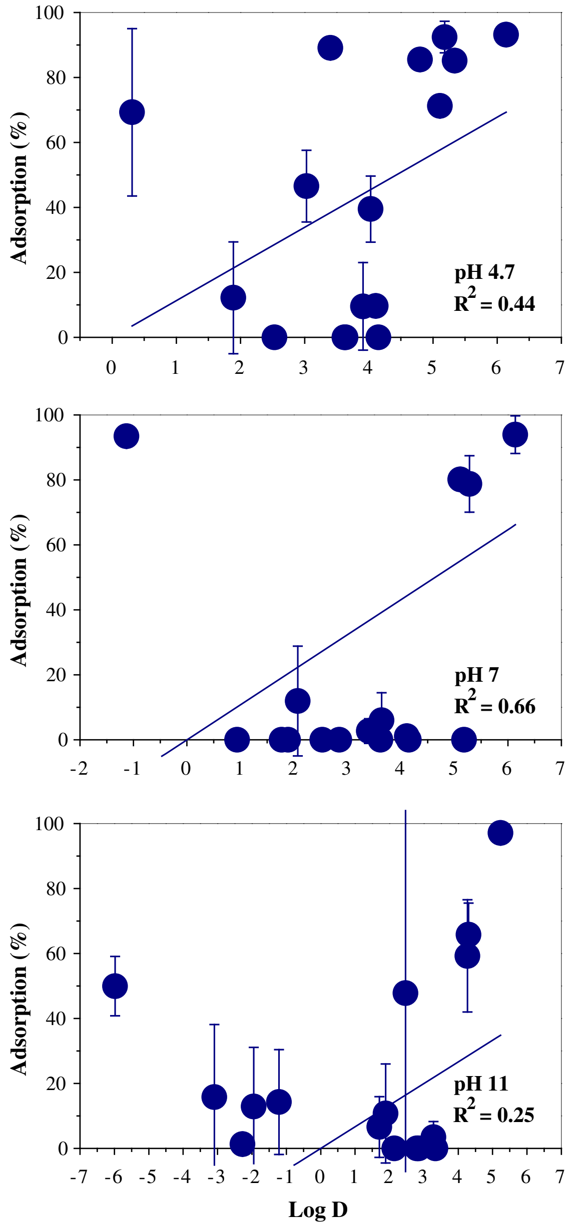

Fig. 5. Adsorption of TrOCs to the ESPA2 membrane as a function of log *D*.

(e.g. 17β-estradiol (0%) and 17α-ethinylestradiol (about 3%)). These findings can be supported by the studies of Boussu et al. [22], who also reported that some exceptions exist where several specific hydrophobic TrOCs did not adsorb inappreciably onto NF and RO membranes. In addition, further reason for this is that at the pH 11 all these compounds exhibited a net negative charge. Therefore, charge repulsion between the negatively charged compounds and the negatively charged membranes was expected to occur, and this may be one of the reasons for the decreased adsorption of almost organic compounds under strong basic pH. These observations have been reported in several previous investigations [15,43].

In addition, for some specific hydrophilic compounds, particularly salicylic acid, there was quite strong adsorption onto both the NF270 and ESPA2 membranes after 24 h of filtration at all pH used. Its adsorption was approximately 60, 81, and 16% at pH 4.7, pH 7, and pH 11, respectively, for the NF270 membrane. For the ESPA2 membrane, these values were approximately 69, 94, and 50% at pH 4.7, pH 7, and pH 11, respectively. This phenomenon can be explained through other factors that can further impact the adsorption capacity. Indeed, surveys conducted by Comerton et al. [18] have shown that TrOCs adsorption was also related to the membrane pore size. Membranes with larger pore sizes allowed organic compound to access their internal adsorption sites, support layer and pore in addition to their surface, whereas access to these internal sites might be limited with tighter membranes. Hence, the average pore diameter of the NF270 membrane was markedly larger than molecular dimension of salicylic acid, which might allow more salicylic acid adsorption onto the membrane surface and within its structure. Apart from these, it is important to note that the ESPA2 membrane exhibited considerable surface roughness [25]. In general, a rough membrane surface morphology would result in more adsorption of TrOCs on the membrane due to the larger surface area, leading to more opportunities for molecular contact [18,44]. Therefore, salicylic acid showed considerable adsorption to both these membranes at all pH conditions used.

4. Conclusions

From the results obtained using the selected compounds, at the pH conditions used, the rejection efficiency of most TrOCs was higher for the ESPA2 membrane than for NF270 membrane. This can be attributed to the fact that the pore size of the ESPA2 membrane is smaller than that of the NF270 membrane, and adsorption can only occur at the surface of the active layer. Among these compounds, many negatively charged compounds showed better rejection efficiencies compared to neutral compounds for both the membranes, due to electrostatic repulsion between solute and membrane. For negatively charged organic compounds, charge repulsion leads to a decrease in solute concentration at the negatively charged membrane surface, and consequently to a higher rejection. However, rejection of some hydrophobic neutral and hydrophobic negatively charged compounds with high log *D* value was observed to be relatively low. This can be due to the adsorption and diffusion of these compounds across membranes. Data in this study also clearly demonstrated that size exclusion might be a major rejection mechanism for hydrophilic compounds as shown by the significant correlation between rejection of these compounds with their molecular weight. There was no strong correlation between the rejection of hydrophobic compounds with their molecular weight. Rejection of these compounds, therefore, could be attributed to the importance of electrostatic repulsion at high pH in addition to the effect of adsorption.

Results reported here also show that the adsorption of many hydrophilic and hydrophobic TrOCs onto the membranes could be predicted based on their hydrophobicity, expressed as log *D*. For TrOCs with higher hydrophobicity as reflected by quite high log *D* values, their adsorption onto membranes after 24 h of filtration was quite significant. However, there was no correlation between adsorption and log *D* of these organic compounds. Especially for some hydrophilic and hydrophobic compounds, log *D* was not always the best tool to model their adsorption levels onto the membranes with time. Therefore, findings in this study has been suggested that other parameters, namely molecular size of compounds, charge repulsion between the negatively charged membranes and the negatively charged compounds as well as surface roughness properties, and pore size of the membranes also had a considerable influence on the adsorption of TrOCs to the membranes.

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References

[1] M. Williams, M. Woods, A. Kumar, G.G. Ying, A. Shareef, M. Karkkainen, R. Kookana, Endocrine Disrupting Chemicals in the Australian Riverine Environment: A Pilot Study on Estrogenic Compounds, Land & Water Australia, Canberra, 2007.

[2] N. Bolong, A.F. Ismail, M.R. Salim, T. Matsuura, A review of the effects of emerging contaminants in wastewater and options for their removal, Desalination 239 (2009) 229–246.

[3] Z.H. Li, T. Randak, Residual pharmaceutically active compounds (PhACs) in aquatic environment–status, toxicity and kinetics: A review, Vet. Med. (Praha) 52 (2009) 295–314.

[4] T. Sirivedhin, K.A. Gray, Comparison of the disinfection by-product formation potentials between a wastewater effluent and surface waters, Water Res. 39 (2005) 1025–1036.

[5] A.M. Comerton, R.C. Andrews, D.M. Bagley, C. Hao, The rejection of endocrine disrupting and pharmaceutically active compounds by NF and RO membranes as a function of compound and water matrix properties, J. Membr. Sci. 313 (2008) 323–335.

[6] C. Rodriguez, P.V. Buynder, R. Lugg, P. Blair, B. Devine, A. Cook, P. Weinstein, Indirect potable reuse: A sustainable water supply alternative, Int. J. Environ. Res. Publ. Health 6 (2009) 1174–1209.

[7] J.Y. Hu, X. Jin, S.L. Ong, Rejection of estrone by nanofiltration: Influence of solution chemistry, J. Membr. Sci. 302 (2007) 188–196.

[8] L.D. Nghiem, A.I. Schäfer, M. Elimelech, Pharmaceutical retention mechanisms by nanofiltration membranes, Environ. Sci. Technol. 39 (2005) 7698–7705.

[9] C. Sagne, C. Fargues, R. Lewandowski, M.L. Lameloise, M. Decloux, Screening of reverse osmosis membranes for the treatment and reuse of distillery condensates into alcoholic fermentation, Desalination 219 (2008) 335–347.

[10] T. Wintgens, T. Melin, A. Schäfer, S. Khan, M. Muston, D. Bixio, C. Thoeye, The role of membrane processes in municipal wastewater reclamation and reuse, Desalination 178 (2005) 1–11.

[11] X. Jin, J. Hu, S.L. Ong, Removal of natural hormone estrone from secondary effluents using nanofiltration and reverse osmosis, Water Res. 44 (2010) 638–648.

[12] A.R.D. Verliefde, E.R. Cornelissen, S.G.J. Heijman, J.Q.J.C. Verberk, G.L. Amy, B. Van der Bruggen, J.C. van Dijk, The role of electrostatic interactions on the rejection of organic solutes in aqueous solutions with nanofiltration, J. Membr. Sci. 322 (2008) 52–66.

[13] M.A. 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.

[14] A.R.D. Verliefde, E.R. Cornelissen, G.L. Amy, B. Van der Bruggen, J.C. van Dijk, Rejection of Organic Micropollutants by High Pressure Membranes (NF/RO), Water Management Academic Press, Netherlands, 2008.

[15] A.I. Schäfer, L.D. Nghiem, T.D. Waite, Removal of the natural hormone estrone from aqueous solutions using nanofiltration and reverse osmosis, Environ. Sci. Technol. 37 (2003) 182–188.

[16] C. Bellona, J.E. Drewes, P. Xu, G. Amy, Factors affecting the rejection of organic solutes during NF/RO treatment—A literature review, Water Res. 38 (2004) 2795–2809.

[17] L.D. Nghiem, A.I. Schäfer, M. Elimelech, Removal of natural hormones by nanofiltration membranes: Measurement, modeling, and mechanisms, Environ. Sci. Technol. 38 (2004) 1888–1896.

[18] 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.

[19] L. Braeken, R. Ramaekers, Y. Zhang, G. Maes, B.V.D. Bruggen, C. Vandecasteele, Influence of hydrophobicity on retention in nanofiltration of aqueous solutions containing organic compounds, J. Membr. Sci. 252 (2005) 195–203.

[20] J.M. Arsuaga, A. Sotto, M.J. López-Muñoz, L. Braeken, Influence of type and position of functional groups of phenolic compounds on NF/RO performance, J. Membr. Sci. 372 (2011) 380–386.

[21] L.D. Nghiem, A.I. Schäfer, M. Elimelech, Role of electrostatic interactions in the retention of pharmaceutically active contaminants by a loose nanofiltration membrane, J. Membr. Sci. 286 (2006) 52–59.

[22] K. Boussu, C. Vandecasteele, B. Van der Bruggen, Relation between membrane characteristics and performance in nanofiltration, J. Membr. Sci. 310 (2008) 51–65.

[23] A.I. Schäfer, I. Akanyeti, A.J.C. Semião, Micropollutant sorption to membrane polymers: A review of mechanisms for estrogens, Adv. Colloid Interface Sci. 164 (2011) 100–117.

[24] L.D. Nghiem, D. Vogel, S. Khan, Characterising humic acid fouling of nanofiltration membranes using bisphenol A as a molecular indicator, Water Res. 42 (2008) 4049–4058.

[25] H. Li, Y. Lin, Y. Luo, P. Yu, L. Hou, Relating organic fouling of reverse osmosis membranes to adsorption during the reclamation of secondary effluents containing methylene blue and rhodamine B, J. Hazard. Mater. 192 (2011) 490–499.

[26] A.A. Alturki, N. Tadkaew, J.A. McDonald, S.J. Khan, W.E. Price, L.D. Nghiem, Combining MBR and NF/RO membrane filtration for the removal of trace organics in indirect potable water reuse applications, J. Membr. Sci. 365 (2010) 206–215.

[27] R. Liu, J.L. Zhou, A. Wilding, Simultaneous determination of endocrine disrupting phenolic compounds and steroids in water by solid-phase extraction-gas chromatography-mass spectrometry, J. Chromatogr. A 2004 (1022) 179–189.

[28] G. Gatidou, N.S. Thomaidis, A.S. Stasinakis, T.D. Lekkas, Simultaneous determination of the endocrine disrupting compounds nonylphenol, nonylphenol ethoxylates, triclosan and bisphenol A in wastewater and sewage sludge by gas chromatography-mass spectrometry, J. Chromatogr. A 1138 (2007) 32–41.

[29] S.Y. Zhang, Q.A. Zhang, S. Darisaw, O. Ehie, G.D. Wang, Simultaneous quantification of polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and pharmaceuticals and personal care products (PPCPs) in Mississippi river water, in New Orleans, Louisiana, USA, Chemosphere 66 (2007) 1057–1069.

[30] Y. Kiso, Y. Sugiura, T. Kitao, K. Nishimura, Effects of hydrophobicity and molecular size on rejection of aromatic pesticides with nanofiltration membranes, J. Membr. Sci. 192 (2001) 1–10.

[31] W.S. Hua, D.B. Zhi, H. Yu, Adsorption of bisphenol A by polysulphone membrane, Desalination 253 (2010) 22–29.

[32] M.J.M. Wells, Log Dow: Key to understanding and regulating wastewater-derived contaminants, Environ. Chem. 3 (2006) 439–449.

[33] L.V. Tetko, G.I. Poda, Application of ALOGPS 2.1 to predict log D distribution coefficient for pfizer proprietary compounds, J. Med. Chem. 47 (2004) 5601–5604.

[34] M.E. Williams, J.A. Hestekin, C.N. Smothers, D. Bhattacharyya, Separation of organic pollutants by reverse osmosis and nanofiltration membranes: Mathematical models and experimental verification, Ind. Eng. Chem. Res. 38 (1999) 3683–3695.

[35] L.D. Nghiem, A.I. Schäfer, Adsorption and transport of trace contaminant estrone in NF/RO membranes, Environ. Eng. Sci. 19 (2002) 441–451.

[36] K.O. Agenson, J.I. Oh, T. Urase, Retention of a wide variety of organic pollutants by different nanofiltration/reverse osmosis membranes: Controlling parameters of process, J. Membr. Sci. 225 (2003) 91–103.

[37] P. Xu, J.E. Drewes, C. Bellona, G. Amy, T.U. Kim, M. Adam, T. Heberer, Rejection of emerging organic micropollutants in nanofiltration-reverse osmosis membrane applications, Water Environ. Res. 77 (2005) 40–48.

[38] K. Kimura, G. Amy, J. Drewes, Y. Watanabe, Adsorption of hydrophobic compounds onto NF/RO membranes:An artifact leading to overestimation of rejection, J. Membr. Sci. 221 (2003) 89–101.

[39] 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.

[40] V. Yangali-Quintanilla, Rejection of Emerging Organic Contaminants by Nanofiltration and Reverse Osmosis Membranes: Effects of Fouling, Modelling and Water Reuse, PhD thesis, Delft University of Technology, Delft, 2010.

[41] H. Ozaki, N. Ikejima, Y. Shimizu, K. Fukami, S. Taniguchi, R. Takanami, R.R. Giri, S. Matsui, Rejection of pharmaceuticals and personal care products (PPCPs) and endocrine disrupting chemicals (EDCs) by low pressure reverse osmosis membranes, Water Sci. Technol. 58 (2008) 73–81.

[42] X. Jin, J. Hu, S.L. Ong, Influence of dissolved organic matter on estrone removal by NF and the role of their structures, Water Res. 41 (2007) 3077–3088.

[43] E.A. McCallum, H. Hyung, T.A. Do, C.H. Huang, J.H. Kim, Adsorption, desorption, and steady-state removal of 17β-estradiol by nanofiltration membranes, J. Membr. Sci. 319 (2008) 38–43.

[44] Q. Li, Z. Xu, I. Pinnau, Fouling of reverse osmosis membranes by biopolymers in wastewater secondary effluent: Role of membrane surface properties and initial permeate flux, J. Membr. Sci. 290 (2007) 173–181.