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Hai Q. Dang

*University of Wollongong*, [hdq686@uowmail.edu.au](mailto:hdq686@uowmail.edu.au)

Long D. Nghiem

*University of Wollongong*, [longn@uow.edu.au](mailto:longn@uow.edu.au)

William E. Price

*University of Wollongong*, [wprice@uow.edu.au](mailto:wprice@uow.edu.au)

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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**

rejection, trace, organic, contaminants, nanofiltration, reverse, factors, osmosis, governing, membranes, GeoQuest, CMMB

## **Disciplines**

Medicine and Health Sciences | Social and Behavioral Sciences

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

Hai Q. Dang <sup>a</sup>, Long D. Nghiem <sup>b</sup>, William E. Price <sup>a,\*</sup>

<sup>a</sup> Strategic Water Infrastructure Laboratory, School of Chemistry, University of Wollongong, Wollongong, NSW, 2500, Australia  
(E-mail: [dangquanghaicn@gmail.com](mailto:dangquanghaicn@gmail.com); [wprice@uow.edu.au](mailto:wprice@uow.edu.au))

<sup>b</sup> Strategic Water Infrastructure Laboratory, School of Civil, Mining and Environmental Engineering, University of Wollongong, NSW, 2500, Australia (E-mail: [longn@uow.edu.au](mailto:longn@uow.edu.au))

\*Corresponding author.

## 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 were 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

## 1. Introduction

Over the last hundred 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 compounds have been released into the environment due to their widespread use [1]. As a result, different classes of TrOCs including endocrine disrupting chemicals (EDCs), pharmaceutically active

compounds (PhACs), disinfection by products (DBPs) and personal care products (PCPs) have been found in leachate from landfill sites, ground water, surface water, drinking water treatment plants and wastewater treatment plants (WWTPs) effluents [2-4]. More recently, the occurrence at trace levels (usually at  $\mu\text{g/L}$  or  $\text{ng/L}$  levels) of these organic contaminants in different water resources has attracted the attention of both scientific and regulatory communities. Several of the 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 the micropollutants in drinking water treatment and water reclamation processes [7]. In particular, NF and 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 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 which may influence their rejection including the physicochemical properties of the compounds, characteristics of the membrane, operating conditions and feed water composition [13,14]. In particular, the feed solution pH can be considered 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 considerably affected by solution pH above its pKa 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 stabilised 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, amongst 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 contaminant. 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. Nanofiltration and reverse osmosis 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 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 as well as 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. Trace organic contaminants, 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 feed waters were prepared with Milli-Q water. Both the solvents used for solid phase extraction and analysis of samples including methanol and dichloromethane, purchased from Sigma-Aldrich (Sydney, Australia). Internal standard of bisphenol A-d<sub>16</sub> and N,O-bis (trimethylsilyl) trifluoroacetamide (BSTFA) containing 1 % of trimethylchlorosilane (TMCS). Pyridine 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 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<sup>2</sup> (4 cm × 10 cm) with a channel height of 2 mm, and a stainless steel feed reservoir of 10 litres. 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 litres per minute was employed. 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 1000, Agilent Technologies, Palo Alto, CA) connected to a PC was utilized to measure permeate flow, and the cross flow was monitored with a manual flow meter.

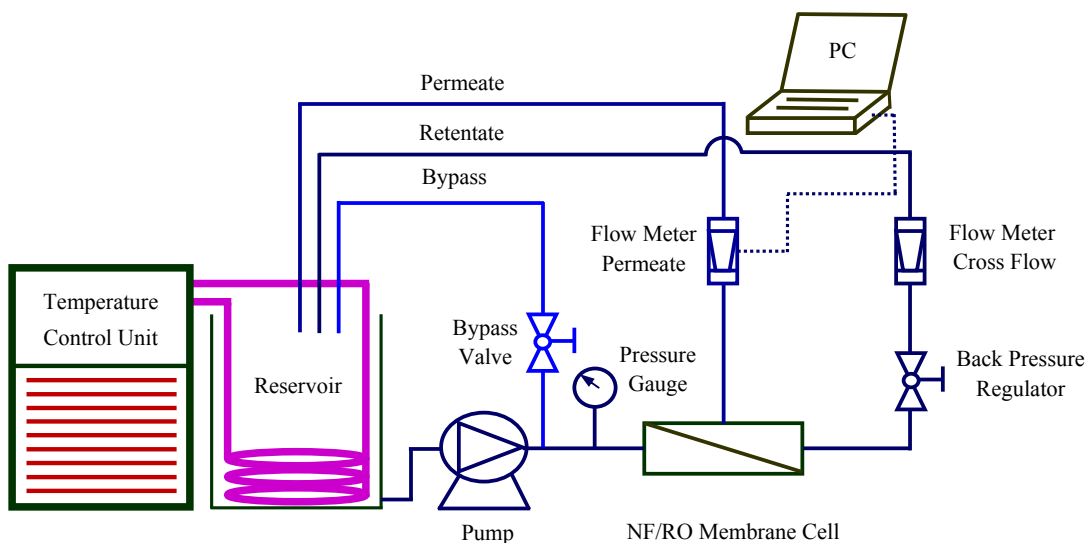


Fig. 1. Schematic diagram of the NF/RO filtration system.

#### 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 hours. 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 litres. For the experiment at pH 4.7, an acetate buffer solution containing 1 mM of  $\text{CaCl}_2$ , 5.5 mM of  $\text{CH}_3\text{COOH}$ , and 5.5 mM of  $\text{CH}_3\text{COONa}$  was utilized. A phosphate buffer solution contained 10 mM of  $\text{NaCl}$ , 1 mM of  $\text{CaCl}_2$ , and 1 mM of  $\text{NaH}_2\text{PO}_4$  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  $\text{NaCl}$ , 0.3 mM of  $\text{NaHCO}_3$ , and 4.5 mM of  $\text{Na}_2\text{CO}_3$ . During the experiment, the feed reservoir temperature and cross flow velocity were kept constant at  $20 \pm 0.1$  °C and 42 cm/s, respectively. The permeate flux was set to the manufacturer's quoted nominal membrane flux of 42 L/m<sup>2</sup>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  $\text{CH}_3\text{COOH}$ , 1 M of  $\text{NaOH}$  and 1 M of  $\text{Na}_2\text{CO}_3$  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 aluminium foil, 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 sulphuric 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 x 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 x 7 mL of Milli-Q water and dried under vacuum for 30 minutes 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<sub>16</sub> 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 (trimethylchlorosilane)) 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 °C to 210 °C, third ramp 2 °C/min to 228 °C, fourth ramp 30 °C to 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 ionisation in full scan mode from 50 to 600 of  $m/z$ , and later on in selected ion monitoring (SIM) 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 1000 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 discussions

#### 3.1. Properties of trace organic contaminants

The major physicochemical properties of the target organic contaminants are shown in Table 1. The compounds selected for this investigation exhibited considerably difference in their physicochemical properties. These compounds have low molecular weight, ranging between 138.12 and 314.42 g/mol for salicylic acid and 17 $\beta$ -estradiol acetate, respectively. However, they are markedly different in their dissociation constants (pKa) and hydrophobicity properties. Most TrOCs are weak acids and will dissociate into an ionic form at pH above the pKa. Based on the selected organic compounds pKa values 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, the other all organic contaminants are uncharged and exist in 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 Kow. However, log D appears to be a better hydrophobicity indicator than log Kow 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 (unionised) or charged species (ionised) depending on the solution pH. For ionisable solutes, the hydrophobicity is dependent on the percentage of uncharged versus charged species, and thus it depends strongly on pH. Log Kow 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 and it reflects the true hydrophobicity behaviour of an ionisable compound in a solution at a given pH value or range. Log D can be calculated from the pKa and log Kow of TrOCs and it thus is accepted as one the principal parameter to evaluate hydrophobicity of TrOCs at any pH value [14,33]. According to Wells [32] and Alturki et al. [26], TrOCs with log D is equal 3 or higher are generally referred to as hydrophobic. TrOCs with log D is 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 (ranging from 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 decrease 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 behaviour. 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: 17 $\alpha$ -ethinylestradiol, 17 $\beta$ -estradiol, 4-tert-octylphenol, 17 $\beta$ -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 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 hours of filtration using the NF270 and ESPA2 membranes at three pH values of pH 4.7, 7 and 11 is illustrated in Fig. 2 and Fig. 3. In most cases, the rejection efficiency of the TrOCs by the ESPA2 membrane was considerably higher than for 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].

Table 1

Physicochemical properties of the selected trace organic contaminants

Organic compounds	CAS number	Molecular formula	Molecular weight (MW) (g/mol)	Log $K_{ow}$ <sup>a</sup>	pKa <sup>a</sup>	Log D <sup>b</sup>			Molecular dimension (nm) <sup>c</sup>		
						pH 4.7	pH 7	pH 11	Length	Width	Height
Salicylic acid	69-72-7	C <sub>7</sub> H <sub>6</sub> O <sub>3</sub>	138.12	2.011	3.01	0.31	-1.13	-5.98	0.615	0.354	0.577
Ibuprofen	15687-27-1	C <sub>13</sub> H <sub>18</sub> O <sub>2</sub>	206.28	3.502	4.41	3.03	0.94	-3.09	0.900	0.354	0.561
Gemfibrozil	25812-30-0	C <sub>15</sub> H <sub>22</sub> O <sub>3</sub>	250.33	4.302	4.75	4.03	2.07	-1.95	0.972	0.354	0.670
Diclofenac	15307-86-5	C <sub>14</sub> H <sub>11</sub> Cl <sub>2</sub> NO <sub>2</sub>	296.15	4.548	4.18	3.91	1.77	-2.27	0.829	0.354	0.767
Carbamazepine	298-46-4	C <sub>15</sub> H <sub>12</sub> N <sub>2</sub> O	236.27	1.895	13.94	1.89	1.89	1.89	0.818	0.354	0.676
Pentachlorophenol	87-86-5	C <sub>6</sub> HCl <sub>5</sub> O	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 <sub>10</sub> H <sub>14</sub> 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 <sub>14</sub> H <sub>22</sub> 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 <sub>15</sub> H <sub>24</sub> O	220.35	6.142	10.15	6.14	6.14	5.23	1.179	0.354	0.519
Triclosan	3380-34-5	C <sub>12</sub> H <sub>7</sub> Cl <sub>3</sub> O <sub>2</sub>	289.54	5.343	7.80	5.34	5.28	2.14	0.926	0.354	0.602
Bisphenol A	80-05-7	C <sub>15</sub> H <sub>16</sub> O <sub>2</sub>	228.29	3.641	10.29	3.64	3.64	2.85	0.876	0.354	0.570
Estrone (E1)	53-16-7	C <sub>18</sub> H <sub>22</sub> O <sub>2</sub>	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 <sub>18</sub> H <sub>24</sub> O <sub>2</sub>	272.38	4.146	10.27	4.15	4.15	3.34	0.697	0.340	0.693
Estriol (E3)	50-27-1	C <sub>18</sub> H <sub>24</sub> O <sub>3</sub>	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 <sub>20</sub> H <sub>24</sub> O <sub>2</sub>	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 <sub>20</sub> H <sub>26</sub> O <sub>3</sub>	314.42	5.111	10.26	5.11	5.11	4.30	0.947	0.354	0.842

<sup>a</sup> Scifinder Scholar, <sup>b</sup> calculated by the equation:  $\log D_{(pH)} = \log K_{ow} - \log (1 + 10^{(pH-pKa)})$ , <sup>c</sup> calculated using Molecular Modeling Pro<sup>TM</sup> Plus software.

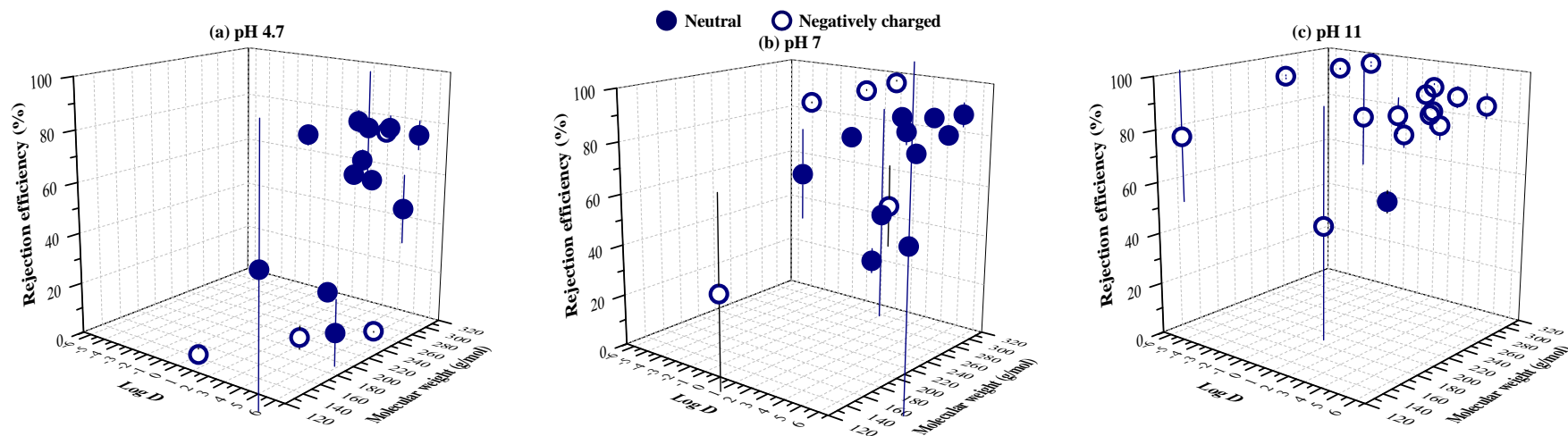


Fig. 2. Correlation between rejection efficiency after 24 hours of filtration, log D and molecular weight of TrOCs by the NF270 membrane at pH 4.7, pH 7 and pH 11.

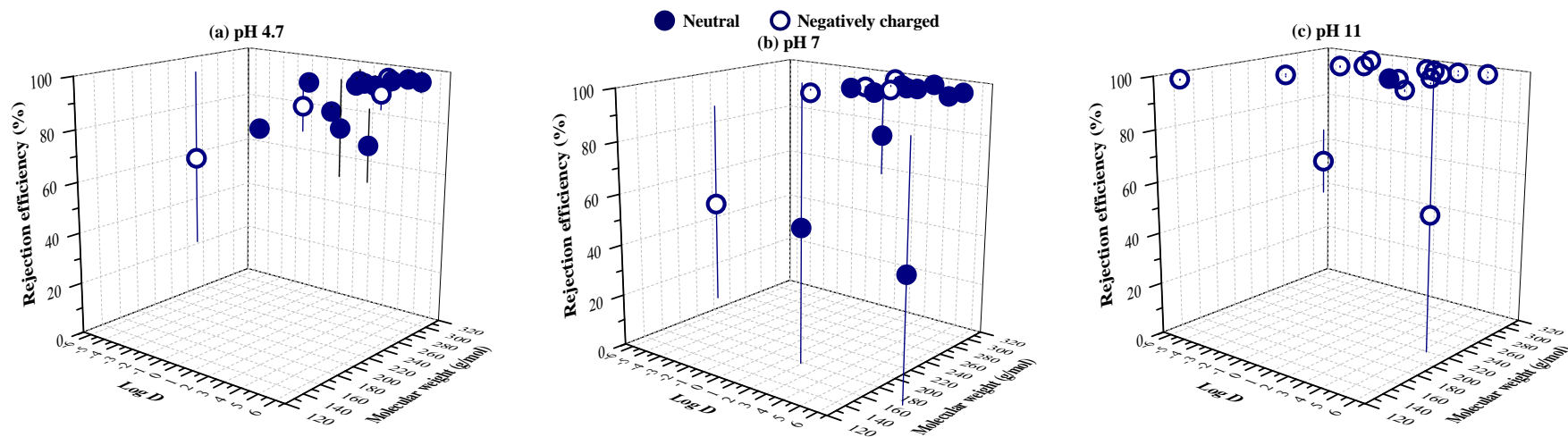


Fig. 3. Correlation between rejection efficiency after 24 hours of filtration, log D and molecular weight of TrOCs by the ESPA2 membrane at pH 4.7, pH 7 and pH 11.

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. It was already reported in most investigations on electrostatic interactions that an increase in rejection of negatively charged compounds compared to 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 Fig. 2 and Fig. 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 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 employed. 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, it was little or no correlation between their rejection 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 next section.

### 3.3. Adsorption of trace organics to NF/RO membranes

Adsorption levels of both hydrophilic and hydrophobic organic compounds illustrated in Fig. 4 and Fig. 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 hours 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 employed. 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-Square in Fig. 4 and Fig. 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 17 $\beta$ -estradiol (0 %) and 17 $\alpha$ -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 (eg 17 $\beta$ -estradiol (0 %) and 17 $\alpha$ -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 in adsorption of almost organic compounds under strong basic pH. These observations have been reported in several previous investigations [15,43].

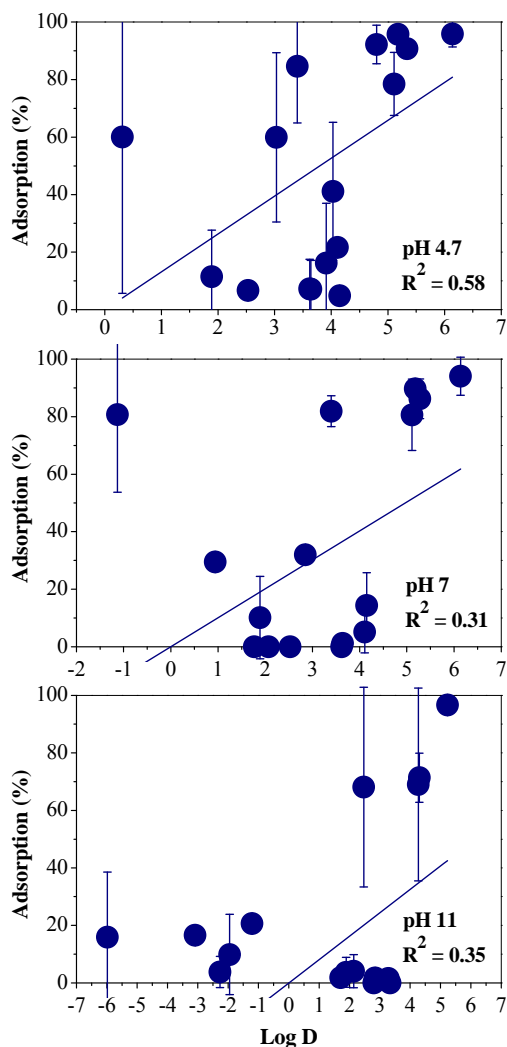


Fig. 4. Adsorption of TrOCs to the NF270 membrane as a function of log D.

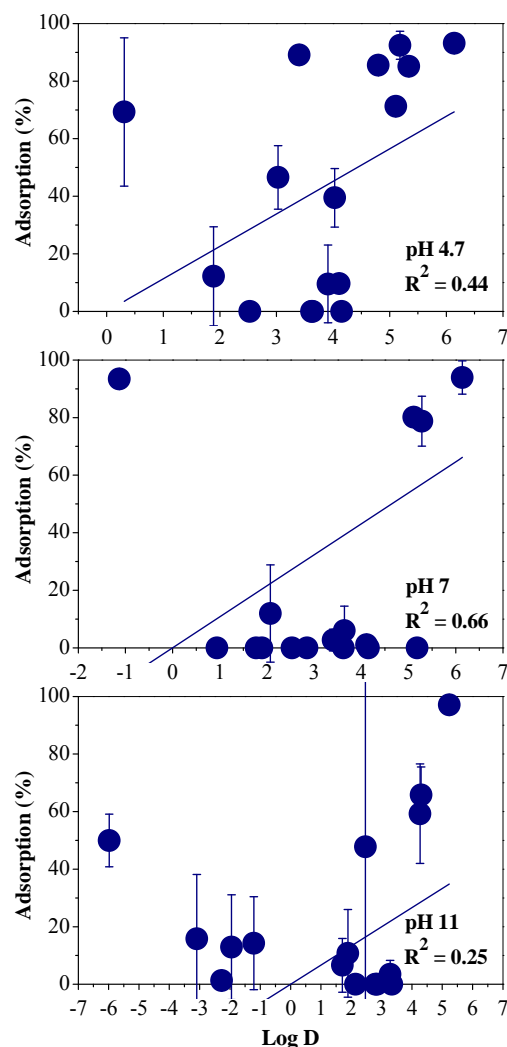


Fig. 5. Adsorption of TrOCs to the ESPA2 membrane as a function of log D.

In addition, for some specific hydrophilic compounds, particularly salicylic acid, there was quite strong adsorption onto both the NF270 and ESPA2 membranes after 24 hours of filtration at all pH employed. 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 such as that 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, may be due to 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 employed.

#### 4. Conclusions

From the results obtained using the selected compounds, at the pH conditions employed, 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 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 hours 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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